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Effect of the microstructure on the corrosion behavior of dissimilar friction stir-welded 304 austenitic stainless steel and Q235 low-carbon steel joints

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Abstract
To investigate the effect of the microstructure on the corrosion behavior of the dissimilar friction stir welded (FSW) joint between 304 stainless steel (SS304) and Q235 low-carbon steel, the microstructure of the joint in this work was characterized by optical microscopy, scanning electron microscopy (SEM), and electron backscatter diffraction. The corrosion behavior in different zones of the joint was evaluated by the electrochemical tests, and the corresponding corrosion morphologies were illustrated via SEM and laser confocal scanning microscopy. According to the results, plenty of low-angle grain boundaries (LAGBs) and a low proportion of twin boundaries (TBs) deteriorated the corrosion resistance on the SS304 side of the joint. The corrosion products of the SS304 side mainly included γ-Fe2O3, FeCrO4, and Cr2O3, while those of the Q235 steel side were α-Fe2O3 and α-FeOOH. The corrosion mechanism in the stir zone (SZ) was galvanic corrosion between proeutectoid ferrite and pearlite on the Q235 steel side, during which the austenite remained uncorroded, whereas the proeutectoid ferrite, pearlite, and bainite were severely corroded. The above results indicated that the uniform distribution of mixed structures and a small area proportion of austenite (cathode) would improve the corrosion resistance in the SZ.

1. Introduction

Owing to the low cost and good corrosion resistance of carbon steel and stainless steel, respectively, their dissimilar steel welded structures have been widely used in the chemical, petroleum, natural gas, nuclear energy, power generation industries, among others [1–4]. The conventional fusion welding methods for carbon steel and stainless steel mainly include tungsten inert gas welding (TIG) [5, 6], laser welding [7], and electron-beam welding [8]. However, these methods tend to produce defects such as solidified cracks, pores, and the coarsening of second phases during welding, resulting in the poor mechanical performance of the resulting joints [2, 9]. To prevent the formation of defects in solidified structures caused by conventional fusion welding technologies, solid-state welding provides an ideal high-quality welding method for dissimilar steels [10].

Friction stir welding (FSW) is a solid-state welding technology for aluminum alloys that was invented by the British Welding Research Institute in the early 1990s [11, 12]. In the FSW process, a high-speed rotating stirring tool is inserted into the seam of weld plates until the shoulder is in close contact with the material to be welded. The material is softened under the action of frictional heat, while the tool’s stirring action causes plastic flow and mixing of materials at the joint, thereby achieving solid-state welding between materials [13]. Compared with fusion welding, FSW requires the lower welding temperature and shorter welding time [14]. Therefore, when FSW is performed on dissimilar steels, the use of a lower heat input prevents the formation of defects in the
In this study, hot-rolled SS304 and Q235 steel plates with dimensions of 100 × 2.1 × 2.1 mm³ were used for FSW butt welding. The plates were placed on the advancing side (AS) and retreating side (RS), respectively. The chemical compositions of the two materials are listed in Table 1. FSW was performed on a modified vertical milling machine with a rotation speed of 475 rpm and a welding speed of 47.5 mm min⁻¹, which enabled one to obtain a workpiece with the sound appearance and appropriate mechanical characteristics. A WC-Co tool had a shoulder of 16 mm diameter, tapered pin diameters of 5.3 and 3.0 mm, and a pin length of 2.7 mm. The tilt angle was 2 deg, at which the friction pressure was 20 kN.

2. Material and experimental process

2.1. FSW experiment

In this study, hot-rolled SS304 and Q235 steel plates with dimensions of 100 × 60 × 3 mm³ were used for FSW butt welding. The plates were placed on the advancing side (AS) and retreating side (RS), respectively. The chemical compositions of the two materials are listed in Table 1. FSW was performed on a modified vertical milling machine with a rotation speed of 475 rpm and a welding speed of 47.5 mm min⁻¹, which enabled one to obtain a workpiece with the sound appearance and appropriate mechanical characteristics. A WC-Co tool had a shoulder of 16 mm diameter, tapered pin diameters of 5.3 and 3.0 mm, and a pin length of 2.7 mm. The tilt angle was 2 deg, at which the friction pressure was 20 kN.

