

Article

Chloride-Induced Stress Corrosion Cracking of Friction Stir-Welded 304L Stainless Steel: Effect of Microstructure and Temperature

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Abstract: Dry storage canisters of used nuclear fuels are fabricated using SUS 304L stainless steel. Chloride-induced stress corrosion cracking (CISCC) is one of the major failure modes of dry storage canisters. The cracked canisters can be repaired by friction stir welding (FSW), a low-heat input ‘solid-phase’ welding process. It is important to evaluate the CISCC resistance of the friction stir welded material. Stress corrosion cracking (SCC) studies were carried out on mill-annealed base materials and friction stir welded 304L stainless U-bend specimens in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature and boiling MgCl₂ solution at 155 °C. The engineering stress on the outer fiber of the FSW U-bend specimen was ~60% higher than that of the base metal (BM). In spite of the higher stress level of the FSW, both materials (FSW and BM) showed almost similar SCC failure times in the two different test solutions. The SCC occurred in the thermo-mechanically affected zone (TMAZ) of the FSW specimens in the 3.5% NaCl + 5 N H₂SO₄ solution at room temperature, while the stirred zone (SZ) was relatively crack-free. The failure occurred at the stirred zone when tested in the boiling MgCl₂ solution. Hydrogen reduction was the cathodic reaction in the boiling MgCl₂ solution, which promoted hydrogen-assisted cracking of the heavily deformed stirred zone. The emergence of the slip step followed by passive film rupture and dissolution of the slip step could be the SCC events in the 3.5% NaCl + 5 N H₂SO₄ solution at room temperature. However, the slip step height was not sufficient to cause passivity breakdown in the fine-grained SZ. Therefore, the SCC occurred in the partially recrystallized softer TMAZ. Overall, the friction-stirred 304L showed higher tolerance to CISCC than the 304L base metal.



Citation: Naskar, A.; Bhattacharyya, M.; Jana, S.; Darsell, J.; Raja, K.S.; Charit, I. Chloride-Induced Stress Corrosion Cracking of Friction Stir-Welded 304L Stainless Steel: Effect of Microstructure and Temperature. *Crystals* **2024**, *14*, 556. <https://doi.org/10.3390/cryst14060556>

Academic Editor: Marek Sroka

Received: 15 April 2024

Revised: 5 June 2024

Accepted: 12 June 2024

Published: 16 June 2024

Keywords: friction stir welding; 304L austenitic stainless steel; chloride-induced stress corrosion cracking

1. Introduction

Austenitic stainless steel (SS) has good formability, weldability, mechanical strength, and excellent general corrosion resistance in various environments. However, austenitic SS is susceptible to stress corrosion cracking (SCC). The SCC occurs when the susceptible microstructure of austenitic SS with adequate tensile stress encounters a chloride-containing environment such as NaCl and MgCl₂ or other specific environments such as H₂S or H₂O₂, resulting in loss of ductility and brittle failure [1–4]. SUS 304L or 316L austenitic steel plates are used for the fabrication of canisters for intermittent dry storage of used nuclear fuels [5]. During dry storage, salts-laden dust in the atmosphere settles on the canisters and subsequently deliquesces as heat generated by radioactive decay declines over time.



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The deliquescence of salt deposits leads to chloride-induced stress corrosion cracking (CISCC) [6]. NaCl-based salt requires a high relative humidity ($RH > 76\%$) to become liquid, while $MgCl_2$ -based salt liquefies at low RH values ($<65\%$) [7]. The SCC crack propagation mechanisms were different in the two chloride media. Preferential dissolution of slip bands resulted in predominantly transgranular cracking (TGSCC) in $MgCl_2$, while mixed-mode cracking (TGSCC + IGSCC) was observed in the NaCl solution without attacking the slip bands [8–10].

Acello and Green reported SCC of U-bend specimens of SUS 304 SS in H_2SO_4 –NaCl solution at room temperature [11]. Other studies relating to the creep–corrosion interaction of 304 SS in 2.5 M H_2SO_4 –0.5 M NaCl have also reported SCC failure of 304 SS tensile sample at 30 °C [12–14]. The SCC susceptibility of SUS304 was investigated in various NaCl (0–4.5 M) and H_2SO_4 (0–5.5 M) concentrations. SCC occurred in all NaCl concentrations above 0.2 M when the concentration of H_2SO_4 was fixed at 0.5 M. Similarly, for 1.5 M H_2SO_4 solution, SCC only occurred between 0.1–0.9 M NaCl concentration. All other NaCl concentrations (1.0–4.0 M) showed only general corrosion, not SCC [14]. The effect of NaCl concentration (with fixed H_2SO_4 concentration) on the SCC crack length was also studied in the same study. For H_2SO_4 concentrations of 1.5 M and 2.5 M, the maximum crack length was observed with a NaCl concentration of 0.1–0.3 M. SCC in austenitic SS in boiling $MgCl_2$ saturated solution was due to high chloride content and temperature (about 155 ± 1 °C) [15–17]. It is well-established that austenitic stainless steels are more susceptible to SCC than ferritic stainless steels [18]. The higher susceptibility of the austenitic phase to SCC could be attributed to the low stacking fault energy that resulted in widely spaced planar slip systems leading to easy breakdown of the passive film [19]. On the other hand, delta ferrite in the austenitic welds and martensite in the cold-worked austenitic stainless steels promoted SCC [20].

To mitigate SCC, a few approaches involving the development of less susceptible microstructure by different surface treatments and microalloying have been investigated. For example, laser shock processing [21], shot peening [22], and ultrasonic impact treatments [23] improved the SCC resistance in 304 SS in various chloride and acid-chloride media. Laser shock processing (LSP) in 304 SS caused severe grain refinement and formation of SCC-resistant deformation twins, improving SCC resistance. Moreover, the compressive stress generated on the 304SS surface due to LSP provided additional resistance to SCC [24]. Another SCC mitigation approach is to apply a cold-spray coating of similar composition material on the fusion welded area where high tensile residual stress is anticipated. The enhanced resistance of cold spray coating to CISCC was attributed to compressive residual stress and a heavily deformed microstructure due to adiabatic shear instability [25].

Friction stir welding or processing (FSW or FSP) is another surface modification process that leads to grain refinement, low-angle grain boundaries, and compressive residual stress distribution on the stirred zone (SZ) [26]. The friction-stirred 304L material showed better resistance to pitting corrosion in the acidified chloride solution than the base metal (BM) in mill-annealed conditions [27,28]. Therefore, FSW and FSP can be beneficial in preventing SCC damage in austenitic SS structures. Moreover, FSW can be utilized for repairing SCC cracks on stainless steel components rather than traditional fusion welding. Traditional welding process is a high-temperature process, degradation of the welded microstructure is common (HAZ grain growth, formation of detrimental secondary phases, etc.), which deteriorates the SCC resistance of austenitic SS. Furthermore, the fusion welding of austenitic stainless steels requires about 2–10 vol% of delta ferrite to prevent solidification cracking of the weld metal, increasing the susceptibility of SCC [29].

Our previous studies showed that friction stir welding of 304L resulted in excessive grain refinement due to heavy plastic deformation and a higher fraction of low-angle grain boundaries due to dislocation rearrangement [27,28]. The low-angle grain boundaries could supply more misorientation dislocations at the metal/film interface, forming anion vacancies by a dislocation-climb process. This leads to oxide formation at these locations

without stressing the substrate. Stress-free passive films were considered to enhance pitting resistance. Because pitting promotes the initiation of SCC, the SCC susceptibility could be controlled by improving the pitting resistance. Therefore, the FSW of 304L SS is anticipated to increase the SCC resistance. The storage canisters of the used nuclear fuels predominantly fail due to chloride-induced SCC. The cracked storage canisters need to be repair-welded. FSW could be a potential repair-welding technique for repairing cracked canisters. Therefore, it is important to know the SCC behavior of the friction stir welded material. Using U-bend specimens, this study investigated the SCC behavior of the as-received 304L SS and friction stir welded 304L in two different environments. The aim of this paper is to compare the SCC resistance of friction-stirred welded (FSW) and wrought 304L SS (BM) in NaCl-H₂SO₄ solution at room temperature and boiling MgCl₂ medium and to show that FSW increases the SCC resistance.

2. Experimental

2.1. Friction Stir Welding (FSW) Process

A hot-rolled plate of 304L with composition (in wt%), C = 0.02, Mn = 1.54, P = 0.06, S < 0.001, Si = 0.32, Cr = 18.34, Ni = 8.17, Mo = 0.32, Cu = 0.43, N = 0.09, Nb = 0.02, and dimensions (330 mm (L) × 149 mm (W) × 12.7 mm (T)) was used for the FSW (bead-on-plate type). The FSW process was carried out at Pacific Northwest National Laboratory (PNNL) using an FSW machine (Formerly Transformation Technologies, Inc., now Bond Technologies Elkhart, IN, USA). A polycrystalline cubic boron nitride (PCBN) tungsten rhenium tool (Q70, Mazak-MegaStir, Provo, UT, USA) of a convex scrolled shoulder stepped spiral design (CS4) with a shoulder diameter of 25 mm and a 5.7 mm long pin was used for the friction stir welding with a tilt angle of -0.5° . FSW was performed in simultaneous force control and temperature control while keeping the transverse speed fixed at 50.8 mm/min. The temperature of the weld during the stirring operation was maintained at 900 °C. The isothermal temperature maintained during the friction stir welding minimized the cooling gradient across the weld, and hence, uniform microstructural features could be expected throughout the weld length. The FSW parameters are listed in Table 1.

Table 1. Parameters of the friction stir welding parameters for isothermal tool temperature.

Isothermal Tool Temperature (°C)	Welding Speed (mm/min)	Tool Rotational Speed (rev/min)	Vertical Forging Load (kN)	Spindle Torque (N.m)	Weld Power (kW)
900	50.8	160–200	55.6	~150	~2.7

2.2. Microstructural Characterization

Small samples (10 mm × 10 mm) of 304L base material (BM) and friction stir welded material from the stir zone were machined using a slow-speed diamond cutter. The samples were sectioned from multiple locations of the weld traverse path for microscopic observation. Samples were then polished using emery sheets from 120 grit down to 1200 grit and 0.1 µm diamond paste for the surface finish. The samples were etched using 10% oxalic acid solution in 6 V for 10 s to reveal the microstructure. Microstructures were examined using an optical microscope (Olympus PMG-3, Tokyo, Japan) and a scanning electron microscope (FE-SEM Zeiss Supra 35VP, Oberkochen, Germany). Electron back scattered diffraction (EBSD) analysis of grain size and grain boundary structure was carried out using a scanning electron microscope (JEOL, Tokyo, Japan, JSL6610LV SEM with attached Hikari camera and TSL OIM v6 data collection software).

EBSD analysis was carried out to generate inverse pole figures, band contrast images, and grain boundary maps. The step size was 0.1 µm. In the grain boundary maps, all the coincidence site lattice boundaries, which mostly appear in the form of annealing twins, were eliminated by setting a range of the misorientation angle. This ensured the mapping of the random high-angle grain boundaries only. With these set values, the TSL OIM software version 7.1.0 calculated the average grain size using the average grain area method.

Grain boundary crystallography is used to determine the total length of a particular grain boundary type to quantify the grain boundary structure. This is done by setting the misorientation angles for low-angle boundaries (LAB) and sigma 3 and 9 boundaries to map them separately. The TSL OIM software v. 7.1.0 calculated the total length covered by each boundary type to correlate with the strain in the microstructure. Microhardness was measured across the weld using 0.2 kg-f (1.96 N) load using a Vickers microhardness tester (LECO LM-100, St. Joseph, MI, USA).

2.3. Electrochemical Studies

Specimens of size 1 cm × 1 cm were cut from the top surface of the (i) SZ and (ii) SZ + BM. Both types of specimens were polished down to a 1 µm surface finish. All electrochemical experiments were conducted using a computer-controlled potentiostat (Gamry Interface 1000, Gamry Instruments Inc., Warminster, PA, USA) in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature. A spiral platinum wire and an Ag/AgCl electrode in saturated KCl (46 mV Vs. SCE) were used as counter and reference electrodes, respectively. No deaeration of the electrolyte was performed. Initially, the specimen was conditioned until a stable open circuit potential (OCP) was recorded. Linear polarization (LP) and potentiodynamic polarization (PDP) experiments were performed after the OCP was stabilized. For LP, the voltage was swept −25 mV_{Ag/AgCl} to +25 mV_{Ag/AgCl} from the OCP at a rate of 0.5 mV/s to determine the polarization resistance. During PDP, the voltage scan started at −250 mV_{Ag/AgCl} below OCP and swept towards more positive potentials at the rate of 0.1667 mV/s until a potential of 1.6 V_{Ag/AgCl} was reached. After PDP, the samples were cleaned using distilled water and acetone in an ultrasonic cleaner, and then the surfaces were examined under optical and scanning electron microscopes. Electrochemical impedance spectroscopy (EIS) experiments were conducted at the open circuit potential. The AC potential of amplitude 10 mV and frequency varied from 10 kHz to 0.01 Hz for all EIS experiments. All the tests were duplicated or triplicated to verify their reproducibility. Only reproducible results are presented in this report. The tabulated values are the average of two or three test results.

2.4. Stress Corrosion Cracking (SCC)

Specimens with dimensions 1.6 cm × 2.5 cm × 0.15 cm were machined out from the BM and the SZ. These samples were formed to a U shape with a two-step loading process following the ASTM G30 [30] standard. Stainless steel nuts and bolts were used to maintain the stress in the U-bend specimens. Figure 1 shows the dimensions of the U-bend samples. The outer surface of the U-bend sample experiences constant tensile strain, whereas the inner surface remains under compressive strain. The relation can express the tensile strain at the outer fiber: $e = t/(2R + t)$, where e = engineering strain, t = thickness of sample (0.15 cm), and R = bend radius (1 cm). The calculated maximum strain is 6.97%. Considering the well-established Hollomon equation for the true stress $\sigma = K\epsilon^n$, and taking the values for strength coefficient $K = 1564$ MPa (wrought) and 1224 MPa (FSW), ϵ = true strain ($\ln(1 + e) = 0.0674$) and $n = 0.625$ (wrought) and 0.256 (FSW) for the 304 SS [31]. The engineering stress ($s = \sigma/(1 + e)$) on the outer fiber of the U-bend specimen could be roughly estimated as 395 MPa for the wrought and 621 MPa for the FSW 304L U-bend specimens. It is noted that the FSW specimen was stressed ~ 60% higher than the wrought specimen. The SCC tests were carried out by immersing the bent portions of U-bend specimens in the test solutions and leaving the unbent arms outside the solutions. The test solutions were (i) 3.5% NaCl + 5 N H₂SO₄ and (ii) 54.3 wt% MgCl₂. The SCC tests in 3.5% NaCl + 5 N H₂SO₄ solution were performed at room temperature (24–26 °C). This electrolyte was employed based on the results of Sunada et al. [14] who investigated the influences of concentrations of H₂SO₄ and NaCl on the SCC of 304 SS in H₂SO₄–NaCl aqueous solutions at 30 °C. The OCP of the specimen was continuously monitored. The SCC in MgCl₂ was carried out in boiling conditions (~155 °C) by refluxing the condensed water. The U-bend samples were taken out of the test solution to observe crack initiation every 12 h under a 10× magnifying

lens. The first crack appearance time and complete failure time were recorded. The tests were duplicated for each test condition. After failure, the specimens were cleaned and ultrasonicated in distilled water to remove the corrosion products, dried, and stored in a desiccator for further analysis under optical and electron microscope.

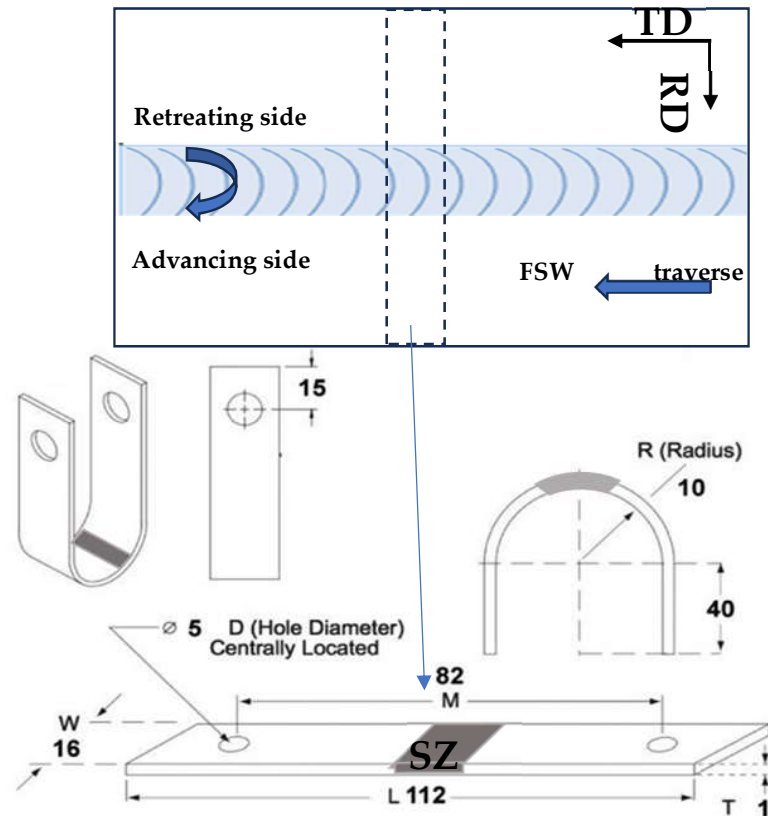


Figure 1. Preparation of U-bend specimens from the FSW plate for SCC testing.

3. Results & Discussion

3.1. Microstructure

Figure 2a shows the SEM and optical micrographs of the 304L wrought or base material (BM). The BM microstructure mostly consists of equiaxed austenite grains with a few twin boundaries. The presence of delta ferrite stringers was also observed. Figure 2b shows the microstructure of the cross-section of the advancing side of the FSW specimen. A banded structure was observed in the SZ, showing the material flow patterns during friction stirring. The delta ferrite stringers observed in the BM were broken down and not visible in the SZ. Figure 2c shows the cross-sectional microstructure of the retreating side of the FSW sample. Flow patterns (banded structure) could not be discerned at the retreating side due to the counter-current flow of the material because the welding direction was opposite to the velocity vector of the tool rotation. Figure 2d shows the microstructure of the SZ where recrystallized finer grains are observed. The region adjacent to the SZ is denoted as a thermo-mechanically affected zone (TMAZ) because the microstructure of this region was influenced by the heavy plastic deformation of the SZ and frictional heat due to the tool shoulder. This region revealed relatively finer grains than BM but coarser grains than SZ. The region next to TMAZ is typically denoted as a heat-affected zone (HAZ), where the microstructure is affected by the frictional heat generated by the FSW process. In this study, HAZ could not be discerned. Therefore, only TMAZ is marked. The width of the TMAZ is about 100 μm . The grain size gradually increases as the distance increases from the SZ boundary toward the unaffected BM. Figure 3a–f show the optical microstructure of the top surfaces of different regions of the FSW 304L specimen. The top surface microstructures

are more relevant because the top surfaces were exposed to the test environment during the corrosion tests. Banded structures or onion rings are observed on the top surfaces of the FSW samples. The formation mechanism of onion rings during FSW of 304L has been reviewed in our earlier work [31,32]. Table 2 summarizes the microstructural features of the BM and the friction-stir welded (FSW) specimens. Figure 2b shows the microstructure of the FSW specimen. The delta ferrite stringers observed in the BM were broken down into small particles and dissolved during etching. The average grain size of the BM is $44 \pm 16 \mu\text{m}$. A grain-refined microstructure is observed in the FSW 304L with an average grain size of $16 \pm 4 \mu\text{m}$. A similar grain size ($\sim 13 \mu\text{m}$) was reported by Reynolds et al. under similar welding conditions [33]. The grain refinement observed in the SZ could be attributed to the dynamic recrystallization mechanism followed by the grain growth due to the higher weld temperature [34]. Generally, discontinuous dynamic recrystallization (DDRX) is observed for low stacking fault energy materials [35,36]. The grain refinement observed in the SZ could be attributed to the DDRX mechanism followed by the grain growth due to the higher weld temperature. A high fraction of $\Sigma 3$ ($\sim 46\%$) grain boundaries and a very low fraction ($\sim 2\%$) of low angle grain boundaries (LABs), angles between $2\text{--}15^\circ$, are recorded in the BM. Figure 3a–c illustrate the inverse pole figure, grain boundary map, and phase boundary map of the FSW, respectively. A very high fraction of LABs ($\sim 66\%$) is observed in the SZ. Due to very high tool rpm during the stirring process, the twin boundaries in the parent microstructure were shattered because of severe plastic deformation. This is evident from Table 2 as well as in Figure 4b. Figure 4c shows the phase map of the stir zone of the FSW specimen. A small fraction of delta ferrite (0.6%) is found in the stir zone. Other researchers have reported the presence of the sigma phase in the friction stir welded 304L SS [37,38]. This study did not detect the sigma phase in the FSW. The formation of the sigma phase in austenitic stainless steel mostly depends on the thickness of the plate, the chromium equivalent of the material, welding parameters, and the peak temperature in the stir zone. Rapid cooling rate favored by low tool rotational speed and a less thick plate of 316L did not form a sigma phase during FSW [39,40]. Figure 5 shows the microhardness profile of the FSW specimen. The hardness of the BM is around 170 HV. The SZ is harder than the BM by about 55 HV because of its finer grain size and higher dislocation density. Marginally higher hardness is observed on the advancing side than on the retreating side. The TMAZ shows hardness values in the range of 185–195 HV. The hardness values of the FSW specimens are lower than the ones reported for FSWed at 750°C and 825°C in our previous studies 33. This could be attributed to the higher isothermal welding condition (900°C) that resulted in larger grains and a higher fraction of LABs.

Table 2. Microstructural features of the 304L SS base material and friction stir welded material.

Sample	Grain Size, μm	LABs, %	$\Sigma 3$, %
Base material (BM)	44 ± 16	2.20	47.70
FSW (bead-on-plate)	16 ± 4	67.85	4.34

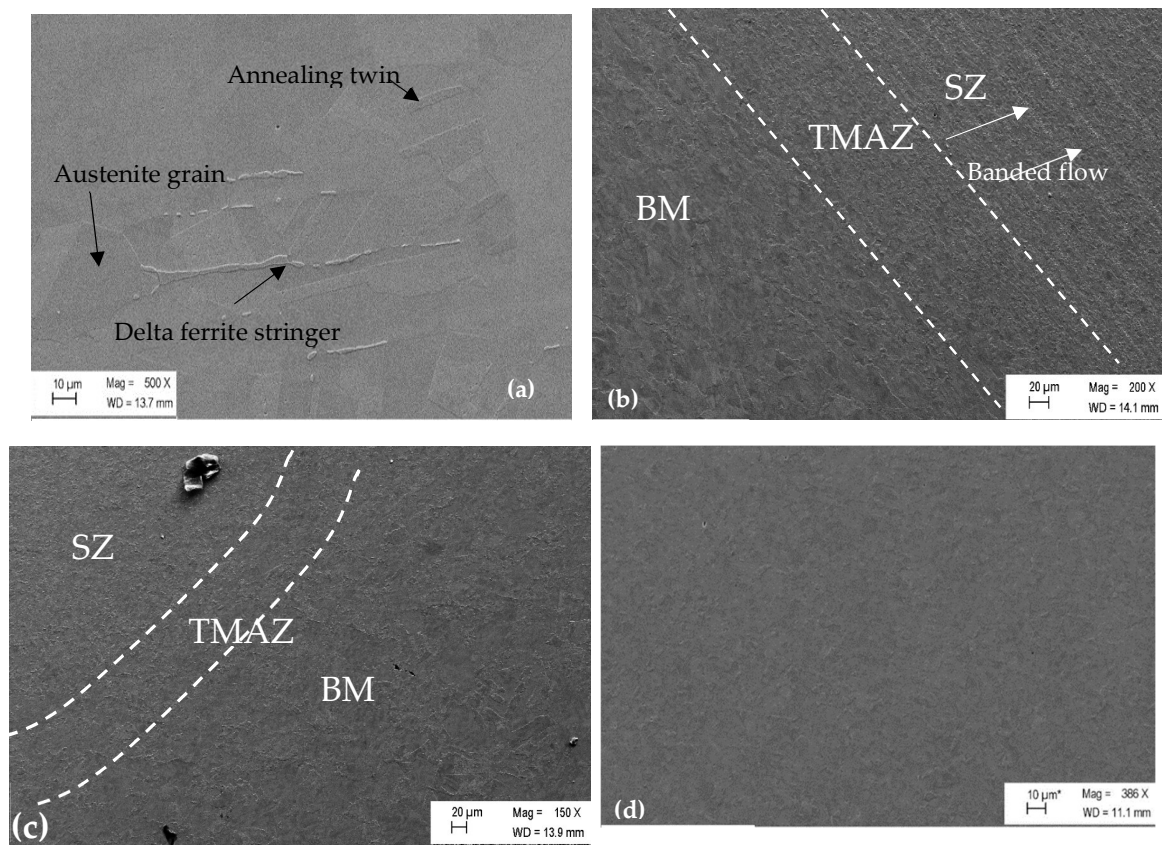


Figure 2. (a) Microstructure of the 304L SS base metal (BM), (b) cross-sectional microstructure of the friction stir welded (FSW) specimen revealing stir zone (SZ), thermo-mechanically affected zone (TMAZ), and base metal (BM) of the advanced side. (c) Microstructure of the receding side. (d) Microstructure of the stir zone (SZ) revealing fine grain austenite.