2.2. Microstructure characterization

After FSW, the metallographic specimens were cut perpendicular to the joint’s welding direction (WD). After mechanical polishing, aqua regia and nitric acid-ethanol solution were used to etch the cross-sections of SS304 and Q235 steel, respectively. Optical microscopy (OM) and scanning electron microscopy (SEM) were applied...
to observe the microstructure after corrosion. Electron backscatter diffraction (EBSD) image acquisition was completed with a fully-automatic HKL-EBSD system connected to a field-emission SEM.

2.3. Electrochemical tests

The joint was processed into square pieces with dimensions of 8 mm x 8 mm x 3 mm. The sampling location, sample dimensions, and division of each area are shown in figure 1. The joint was divided into five macro-zones: SS304 and Q235 steel base materials (BM304 and BMQ235), the retreating side (RS304), the stir zone (SZ), and the advancing side (ASQ235), where the RS304, SZ, and ASQ235 each included two micro-zones. RS304 was composed of a heat-affected zone (HAZ304) and a thermomechanically-affected zone (TMAZ304) on the retreating side. The SZ was presented by SZ304 on the retreating side and SZQ235 on the advancing side. ASQ235 included TMAZQ235 and HAZQ235 on the advancing side.

The test surface of the macro-zones of electrochemical samples was the WD-TD surface with a scan area of 0.64 cm². The samples were exposed to 3.5 wt% NaCl solution at room temperature, which contained deionized water and analytically pure NaCl. The open-circuit potential, potentiodynamic polarization, and electrochemical impedance tests were carried out by means of a three-electrode system. The auxiliary electrode was a platinum plate, the reference electrode was 1 M KCl Ag/AgCl, and the working electrode was the sample. A CST520 electrochemical workstation was used for tests. During the tests, the working electrode was first immersed in the test solution for 1 h, and the potentiodynamic polarization measurements were performed after the open-circuit potential (OCP) stabilized. The time for collecting the polarization curves was 1 h. The scan rate was 0.3333 mV s⁻¹, and the scan range was −0.5 V versus OCP ~ +1.0 V versus OCP. The scanning frequency range of electrochemical impedance spectroscopy (EIS) was from 100 kHz to 5 mHz, and the disturbance signal was 5 mV.

2.4. Corrosion morphology characterization

SEM was used to examine the corrosion morphology of the above zones after the joint was corroded. A laser confocal scanning microscope (Keyence vk9710) was employed to determine the surface roughness characteristics and to quantitatively assess the corrosion resistance of each zone by measuring the root mean square (RMS) roughness. The corrosion products in the zones were qualitatively analyzed with a Raman spectrometer (LabRAM HR Evolution) coupled with an Ar⁺ laser (532 nm wavelength) within a spectral range of 100–2000 cm⁻¹.

3. Results and discussion

3.1. Microstructures

Figure 2 displays the microstructures of the BM304 and BMQ235 zones. The main phase in BM304 was austenite (γ) with coarse grains whose average size was 10.9 μm (including twins, TBs) (figure 2(a)). The fraction of low-angle grain boundaries (LAGBs) was 14% (except for TBs) (figure 2(b)). Many TBs (25%) could be observed...
inside the $\gamma$ grains, which are marked with black arrows in figures 2(a) and (b). In addition, the microstructure of BMQ235 mainly included ferrite and pearlite. Pearlite was distributed on the ferrite’s grain boundaries, with an area proportion of 15.6\% (figure 2(c)). Pearlite was composed of eutectoid ferrite (EF) and cementite ($\text{Fe}_3\text{C}$), showing a predominantly lamellar texture. According to figure 2(d), the lamellar pearlite had an irregular morphology, with an interlamellar spacing of 0.7–0.8 $\mu$m, and $\text{Fe}_3\text{C}$ existed as intermittent rods or granules.

Figure 3 depicts the microstructure on the RS304 side of the FSW joint (i.e., the SS304 side). After undergoing thermal cycling during welding, the $\gamma$ structure in HAZ304 recovered, and the grains were coarsened, with an average grain size of 11.3 $\mu$m (Zone b in figure 3(a)). Compared with the BM304, the LAGBs proportion increased (figure 3(b)). This can be related to the dislocation rearrange under high temperature and the formation of low-angle grain boundaries (LAGBs) within the major grains [31]. Figure 3(b) shows a decrease in the TBs proportion (marked with a black arrow). TMAZ304 (Zone c in figure 3(a)) exhibited plastic deformation, mainly due to the action of shouldering. As a result, grains were elongated and to enrich the average size of 6.5 $\mu$m, and some of them revealed the emergence of DRX [32]. Compared with the HAZ304, the LAGBs proportion decreased. This was because the LAGBs were transformed into high-angle grain boundaries (HAGBs) as the deformation proceeded, and the microstructure with small grains was developed [33]. Meanwhile, as seen in figure 3(c), the TBs proportion increased (marked with a black arrow).

Figure 4 shows the SZ microstructure of the FSW joint. Due to the rotation during FSW, the mixed textures in the center of the weld exhibited two morphologies. In the left region (SZ304), SS304 was rolled into Q235 steel to form a river-like morphology. The structure was composed of face-centered cubic (FCC) $\gamma$, body-centered cubic (BCC) proeutectoid ferrite (PF), and pearlite. The distribution of the mixed texture was non-uniform, and the area fraction of $\gamma$ phase was large (figures 4(a) and (b)). On the right region (SZQ235), the Q235 steel structure underwent a phase transformation, forming PF and bainite (B), which were afterward mixed with $\gamma$ phase in the SS304 of Q235 steel. The mixed texture was more uniformly distributed, and the area proportion of $\gamma$ phase was low (figure 4(c)).

Figure 5 depicts the microstructure of ASQ235 (i.e., the Q235 low-carbon steel side) of the FSW joint. TMAZQ235 was composed of PF and pearlite. Here, PF includes bulk ferrite (BF), grain boundary ferrite (GF), and acicular ferrite (AF). Compared with BMQ235, pearlite grains were much coarser, with an area proportion of

![Figure 2. Microstructures of BM$_{304}$ and BM$_{Q235}$: (a) EBSD image of BM$_{304}$; (b) misorientation angle distribution of BM$_{304}$; (c) OM images of structures in BM$_{Q235}$; (d) SEM images of pearlite (Zone d in figure 2(c)). The misorientation angle of HAGBs was greater than 15 deg and that of LAGBs was between 2 and 15 deg, as marked with white lines.](image-url)
55% (figure 5(a)). The interlamellar spacing in pearlite decreased, and the distribution became more uniform, showing an interlamellar spacing of 0.4–0.5 μm (figure 5(b)). HAZQ235 was composed of ferrite and pearlite. Compared with BMQ235, the area proportion of pearlite increased slightly to 17.7% (figure 5(c)). Also, pearlite in HAZQ235 had the smallest interlamellar spacing of 0.2–0.3 μm and was uniformly distributed (figure 5(d)).

### 3.2. Corrosion behavior

#### 3.2.1. Open-circuit potential and potentiodynamic polarization curves

Figure 6 displays the open-circuit potentials and potentiodynamic polarization curves acquired at each macrozone of the joint sample in 3.5 wt% NaCl solution. It can be seen from figure 6(a) that BM304 had the highest open-circuit potential, followed by RS304, and finally by SZ, BMQ235, and ASQ235, which had similar values. This means that BM304 and RS304 were less active compared to SZ, BMQ235, and ASQ235. In a word, BM304 and RS304 had the nobler corrosion potentials as negative electrodes, while SZ, BMQ235, and ASQ235 had the lower...
potentials as positive electrodes, hence a galvanic coupling effect could have formed in the case of couples of welded joints [34]. According to figure 6(b), BM304 and RS304 exhibited anodic passivity during the corrosion process, whereas the cathodic part of SZ, BMQ235, and ASQ235 had the typical characteristics of a diffusion-controlled oxygen reduction reaction [35, 36].