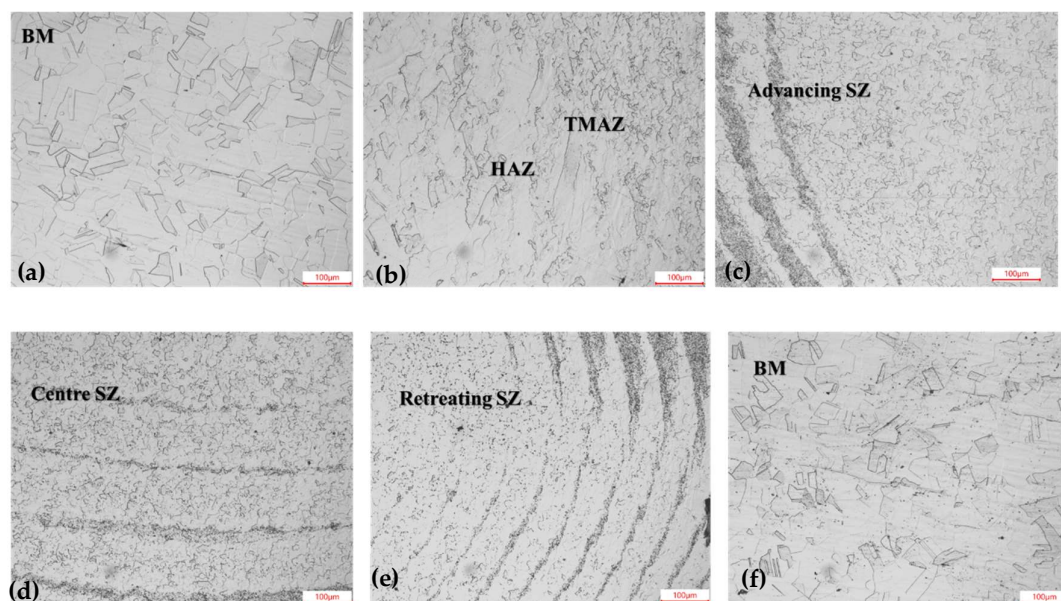


Figure 3. Optical microstructures of the top surface of the BM and FSW specimens at different regions. (a) BM near advancing side, (b) top surface of TMAZ and HAZ of the advancing side, (c) SZ near the advancing side, (d) microstructure at the center of the SZ, (e) SZ near the retreating side, and (f) BM near the retreating side.

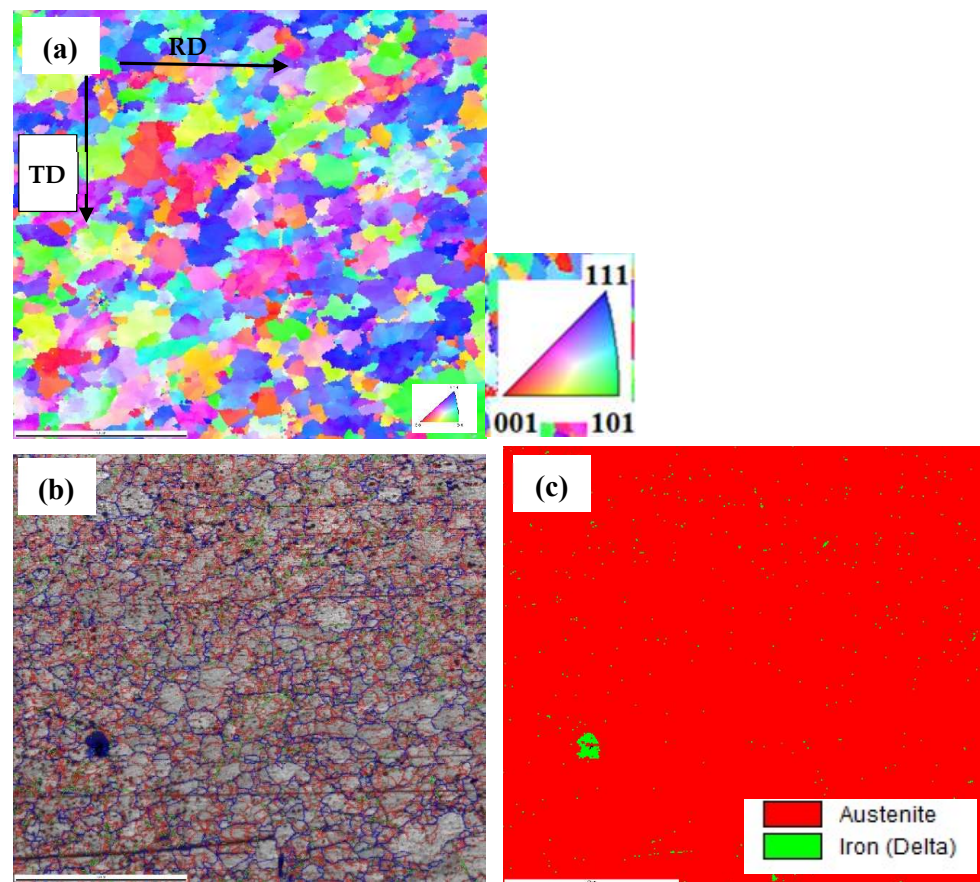


Figure 4. SEM-EBSD analysis showing (a) inverse pole figures (IPF), (b) grain boundary maps, and (c) phase map of the FSW specimens. RD: rolling direction; TD: transverse direction. Note that the length of the marker scales in the above figures is 90 μm .

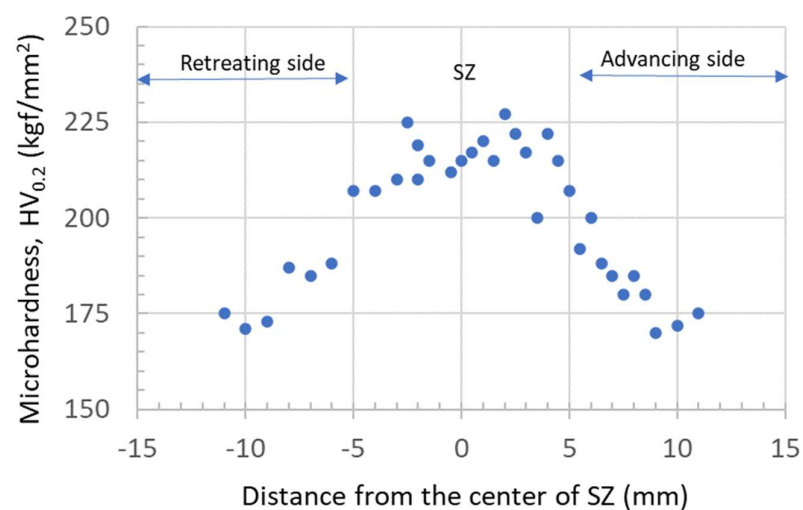


Figure 5. Vickers microhardness profile of the 304L SS FSW specimen friction-stirred at a constant weld temperature of 900 $^{\circ}\text{C}$.

3.2. Corrosion Characterization at Open Circuit Potential (OCP)

3.2.1. Open Circuit Potential (OCP) and Polarization Resistance (R_p)

Figure 6 shows the change in open circuit potential (OCP) with time during the immersion test in 3.5% NaCl+ 5 N H_2SO_4 solution. More noble OCP was observed for the FSW specimen ($-320 \text{ mV}_{\text{Ag}/\text{AgCl}}$) than the BM ($-345 \text{ mV}_{\text{Ag}/\text{AgCl}}$). Linear polarization

tests were carried out to determine the polarization resistance of both specimens, which indicates their ability to resist charge transfer during corrosion. Table 3 shows that the average polarization resistance (R_p) of the FSW specimen (880 ohms) is higher than the BM (575 ohms). As R_p is directly related to corrosion resistance, a higher R_p value of FSW signifies better corrosion resistance. Hence, both OCP and R_p measurement indicates FSW is less susceptible to corrosion than BM, which can be linked to the stability passive film formed on BM and FSW specimens at OCP. As R_p is directly related to corrosion resistance, a higher R_p value of FSW signifies better corrosion resistance. Hence, both OCP and R_p measurements indicate FSW is more corrosion-resistant than BM.

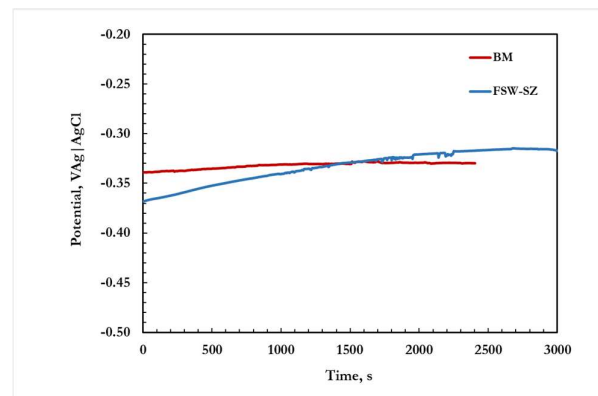


Figure 6. Open circuit potentials (OCP) of 304L SS base material (BM), and friction stir welded (FSW-SZ) specimens in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature.

Table 3. Summary of the results of OCP, LP, and PDP tests in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature.

Sample	OCP, $V_{Ag/AgCl}$	R_p , ohm	β_{anodic} V/dec.	$\beta_{cathodic}$ V/dec.	i_{corr} , $\mu A/cm^2$	i_{pass} , $\mu A/cm^2$	i_{crit} , mA/cm^2	E_{pit} $V_{Ag/AgCl}$
Base material (BM)	0.345 ± 0.05	575 ± 45	104 ± 3.32	90 ± 6.65	103.38 ± 9.25	260.38 ± 30	50.36 ± 4.16	1.071 ± 0.04
FSW (bead-on-plate)	0.320 ± 0.03	880 ± 67	20 ± 4.5	110 ± 3.80	60.35 ± 12.40	270.30 ± 20	115.2 ± 4.2	1.092 ± 0.03

3.2.2. Electrochemical Impedance Spectroscopy (EIS) at OCP

EIS experiments were carried out at OCP to further probe into the overall stability of the passive film. Figure 7a,b show the EIS measurements in Nyquist and Bode plots, respectively. Experimentally obtained EIS spectra were fitted with the electrochemical equivalent circuits (EEC). Figure 7C₁ and C₂ show the EEC circuits used for the BM and FSW specimens, respectively. For BM, the EEC comprised the solution resistance, R_s , the interfacial capacitance at the specimen/electrolyte, Q_1 , the charge transfer resistance at the interface or polarization resistance, R_1 , the resistance of a porous structure of film, R_F , and a leaky capacitance of the porous film, Q_2 . The components Q_1 and Q_2 are constant phase elements (CPE) because the phase angle was less than 90°. The impedance of the CPE can be formulated as $Z_{CPE} = [CPE(j\omega)^n]^{-1}$, where $j = \sqrt{-1}$, ω = frequency, and n is the exponent of the CPE, which varies from 0 (pure resistor) to 1 (pure capacitor). EEC of the FSW specimen has similar components like BM and an additional component inductance, L , which indicates the adsorption of ions on the surface of the working electrode. Two-time constants were observed for the BM, which is common for most self-passivating alloys like stainless steel. On the other hand, a one-time constant and an inductor at low frequencies were observed in the FSW specimen. The bode plot shows the higher impedance, $|Z|$ value for the FSW and, hence, better overall corrosion resistance than the BM. Tables 4 and 5 summarize the values of the EEC components of the BM and FSW, respectively. It is noted that R_1 values (charge transfer resistance) and R_F (film resistance) values of the BM and

FSW from the EIS results were analogous to the polarization resistance measured by the linear polarization method. The EIS results showed that FSW has a better resistance to corrosion at OCP than the BM. However, the impedance values of 304L SS recorded in the 5 N H₂SO₄ + 3.5% NaCl solution at room temperature are an order of magnitude lower than that reported in the hot nitric acid solution [41]. This observation indicates that the 304L specimens were not in a passive state. Luo et al. [42] also reported lower impedance values (<1000 Ω cm²) of the cold-worked 304L SS in contaminated sulfuric acid solution. The Q_1 and Q_2 values are given in the units of S.s^a, and S.s^b respectively, where S represents siemens, s represents second, and a and b are the exponents. The exponent will be unity for a pure capacitor, and a diffusion-controlled CPE component will have an exponent of 0.5. Higher the value of CPE (Q_1 or Q_2) higher is the conductivity and therefore lower the corrosion resistance.

Table 4. The values of electrical equivalent circuit (EEC) elements fitted with the EIS data of the 304L BM specimen after 1 h immersion in 3.5% NaCl + 5 N H₂SO₄ solution at OCP and room temperature.