Table 2 shows the Tafel fitting results of the potentiodynamic polarization curves from each macro-zone of the joint. It can be seen that the corrosion current of BM304 was the lowest, indicating the best corrosion resistance. The corrosion current then increased in a sequence of RS304, SZ, BMQ235, and ASQ235, which meant there was an increase in their corrosion rates and the deterioration in corrosion resistance.
3.2.2. EIS test

Figure 7(a) depicts the EIS Nyquist plots of the joint’s macro-zones in 3.5 wt% NaCl solution. It can be seen from the figure that the impedance spectra have a time constant, and there are capacitive reactance lines elated to charge transfer occurring on the electrode surface in each macro-zone of the joint [37]. The capacitive reactance lines of BM304 and RS304 have the larger diameters and both show an arc shape, which indicates that these zones possess similar corrosion resistance mechanisms. The diameters of the high-frequency zone of the capacitive reactance arcs of SZ, BMQ235, and ASQ235 sequentially decreased compared to those of BM304 and RS304. Their

Table 2. Potentiodynamic polarization curve parameters for each macro-zone in the FSW joint in 3.5 wt% NaCl solution.

| Sample   | $E_{corr}$ (mV versus Ag/AgCl) | $i_{corr}$ ($\mu$A cm$^{-2}$) | $\beta_a$ (mV decade$^{-1}$) | $\beta_c$ (mV decade$^{-1}$) | CR$_{Tafel}$ (mmpy) |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------|
| BM304    | $-139.5$                      | 0.0227                        | 137.7                         | 98.9                          | 0.0003              |
| RS304    | $-186.9$                      | 0.119                         | 88.6                          | 120.9                         | 0.001               |
| SZ       | $-448.5$                      | 5.35                          | 16.5                          | 160.5                         | 0.06                |
| BMQ235   | $-448.9$                      | 6.91                          | 21.4                          | 265.9                         | 0.07                |
| ASQ235   | $-450.8$                      | 7.12                          | 22.1                          | 204.4                         | 0.08                |

3.2.2. EIS test

Figure 7(a) depicts the EIS Nyquist plots of the joint’s macro-zones in 3.5 wt% NaCl solution. It can be seen from the figure that the impedance spectra have a time constant, and there are capacitive reactance lines elated to charge transfer occurring on the electrode surface in each macro-zone of the joint [37]. The capacitive reactance lines of BM304 and RS304 have the larger diameters and both show an arc shape, which indicates that these zones possess similar corrosion resistance mechanisms. The diameters of the high-frequency zone of the capacitive reactance arcs of SZ, BMQ235, and ASQ235 sequentially decreased compared to those of BM304 and RS304. Their
shape changed from an arc to a semicircle, indicating that BM304 had the best corrosion resistance, followed by RS304, and the corrosion resistance then decreased in a sequence of SZ, BMQ235, and ASQ235. This variation is consistent with the polarization curves.

Figures 7(b) and (c) display the Bode magnitude plots and Bode phase plots of the joint’s macro-zone, respectively. Both plots exhibit three distinct regions: low-frequency, mid-frequency, and high-frequency regions. In figure 7(b), the low-frequency region (10^{-2}–10^{2} Hz) represents the polarization resistance of the sample. The polarization resistance of the macro-zones followed the order of BM304 > RS304 > SZ > BMQ235 > ASQ235, which is consistent with the polarization curves. In the mid-frequency region (10^{4}–10^{6} Hz) (figure 7(c)), the phase angles of BM304 and RS304, as well as those of SZ, BMQ235, and ASQ235, were similar. This indicates that the micro-structures of BM304 and RS304, as well as those of SZ, BMQ235, and ASQ235, were identical, meaning there were similar electrical double-layer characteristics. The high-frequency region (10^{6}–10^{7} Hz) was attributed to the resistance of the test solution.