Specimen ID	R_{sol} (ohm)	$Q_1/10^{-6}$ (S.s ^a)	a	R_1 (ohm)	$Q_2/10^{-6}$ (S.s ^b)	R_F (ohm)	b
Base metal	0.8 ± 0.01	135 ± 5.9	0.8763	160 ± 45	287 ± 23.4	610 ± 84	0.9035

Table 5. The values of electrical equivalent circuit (EEC) elements fitted with the EIS data of the FSW 304L specimen after 1 h immersion in 3.5% NaCl + 5 N H₂SO₄ solution at OCP and room temperature.

Specimen ID	R_{sol} (ohm)	$Q_1/10^{-6}$ (S.s ^a)	a	R_1 (ohm)	R_F (ohm)	L (H)
FSW (bead-on-plate)	0.6 ± 0.01	230 ± 3.2	0.8408	475 ± 15	677 ± 13	1800 ± 126

3.2.3. Potentiodynamic Polarization Scan (PDP)

The potentiodynamic polarization scan results for BM and FSW are shown as the I - V plot in Figure 8. Data obtained from the PDP plots are summarized in Table 3. The FSW specimen shows more positive E_{corr} than the BM. Corrosion current density (I_{corr}) was calculated by extrapolating the linear portion of the cathodic and anodic portions of the polarization plots. The I_{corr} of the FSW (~ 60 μ A/cm²) is significantly lower than that of the BM (~ 103 μ A/cm²). A lower I_{corr} value and more positive corrosion potential indicate that FSW had a better corrosion resistance than BM. The polarization plots show a well-defined active-passive region. Even though the FSW shows lower passive current density than the BM, the passive current density (i_{pass}) values are almost the same for both materials, at around 260 μ A/cm². A slight increase in the passive current density is observed in the potential window of 445 mV_{Ag/AgCl} to 600 mV_{Ag/AgCl} on the FSW specimen, which could be associated with metastable pit formation. The FSW specimen required a higher critical current density for transitioning to the passivation state than the BM (0.115 A/cm² versus 0.05 A/cm²). The high critical current density to achieve passivation indicates that the species are in an active state at the OCP. The anodic Tafel slope of the FSW is much lower than that of BM, while the cathodic Tafel slope is similar in both specimens. The transpassive region starts after reaching an E_{pit} potential, where the current density increases rapidly due to the complete breakdown of the passive film. A more positive E_{pit} signifies better pitting resistance. The E_{pit} potential of the FSW, 1070 mV_{Ag/AgCl}, is marginally higher than the E_{pit} potential of the BM, 1050 mV_{Ag/AgCl}. The measured pH of the 3.5% NaCl+ 5 N H₂SO₄ solution is ~ -0.32 . The redox potential for the oxygen evolution reaction is calculated as 1.049 V_{Ag/AgCl}. Therefore, passivity breakdown and oxygen evolution reaction (OER) overlap in the acidified chloride solution at room temperature. It is noted that the OER requires a significant overpotential. Therefore, the increase in the current at E_{pit} is attributed to the passivity breakdown and a break observed in the polarization plots at around 1.2 V_{Ag/AgCl}, and a surge in the current density could be attributed to the OER.

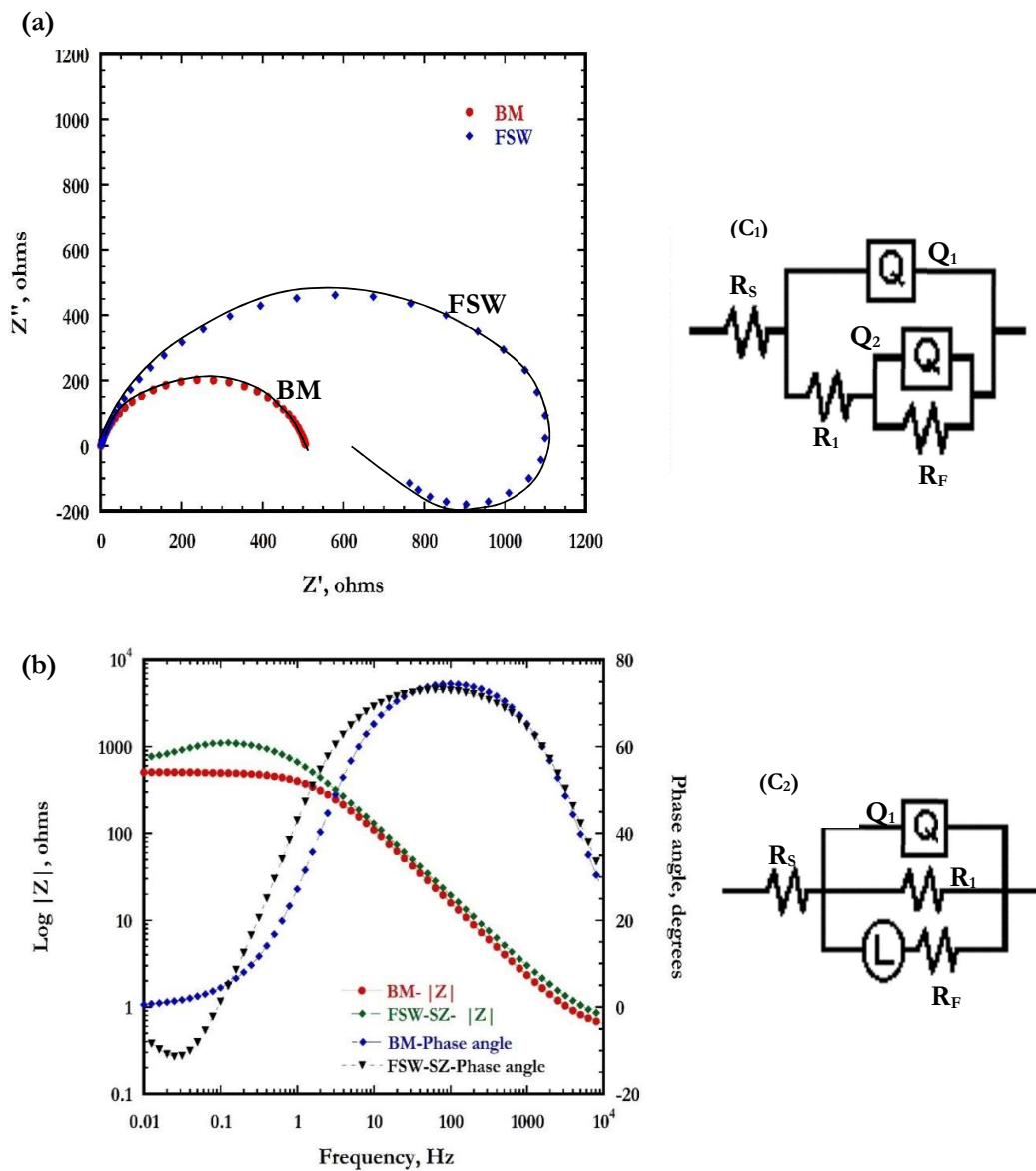


Figure 7. Electrochemical impedance spectroscopy (EIS) of 304L SS base metal (BM) and friction stir welded (FSW-SZ) specimens at open circuit potential in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature. (a) Nyquist and (b) Bode plots, and (C₁,C₂) is the electrical equivalent circuit used for fitting EIS data (C₁) for BM and (C₂) FSW-SZ. The lines connecting the data points of the Nyquist plots are fitted data of the EEC models.

3.2.4. Surface Morphology after Potentiodynamic Polarization

Figure 9a,b show the SEM secondary electron images of the surface of the BM after the potentiodynamic polarization test. Pits are observed to be equally distributed throughout the matrix. Larger pits are mostly formed at the grain boundary of the austenite grains, whereas smaller pits are found inside the austenite grains. Pits are seen at the annealing twins as well. Figure 9c shows a uniform pit formation (mostly dissolution of finer delta-ferrite particles) on the FSW specimen after the potentiodynamic test. The attack appears more of general corrosion than pitting at higher magnification, as seen in Figure 9d.

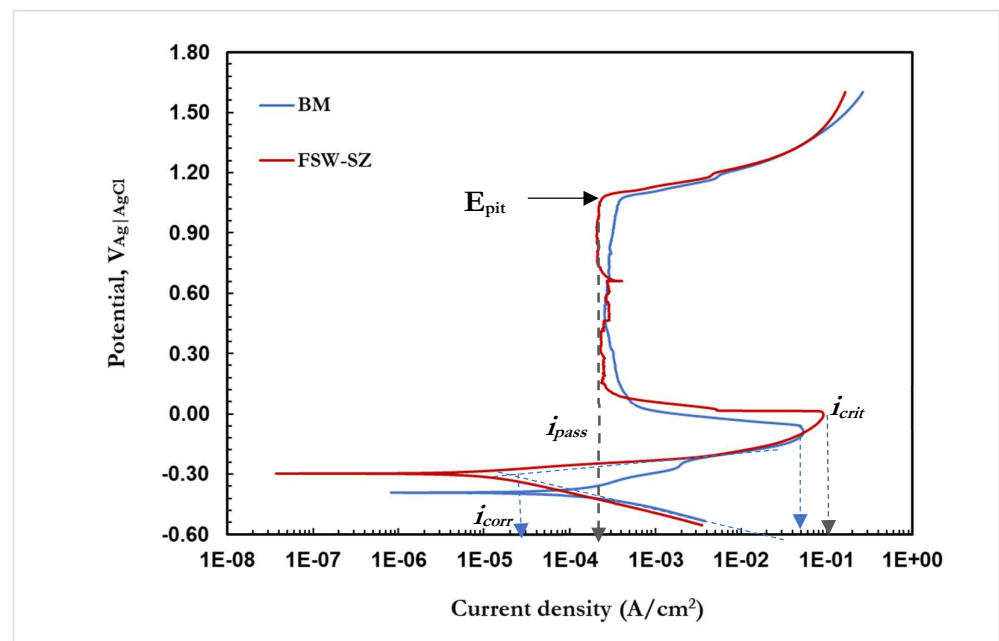


Figure 8. Potentiodynamic polarization scan of 304L SS base metal (BM) and friction stir welded (FSW-SZ) specimens in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature.

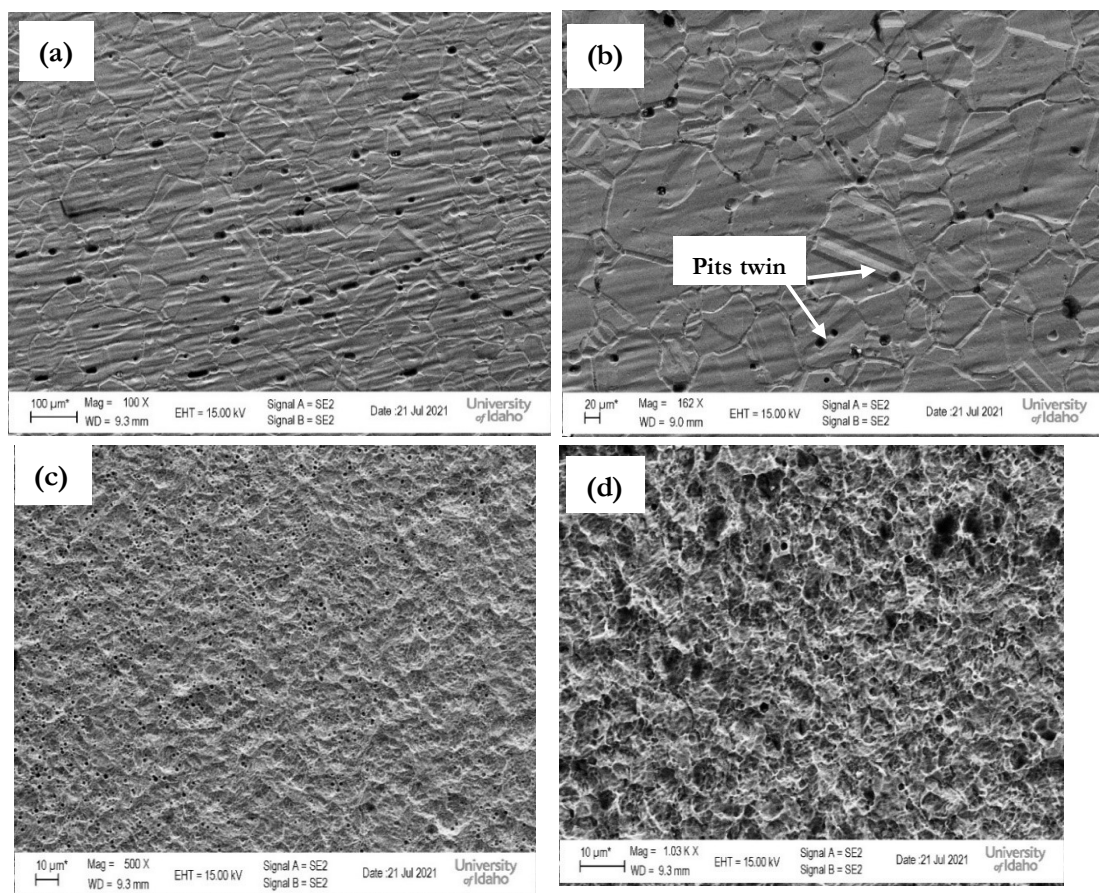


Figure 9. SEM secondary electron images of the surfaces after potentiodynamic polarization scan in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature. (a,b) BM and (c,d) FSW.

3.3. Stress Corrosion Cracking (SCC) in Acidified Chloride Solution

3.3.1. OCP and Failure Time

U-bend specimens of BM and FSW materials were exposed to an acidified chloride solution containing 3.5% NaCl + 5 N H₂SO₄ at room temperature to understand the effect of the FSW process on the SCC susceptibility of 304L SS. Table 6 summarizes the OCP results and time-to-failure of the U-bend specimens. Figure 10a,b show the OCP results of the BM and FSW U-bend specimens during the SCC tests, respectively. The OCP shifted to more positive values with time for both materials. Interestingly, the OCP values are in the active region of the polarization plots given in Figure 8. Therefore, SCC failure was observed not in the passive region or active-to-passive transition region as generally expected but in the active region of the polarization. The U-bend samples of both materials failed almost after 5–6 days with a 6–8 h difference when exposed to the acidified chloride solution. Figure 11a shows the appearance of the failed BM U-bend sample. The BM failed at the center of the bent region. On the other hand, the FSW U-bend specimen did not fail in the middle of the bent region where the stirred zone was located (Figure 11b,c). The FSW U-bend specimens failed at the boundary between the stir zone (SZ) and the BM, more likely in the thermo-mechanically affected zone (TMAZ). Typically, the SZ showed a higher hardness (Vickers hardness number around 240 (kg(f)/mm²)) than the BM (~170 VHN). A hardness gradient is observed in the TMAZ between these two hardness values, as seen in Figure 5. The hardness gradient and associated microstructural changes could drive SCC crack propagation along the TMAZ in the acidified chloride solution at room temperature. Furthermore, it is noted that the estimated maximum outer fiber stress on the FSW is about 60% higher than the BM, even though the strain values are similar. The BM specimen had a uniform microstructure. Therefore, no stress gradient was expected along the bent region. However, non-uniform microstructures along the bent region of the FSW could have resulted in a non-uniform stress field, which rendered the TMAZ more susceptible to SCC.

Table 6. Summary of U-bend SCC tests in 3.5% NaCl + 5 N H₂SO₄ bulk solution at room temperature.

U-Bend Sample	Time to Failure, Hours	Initial OCP, V _{Ag/AgCl}	Final OCP, V _{Ag/AgCl}
Base material (BM)	144 ± 8	−0.341	−0.264
FSW (bead-on-plate)	132 ± 6	−0.294	−0.246

3.3.2. Metallographic Study

Figure 12a–d show low-magnification SEM images of the U-bend samples across their thickness. The BM specimen shows several cracks, and the branching of cracks is also observed, as seen in Figure 10a. SZ did not show cracks, as seen in Figure 12b, in general. However, a few cracks were seen at the center of the thickness (Figure 12c) generated by the corroded delta ferrite in the matrix. Crack lengths in the SZ are not large enough to fail the material across the SZ. The TMAZ portion showed many long and branched cracks, which explains the failure of FSW samples from the TMAZ portions. Figure 13a shows the mode of crack propagation in BM. Predominantly transgranular cracks were observed. The presence of deep pits also led to the branching of stress corrosion cracks. Delta ferrite plays a major role in crack generation in the BM, as seen in Figure 13a. The dissolved delta ferrite regions acted as crack initiation and branching sites [43]. Stress corrosion cracks did not propagate through most of the Σ3 twin boundaries. No cracks were observed in the majority of the stir zone, as seen in Figure 13b. SZ contains a very small amount of delta ferrite, which dissolved, and the vacant sites acted as crack initiation sites. Figure 13c shows the optical microscopy of the crack propagation predominantly in the TMAZ of the FSW U-bend sample. Figure 13d shows the crack transitioning to the base metal region of the FSW U-bend specimen.

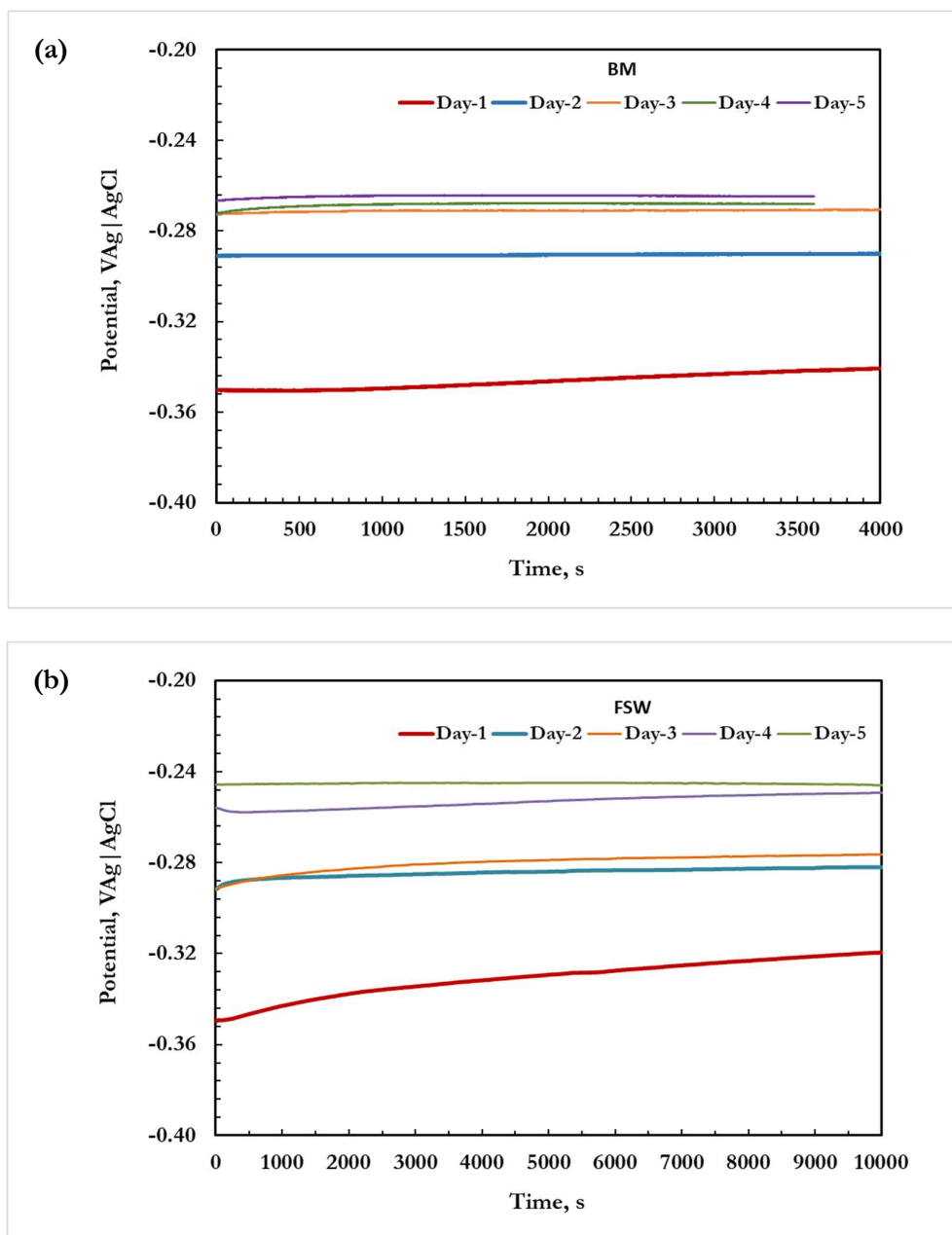


Figure 10. Open circuit potential (OCP) during SCC test in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature. (a) BM and (b) FSW U-bend specimen.

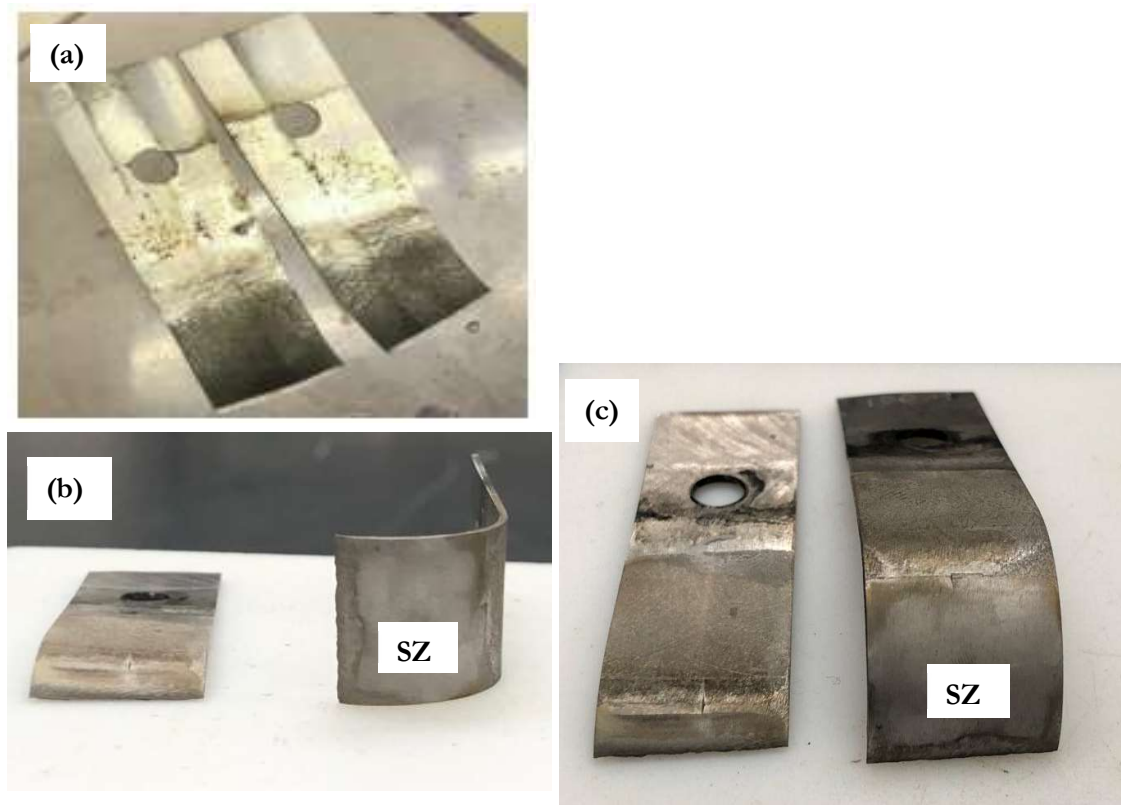


Figure 11. (a) 304L base material (BM) and (b,c) FSW U-bend specimens after the test in 3.5% NaCl + 5 N H₂SO₄ solution at room temperature. No cracks were observed in the SZ. The failure occurred along the TMAZ/BM.

3.3.3. Fractography

Figure 14a–d shows the FE-SEM fractography of the failed U-bend samples in the acidified chloride solution at room temperature. The BM specimens showed a brittle transgranular mode of failure. The fracture surface showed some corrosion pits and secondary cracking in the quasi-cleavage planes. Dislocation channel or slip line-like features could be observed on the fracture surface in Figure 14a,b. The secondary cracks could be attributed to the dislocation pile-up along a slip plane that was not properly oriented in the loading direction initially, but later dislocations became mobile due to the creep–corrosion interaction. Figure 14c shows mixed-mode cracking of the FSW specimen. Figure 14d illustrates the quasi-cleavage planes of the fracture surface in the TMAZ/BM portions of the FSW specimen.