Figures 7(d) and (e) respectively show the equivalent circuit diagrams used to simulate the EIS data of the SS304 and Q235 sides. In the equivalent circuit diagram, $R_c$ denotes the solution resistance; $Q_d$ stands for the constant-phase element (CPE) of the double-layer capacitor; $R_{ch}$ is the charge-transfer resistance. The constant-phase elements reflect the capacitive behavior of non-ideal interfaces. The impedance of the constant-phase element is expressed as follows [38]:

$$Z_{CPE} = [Y_0(j\omega)^n]^{-1}$$

where $Y_0$ denotes the scale factor; $j^2 = -1$ and $w = 2\pi f$; $n$ is the dispersion coefficient, which is related to the surface non-uniformity. If $n = 0$, the constant-phase element represents a resistor $R = Y_0^{-1}$; if $n = 1$, the constant-phase element refers to a capacitor $C = Y_0$. The EIS parameters of each macro-zone of the joint can be calculated using the circuit diagrams from figures 7(d) and (e), and the results are listed in table 3. It can be seen from the table that the EIS parameters of each macro-zone were significantly different. The charge-transfer resistance $R_{ch}$ had the largest difference, where a higher $R_{ch}$ indicated better corrosion resistance [38]. Moreover, the corrosion resistance of each macro-zone changed as follows: BM304 > RS304 > SZ > BMQ235 > ASQ235. This result is also consistent with the measured polarization curves. In addition, given the least Chi-square ($\chi^2$) value, the experimental EIS data show excellent agreement with an equivalent circuit corresponding to $R_c$ ($Q_d$, $R_{ch}$).

### 3.2.3. Corrosion morphology

Figure 8 displays the corrosion morphology evolution of each micro-zone of the FSW joint. Figures 8(a)–(c) depict the corrosion morphologies of BM304, HAZ304, and TMAZ304, respectively. Different degrees of pitting corrosion occurred in the above three zones on the sample’s surface, revealing pits with porous lacy covers due to the accumulation of CI^{-}-rich salt solution therein. In a word, CI^{-} ions penetrated the surface film to the metal/film interface, causing a local damage to the film and forming tiny pits [39]. After the initiation of such pits, metal ions at the edges of the pits entered the salt solution faster, reducing its local concentration below the critical value, and passivation occurred. In contrast, the active dissolution at the bottom of pits continued until the intact surface film surrounding the pits was destroyed and new pits formed. However, metal ions diffused rapidly through the new corroded pores, which again decreased the local concentration of the salt solution and induced passivation at the edges. Therefore, during the film destruction and passivation at the pit edges, the pits continued to grow, causing the film to be destroyed repeatedly before finally forming corrosion pits with porous lacy covers [40–43].

It can be seen from figure 8 that the area of the pit with a lacy cover in BM304 was small, indicating less corrosion and, thus, better corrosion resistance. The pit with a lacy cover in RS304 had a larger area, meaning there were more serious corrosion and poorer corrosion resistance. This was because the LAGBs proportion of RS304 (HAZ304 and TMAZ304) significantly increased after FSW (figures 3(b) and (c)), which resulted in a higher dislocation density. Balusamy et al [44] showed that an increase in dislocation density provides more active sites, which will accelerate corrosion [45]. In addition, the microstructure characterization results showed that, compared with BM304, the proportions of TBs in HAZ304 and TMAZ304 were significantly lower. Husain et al.