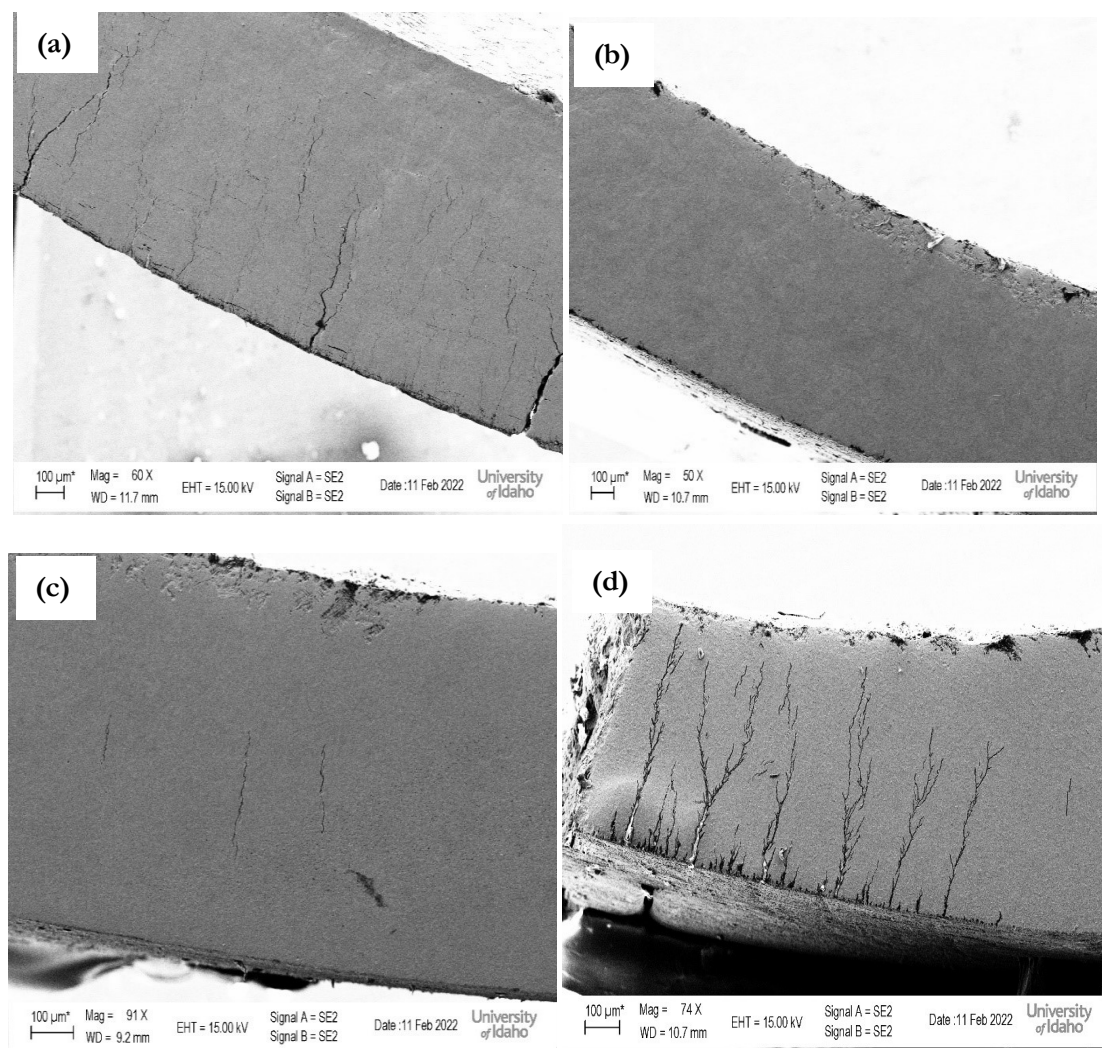


Figure 12. Cross-sectional view of the cracking of U-bend specimens tested in 3.5% NaCl+ 5 N H₂SO₄ solution at room temperature. (a) Multiple cracks in 304L BM; (b,c) center cracks in the stirred zone (SZ) boundary; and (d) crack branching in the TMAZ of the FSW.

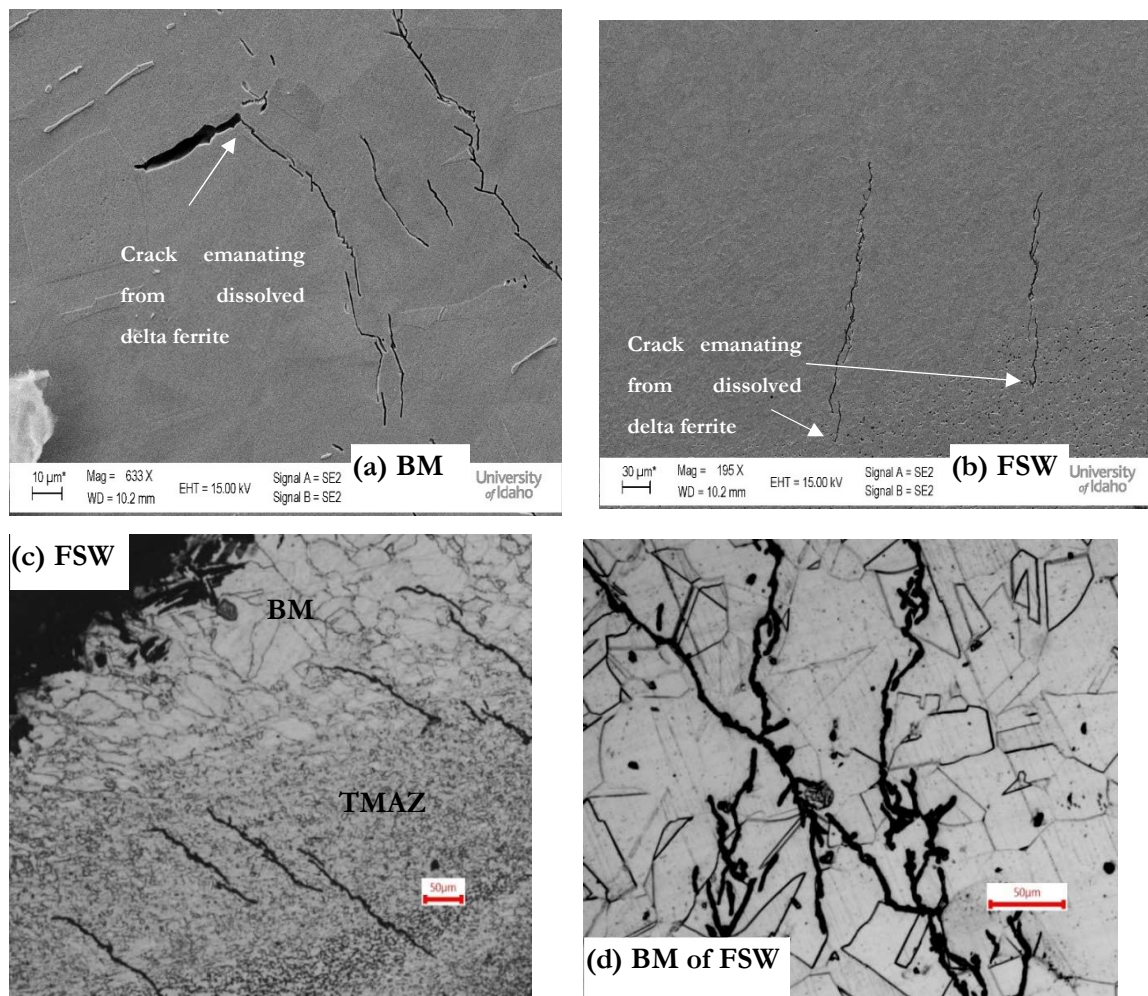


Figure 13. Cross-sectional view of the cracking of U-bend specimens tested in 3.5% NaCl+ 5 N H₂SO₄ solution at room temperature. (a) Multiple cracks in 304L BM; (b) center cracks in the stirred zone (SZ) boundary emanating from the dissolved delta ferrite regions; (c) cracks observed in the TMAZ of the FSW; and (d) crack branching in the BM region of the FSW.

3.4. Stress Corrosion Cracking (SCC) in Boiling MgCl₂ Solution

The BM and FSW U-bend specimens failed within 24 h in the boiling MgCl₂ solution. Crack initiation was observed within 18 h of the experiment in both specimens. The FSW showed fewer cracks than the BM, but both samples failed within 24 h. Crack propagation in BM shows mostly transgranular cracks, as seen in Figure 15a. A few intergranular cracks are also observed (Figure 15a,b). In the FSW sample, the delta ferrite in the SZ corroded, and large cracks with branching originated and propagated from that region, as seen in Figure 15c,d. Figure 16a,b show the fractography of the BM, which revealed quasi-cleavage type fracture with cracking by the emergence of slip steps and their dissolution. The fracture surface of the FSW specimens indicated a mixed mode of cracking with intergranular and transgranular modes of cracking. The IGSCC could have occurred along the random grain boundaries.

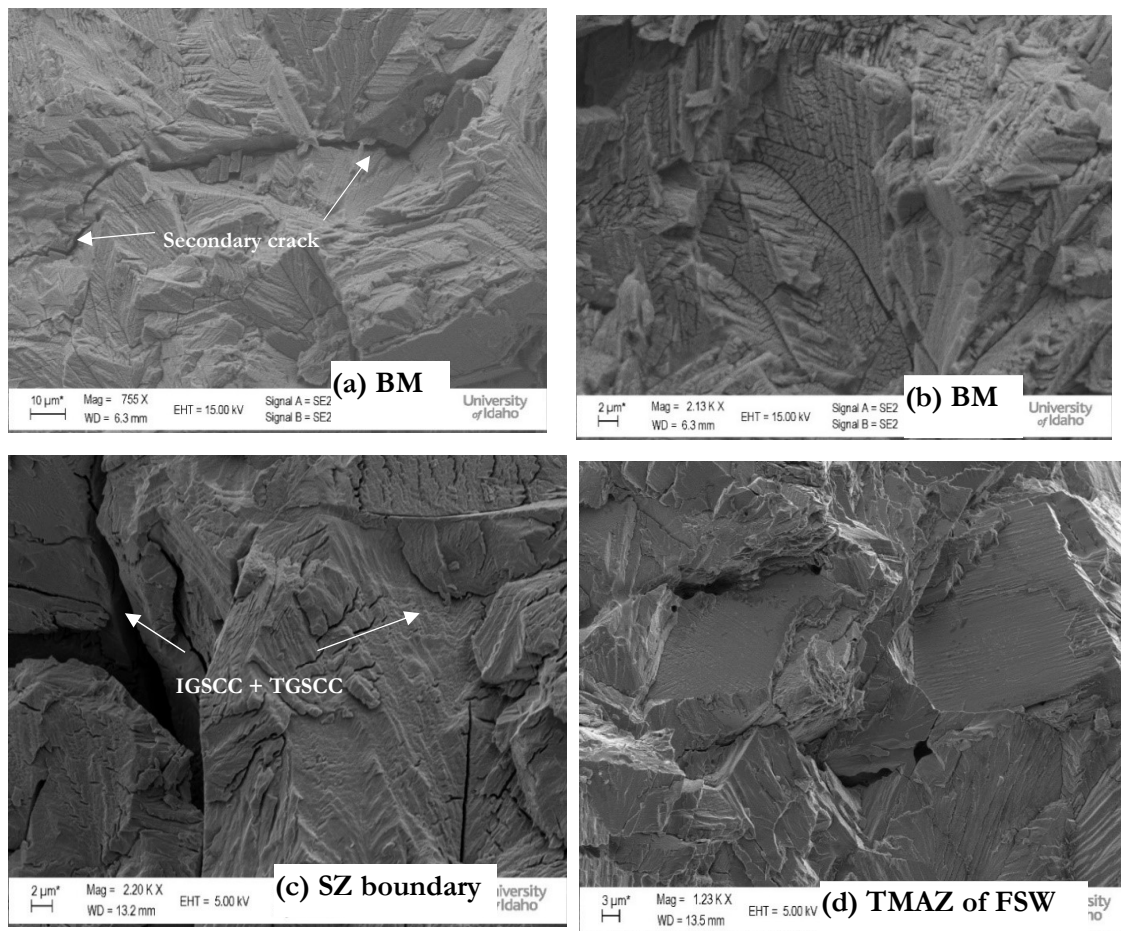


Figure 14. FE-SEM fractographs of the cracked U-bend specimens tested in 3.5% NaCl+ 5 N H₂SO₄ solution at room temperature. (a) TGSCC in 304L BM; (b) secondary cracking in the BM; (c) mixed-mode cracking along the SZ boundary; and (d) cleavage-type fracture in the thermos-mechanically affected zone (TMAZ) of the FSW.

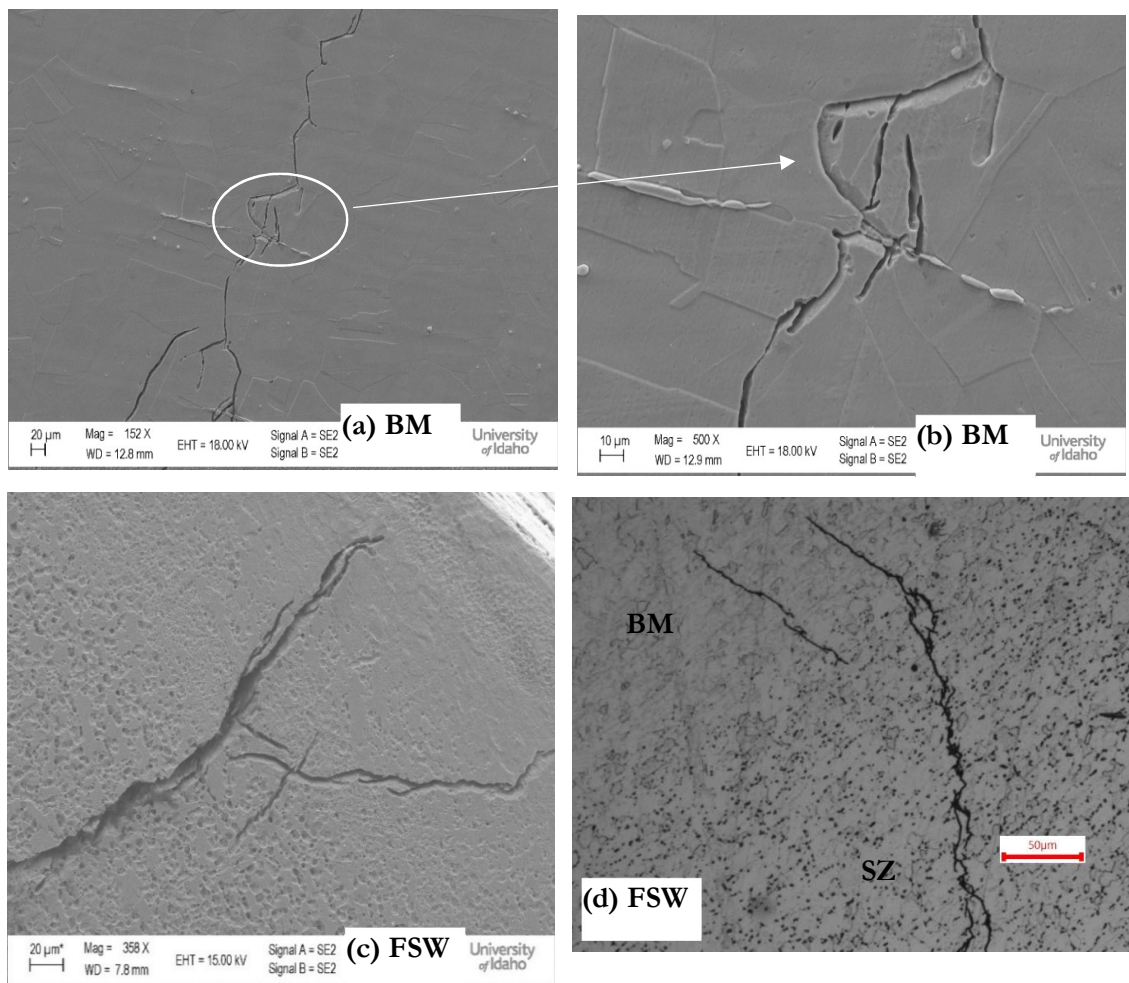


Figure 15. Cracking of U-bend specimens tested in the boiling MgCl_2 solution at 155°C : (a) mixed-mode cracking in the 304L BM; (b) crack branching in the BM; (c) cracking of the FSW; and (d) cracks propagate through SZ, TMAZ, and BM of the FSW.

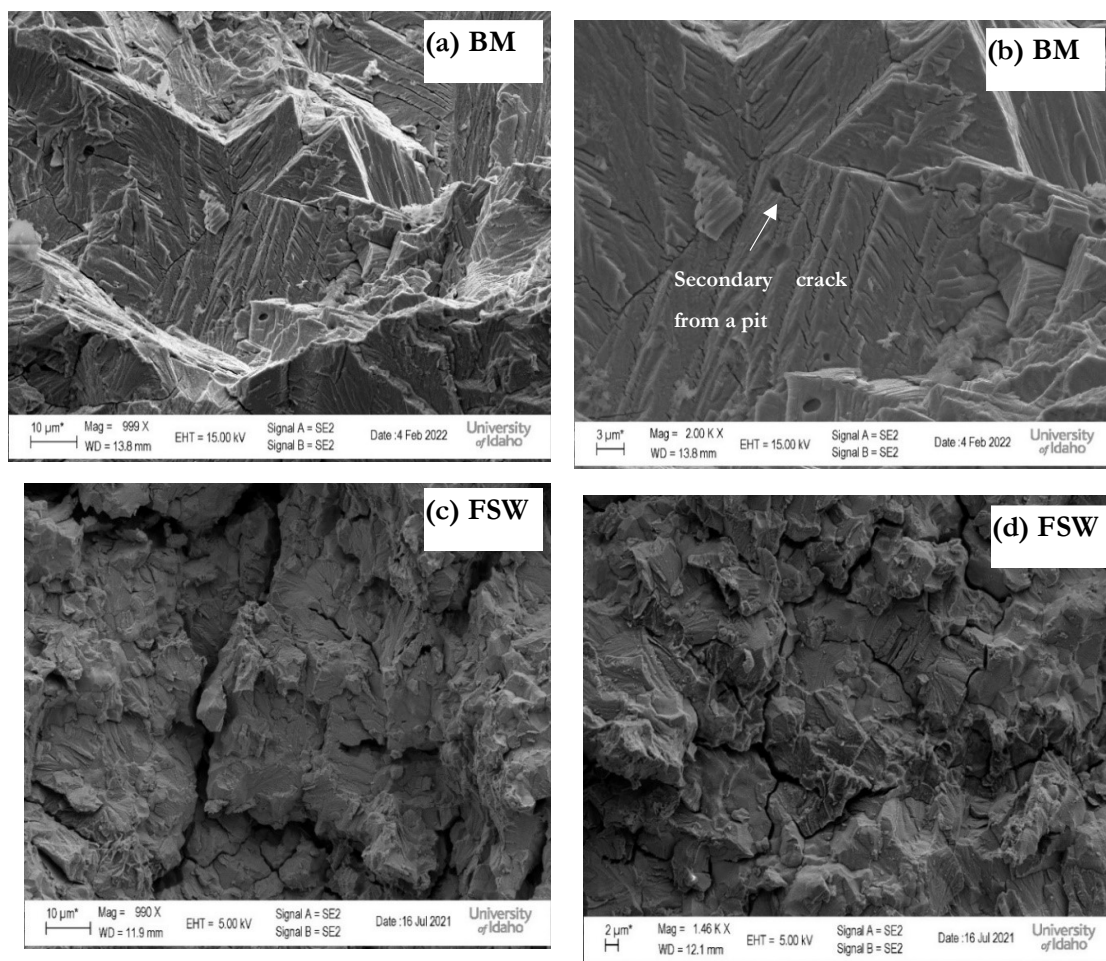


Figure 16. FE-SEM fractographs of the cracked U-bend specimens tested in the boiling MgCl_2 solution. (a) TGSCC in 304L BM; (b) secondary cracking in the BM; (c,d) mixed-mode cracking of the FSW.

4. Discussion

4.1. Role of Microstructures

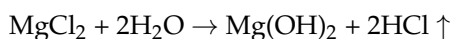
The corrosion resistance of FSW in the acidified chloride solution was marginally better than that of BM. The better corrosion performance of the FSW can be attributed to its finer grain size and a higher fraction of low-angle grain boundaries. The effect of grain refinement on the corrosion resistance of austenitic stainless steels in both chloride and sulfuric acid solutions has been studied by a few researchers, who have reported both positive and negative findings [44,45]. Di Schino and Kenny [44] studied the effect of grain refinement of AISI 304 austenitic stainless steels in different chlorides FeCl_3 and NaCl , boiling H_2SO_4 medium. They observed that the intergranular corrosion and pitting resistance have improved with grain refinement but reduced general corrosion resistance with grain refinement. Aughuy et al. [45] tested 304L stainless steel samples with 5 μm , 11 μm , and 28 μm grain sizes in 3.5% NaCl solution and found no such improvement in pitting potential (E_{pit}) was observed. However, the frequency of metastable pit formation was decreased in smaller grain-size samples due to stable passive film formation [45]. The grain refinement during a plastic deformation process like friction stir welding involves more complex changes in the microstructure, such as secondary phase participation, formation of banded structure, and alteration of grain boundary structures along with the grain refinement [46,47]. Secondary phases, such as sigma phase formation, have detrimental effects on the corrosion resistance of 304L SS [48]. The grain refinement in the 304L FSW sample improves the general corrosion resistance, but E_{pit} or pitting corrosion resistance did not improve significantly. The presence of a higher fraction of

corrosion-resistant $\Sigma 3$ special grain boundaries in 304L BM compensates for the negative effect of its larger grain size on general corrosion or pitting resistance. 304L FSW, on the other hand, has a grain-refined microstructure along with a larger area of low-angle grain boundaries (LABs), which provide better general corrosion resistance [39,49] than the BM.

An inductive loop in the EIS of FSW showed that the absorption of SO_4^{2-} ions competed with the Cl^- ions and thus minimized the effect of Cl^- ions. Generally, the ions may be categorized as (i) water-structure-making ions referred to as kosmotropes and (ii) water-structure-breaking ions or chaotropes according to the properties of their surrounding hydration shell [50]. Kosmotrope ions exhibit a relatively high surface charge density and form high electric fields at short distances, which helps bind water molecules strongly in their vicinity. The chaotropic ions are usually large, and the electric fields around them are weak, leading to a loose hydration shell that can be easily removed. The SO_4^{2-} ions are considered kosmotropic, and due to their high charge density, they remain preferentially adsorbed to preserve their hydration state. This helps prevent aggressive anions, such as Cl^- which is considered chaotropic, from accessing the surface of the specimen [51,52]. The adsorption was not predominant in the BM. The increased adsorption of ions on the FSW specimens could be attributed to the increased grain boundary areas and banded microstructures. A similar type of behavior was observed by other researchers; for example, Luo et al. [42] noted that the cold working of 304L showed increased adsorption of OH^- ions.

In this study, the grain refinement and increase in the LABs fraction in FSW improved the stability of the passive film. The EIS measurement at the OCP revealed that the FSW had higher passive film resistance. It was also reported that with the increasing concentration of the SO_4^{2-} ions the 304L SS showed more resistance towards passivity breakdown [53]. The SZ was relatively free of stress corrosion cracks in the acidified chloride solution tested at room temperature. This could be due to the fine grain size and a large fraction of low-angle grain boundaries that prevented the formation of large slip steps. When the slip steps emerge from the surface, if the height is not sufficient, it will not cause a rupture of the passive film. Therefore, the SCC occurred in the TMAZ where the grain size was larger due to recrystallization leading to planar slips.

The IGSCC and TGSCC failure morphologies were reported in the literature for 304 SS, depending on the temperature and strain rates. A decrease in the boiling point (at low MgCl_2 concentrations (30–40 wt%) or 115–135 °C) resulted in a higher fraction of IGSCC [54,55]. TGSCC was observed at strain rates slower than 10^{-5} s^{-1} , while IGSCC was observed at higher strain rates in a boiling 42% MgCl_2 solution at 143 °C [56]. Predominantly, TGSCC was observed at a low-stress level (~150 MPa) at 143 °C. When the stress increased to 300 MPa, the fracture morphology transitioned to predominantly IGSCC [57]. The TGSCC was associated with anodic polarization of the sites, while the IGSCC was related to hydrogen fugacity due to cathodic polarization. The difference in fracture morphology in the MgCl_2 solution could be attributed to the pH condition of the solution due to hydrolysis, as follows:



The freshly prepared solution will be more acidic, while the solution boiled for longer periods will lose the HCl by evaporation and become more alkaline. TGSCC is observed at higher pH, and IGSCC is related to low pH conditions. It is interesting to note that predominantly, hydrogen reduction reaction has been reported as the primary cathodic reaction and not oxygen reduction despite the presence of oxygen [58]. The boiling condition purges out the dissolved oxygen in the MgCl_2 solution. Therefore, hydrogen reduction was the predominant cathodic reaction. The hydrogen reduced on the surface of the U-bend specimens could have diffused into the austenite lattice. The stirred zone of the FSW contained high dislocation density due to severe plastic deformation [28]. The dislocations are reversible traps for hydrogen with a binding energy of about 0.272 eV [59]. The reversible traps increase the hydrogen solubility and decrease the hydrogen diffusivity [51]. Hydrogen can

easily be transported by the mobile dislocations. When the mobile dislocations are pinned at the grain boundaries, hydrogen could irreversibly be trapped by the grain boundaries. Segregation of hydrogen at the random grain boundaries could decrease the surface energy of the grain boundaries by the Gibbs surface excess relation:

$$-\frac{d\gamma}{dC} = \frac{RT\Gamma_H}{C_H} \quad (1)$$

where $-d\gamma/DC$ is the decrease in the grain boundary (GB) energy with the concentration of hydrogen, Γ_H is the surface excess of hydrogen at the GB, C_H is the bulk concentration of hydrogen in the SZ, R is the universal gas constant, and T is the absolute temperature. The decrease in the GB energy would promote intergranular fracture. Therefore, the observed mixed-mode cracking of the FSW in the boiling $MgCl_2$ could be attributed to the hydrogen-assisted SCC in the SZ.

The SCC initiation of U-bend specimens of 304 SS bare and FSW in the acidified chloride solution at room temperature can be described by linear perturbation theory initially proposed by Asaro and Tiller [60] and later extended to morphological analyses of anodic surface films by several other groups [61–63]. Early stages of chloride-induced pitting or passivity breakdown are also explained by the perturbation theory, where morphological instability is related to a reduction in surface energy due to chloride adsorption [64]. The SCC propagation shall be explained by the film rupture-dissolution model described widely in the literature [46–50].

4.2. SCC Initiation

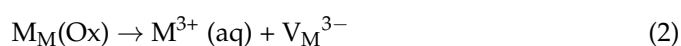
A qualitative phenomenological discussion will be presented here to explain the SCC initiation. It is well-accepted that an impervious barrier-type oxide layer with uniform thickness forms during the initial stages of passivation. The thickening of this barrier-type oxide layer is associated with growth-related compressive stresses. The parameters that promote the compressive stresses are (a) high Pilling–Bedworth ratio (~ 2.01 for Cr_2O_3) and (b) electrostriction stress due to the applied field and changing dielectric constants due to the compressive growth stress as well as variation in the concentration of ionic defects such as oxygen vacancies across the oxide layer thickness [65]. The compressive stresses acting on the film would cause buckling and affect the planar nature of the film [66]. A planar metal/oxide interface is considered to be stable. Any perturbation at the interface implies instability. A sinusoidal morphological instability is introduced at this stage. The instabilities could be attributed to the variations or fluctuations of the following conditions: fluctuations of adsorption and desorption of chloride or hydroxyl ions, competitive adsorption between Cl^- and OH^- ions, fluctuations in the anodic and cathodic sites, localized fluctuations in the pH and temperature, variations in the ionic concentration, variations in the valence state of ions, and localized transition from disordered (amorphous) state to short-range ordered or crystalline state.

The oxide growth stresses and service stresses (or applied strain in terms of U-bending) lead to instability. This instability increases the surface area of the film which will be counteracted by the surface energy of the film. The wavelength and amplitude of the instability are determined by these competing parameters. Under favorable conditions, the perturbation grows, leading to easy crack initiation. The perturbation occurs both at the oxide/electrolyte interface and at the metal/oxide interface as well. Yu et al. [67] reported roughening of the oxide surface when chlorides are present, indicating perturbation of the oxide/electrolyte interface. On the other hand, Zhang et al. [68] showed that transportation of chloride across the passive film resulted in perturbation of the oxide/metal interface, while a planar metal/oxide interface was observed without chloride. These authors evaluated single crystalline FeCr15Ni alloy in 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 0.3 M NaCl electrolytes at room temperature. A bi-layered (bottom Cr-rich and top Fe-rich oxide) passive film of about 4–5 nm thick was observed. The film/metal interface was sharp and straight in the chloride-free solution, while an undulated metal/oxide interface was

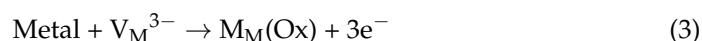
observed in the chloride-containing solution. The metal/film interface contained about 1% chloride, while the outer layer contained only 0.1%. Therefore, the trigger for undulation or perturbation was the chloride excess that decreased the surface energy of the metal/oxide interface. The chloride ions were considered to have permeated along the amorphous-nanocrystal interfaces. The metal/oxide interface was perturbed only when the chloride ions arrived at the interface. This required a connected pathway (nanocrystal/amorphous interface) traversing the oxide layer thickness. In the absence of a connected pathway, no chloride reached the interface, and therefore, no perturbation of the metal/oxide interface was observed. Therefore, the crack or pit initiation event could be related to the aging of the amorphous film nucleating nanocrystals and coalescence of the nanocrystals at select locations that form a continuous path for chloride ions to permeate and reach the metal/film interface.

The SCC initiation time includes the time accumulated for the following activities:

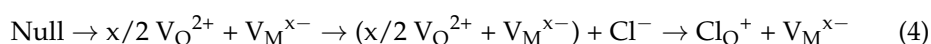
- Formation and growth of planar passive film.
- Development of passive film growth stresses as a function of time ($d\sigma/dt$) superimposed on applied stress and reaching a threshold value.
- The growth stress includes electrostriction stresses due to changes in the dielectric constant, which is time-dependent on the migration of ionic defects.
- Surface diffusion of chloride or hydroxyl ions and adsorption at critical sites result in reduced surface energy and undulation of the oxide/electrolyte interface.
- Aging of the passive film: activities include the annihilation of point defects, nucleation of the short-range ordering of nanocrystals from the amorphous structure, and formation of the continuous pathway of the interface between amorphous and nanocrystals in the passive film across its thickness.
- Migration of chloride ions along the interface between the nanocrystal and amorphous. When there is a continuous path, the chloride ions reach the metal/oxide interface and undulate it. If the interface pathway is not continuous, the chloride ions will not reach the metal/oxide interface, and there will not be any undulation. Therefore, pit initiation or crack initiation sites depend on the continuous pathway for chloride ion migration.
- The alternate mechanism of pit initiation could be based on the point defect model proposed by Macdonald [69]. According to this model, cation vacancies are created at the oxide/electrolyte interface by the reaction:



- The cation vacancies migrate to the metal/oxide interface due to the potential gradient across the passive film and consumed by the film formation reaction:



- Adsorption of chloride ions on the oxide surface leads to interaction with oxygen vacancies, which in turn releases more cation vacancies by autocatalytic reactions:



- When the concentration of cation vacancies reaching the metal/oxide interface is higher than the concentration of cation vacancies consumed by reaction (3), the surplus vacancies condense and form voids at the metal/oxide interface. The voids detach the oxide layer from the metal substrate, and the growth is arrested at that location. However, the dissolution reaction (2) continues which ultimately results in pit initiation at that location.

The diffusivity of point defects (majority charge carriers) can be calculated using the relation:

$$D = \frac{k_b \times T}{\rho \times n \times z \times q^2} \quad (5)$$

where k_b is the Boltzmann constant, T is the temperature in K, ρ is the resistivity of the oxide, n is the charge carrier density, z is the valance state, and q is the elementary charge.

For an oxygen vacancy concentration of 10^{21} cm^{-3} , the diffusivity of oxygen at room temperature, assuming that oxygen ion diffusion entirely occurs by transport of oxygen vacancies, can be estimated on the order of $10^{-16} \text{ m}^2/\text{s}$. When metal cation and oxygen species show a similar order of magnitude diffusivity, one should expect a planar metal/oxide interface. Wide variations in the diffusivities of these species would result in a corrugated interface, as observed in the case of high-temperature oxidation of alloys [70].

4.3. SCC Propagation

The SCC propagation in the acidified chloride solution at room temperature occurs by slip-step emergence, passive film breakdown, and slip-step dissolution mechanism that results in brittle crack propagation in cleavage or low-energy planes. Planar slip systems in the 304 SS BM are considered due to their low stacking fault energy. However, the dislocation cell structure would make the slip planes wavy in the FSW condition. A planar slip system may not be present in the FSW material. Therefore, the SCC occurred predominantly in the TMAZ, which showed a partially recrystallized grain structure. It is envisaged that dislocations are pinned by the passive film on high-density {111} planes. However, as described earlier, surface perturbation due to stresses and reduced surface energy due to chloride adsorption would weaken the passive film. Therefore, the dislocations emerge from the passive film at the low surface energy sites, exposing bare metal surfaces to corrosion attack. Furthermore, the adsorption of anions on the bare surface decreases the surface energy of low-density planes such as {100} or {110}, and the tensile stress component leads to brittle fracture. The active metal dissolution results in the creation of metal vacancies at the crack tip. The dislocation–vacancy interaction helps the emergence of dislocations and increases the localized plasticity and creep strain. The creep strain manifests into crack tip strain. The crack tip strain rate can be a function of the interaction between the metal vacancy creation rate and the interaction between the dislocation, making it mobile. However, the emergence of slip steps in the fine-grained SZ might not result in the breakdown of the passive film due to insufficient step heights [71]. Therefore, no SCC was observed in the SZ.

The brittleness of 304 SS in the boiling MgCl_2 or in the acidified chloride solution could be related to Cottrell's equation [72]:

$$(\tau_i D^{\frac{1}{2}} + k')k' = G\gamma_s\beta \quad (6)$$

where τ_i = the resistance to dislocation movement, D = grain size, k' = microscopic stress intensity factor related to release of dislocation from a pile-up, G = shear modulus, γ_s = effective surface energy or crack extension force, β is constant related to ratio of shear stress to normal stress, $B = 0.5$ for tension, and 0.33 for a notch.

If the value of LHS of Equation (5) is lower than the RHS ($G\gamma_s\beta$), a microcrack can form but will not grow. If the RHS is lower than the LHS, it leads to brittleness. High values of τ_i , k' , or D would increase brittleness. Low values of γ_s will also result in brittleness. In this investigation, brittle fractures are associated with low surface energy. Comparing the brittleness between the annealed and FSW materials, it is considered that the FSW may have a higher τ_i value due to very high dislocation densities and deformed structures but a lower D value than that of the annealed material. Despite having higher τ_i and k' values, the FSW showed slightly better SCC resistance than the annealed base material because of its finer grain size. The absence of cracking in the stirred zone of the FSW in the acidified chloride solution at room temperature could be associated with the balance

between the τ_i , D , and γ_s values. At low temperatures, a slightly high surface energy is anticipated. Therefore, the region (TMZ) having a larger grain size is more susceptible to cracking than the region having a smaller grain size (stirred zone). Even though the FSW and BM specimens showed almost similar failure times, the U-bend specimens of the FSW were subjected to 60% more stress at the outer fiber than the BM specimens. Therefore, overall, the FSW specimens showed better tolerance to SCC than the base metal 304 SS.

5. Conclusions

Friction stir welding was carried out on a 12.7 mm thick hot rolled 304L stainless steel plate under an isothermal condition by maintaining the weld temperature at 900 °C using a polycrystalline boron nitride tool. Microstructural, microhardness, electrochemical polarization, and stress corrosion cracking studies were performed on the FSW specimens and unaffected base metal (BM). Based on this study, the following conclusions are drawn:

1. The FSW of 304 SS resulted in finer grains (12–20 μm), a higher fraction of low-angle grain boundaries (67%), and a breakdown of delta ferrite stringers to small particles, whereas the BM showed longer delta ferrite stringers, larger grains (32–60 μm), and a lower fraction of low-angle grain boundaries (2.2%).
2. The stir zone of the FSW specimen showed a hardness value of 225 HV, while the hardness of BM was $\sim$ 170 HV.
3. The electrochemical polarization behaviors of the FSW and BM in the 5 N H_2SO_4 + 3.5% NaCl at room temperature (24 °C) were almost similar.
4. The FSW U-bend specimens were subjected to 60% more outer fiber stress than the BM specimens.
5. FSW and BM U-bend specimens failed due to stress corrosion cracking in the acid-chloride solution (room temperature) and the boiling MgCl_2 solution.
6. The FSW and BM specimens failed within 24 h in the boiling MgCl_2 solution. On the other hand, a five-fold increase in the failure time was observed in the acidified chloride solution at room temperature.
7. No cracking was observed in the stirred zone of the FSW specimens in the acidified chloride solution at room temperature, which was attributed to the benefits of optimal grain size and grain boundary characteristics.
8. Fractography shows mostly transgranular modes of failure for both BM and FSW when tested at room temperature, while mixed-mode cracking was observed in the boiling MgCl_2 solution. The presence of delta ferrite negatively affected the SCC resistance in both the acid-chloride and boiling MgCl_2 solutions.
9. Hydrogen-assisted SCC could be the failure mechanism in the boiling MgCl_2 solution, while predominantly passive film rupture and slip-step dissolution occurred in the acidified chloride solution at room temperature.
10. The FSW specimens showed higher tolerance to SCC than the base metal.

Author Contributions: Conceptualization, K.S.R., I.C. and S.J.; methodology, A.N., M.B. and J.D.; software, J.D. and S.J.; validation, A.N., M.B. and J.D.; formal analysis, I.C. and K.S.R.; investigation, A.N. and M.B.; resources, I.C., K.S.R. and S.J.; data curation, A.N. and M.B.; writing—original draft preparation, A.N. and K.S.R.; writing—review and editing, M.B. and I.C.; visualization, A.N.; supervision, I.C. and K.S.R.; project administration, I.C.; funding acquisition, I.C., K.S.R. and S.J.; All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the United States Department of Energy’s Office of Nuclear Energy under award number DE-NE0008776.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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