### Table 3. EIS parameters of each micro-zone of the FSW joint.

| Circuitry | BM304 | RS304 | SZ | BMQ235 | ASQ235 |
|-----------|-------|-------|----|--------|--------|
| $R_c$ (Ω·cm²) | 1.111 | 1.526 | 1.788 | 2.583 | 2.052 |
| $Q_d$ (S°Cm) | 0.000024 | 0.00008 | 0.00052 | 0.00081 | 0.000641 |
| $n$ (0<=n<1) | 0.8446 | 0.8665 | 0.7967 | 0.7997 | 0.7854 |
| $R_{ch}$ (Ω·cm²) | 9.86 × 10⁸ | 27450 | 1284 | 1133 | 1049 |
| $\chi^2$ (chi-square) | 0.080 | 0.016 | 0.011 | 0.0055 | 0.004 |
reported a decrease in the proportion of TBs and the tendency of the sample to corrode. Therefore, the increase in the LAGBs proportion and the decrease in the TBs proportion were the main reasons why RS304 had worse corrosion resistance than BM304. In turn, HAZ304 included a higher LAGB proportion and a smaller TB content than TMAZ304, indicating that the former one had worse corrosion resistance than the latter one.

Figures 8(d) and (e) show two different corrosion morphologies in the SZ. One is a river-like morphology (figure 8(d)) with a more serious corrosion, which is consistent with the structure and morphology shown in the OM images of SZ304 (figure 4(a)). Because of the poor distribution uniformity of the PF-pearlite mixed texture in the γ phase of SS304 and Q235 steel, as well as the higher corrosion potential and the larger area proportion of γ phase compared to those of PF and pearlite, strong galvanic corrosion occurred between γ as the cathode and PF and pearlite as the anodes, resulting in the river-like morphology. PF and EF in pearlite were prone to corrosion, but γ and Fe3C in pearlite remained after corrosion. The other morphology is craquelure (figure 8(e)), indicating relatively light corrosion because the microstructure in SZQ235 was composed of PF, B, and γ. Since the mixed texture is more uniformly distributed and the area proportion of γ as the cathode is small (figure 4(c)), galvanic corrosion was relatively weak. The craquelure morphology means that B and PF were preferentially corroded in sequence.

Figure 8. SEM surface corrosion morphology of each micro-zone of the FSW joint after potentiodynamic polarization in 3.5 wt% NaCl solution: (a) BM304; (b) HAZ304; (c) TMAZ304; (d) SZ304; (e) SZQ235; (f) TMAZQ235; (g) HAZQ235; (h) BMQ235.
According to figure 8(f), TMAZQ235 was seriously corroded, revealing coarse intergranular cracks and fine intragranular cracks. The microstructure of TMAZQ235 was composed of GF, AF, and pearlite, and the area proportion of pearlite was relatively large (55%) (figure 5(a)). The formation of corrosion cracks in TMAZQ235 was due to galvanic corrosion. In the entire TMAZQ235, GF, AF, and BF served as the anodes, and pearlite was the cathode, while EF and Fe3C in pearlite were the anode and cathode, respectively. Therefore, the anodes (GF, AF, BF, and EF in pearlite) were preferentially corroded [48, 49], which exposed the remaining Fe3C cathode to the solution. Intergranular cracks formed due to the corrosion of GF and BF, whereas small intragranular cracks emerged owing to the corrosion of AF and EF. During corrosion, on account of the high area proportion of pearlite, the reaction area of Fe3C as the cathode increased upon prolonging the corrosion time, which promoted galvanic corrosion and caused the corrosion rate within the zone to increase. As a result, TMAZQ235 experienced severe corrosion [50].

Figure 8(g) displays the corrosion morphology of HAZQ235. The non-uniformly distributed ferrite cavities (marked with a white circle) surrounded with various corrosion products can be seen in the figure. The morphology shows that the corrosion of HAZQ235 was mainly due to the dissolution of ferrite, and galvanic corrosion was secondary corrosion. Most corrosion products were produced since HAZQ235 had a lower area proportion of pearlite than the adjacent TMAZQ235, and the entire surface was equivalent to an anode. Accordingly, a galvanic pair formed with the TMAZQ235 as the cathode [35], which accelerated corrosion in HAZQ235. Due to the larger cathode area of TMAZQ235, Fe2+ diffused relatively easy, leading to an increase in the Fe2+ concentration on the surface of HAZQ235. As a result, HAZQ235 generated more corrosion products on the surface of Fe3C and also on the surface of ferrite. Sun et al [50] showed that corrosion products can prevent the solution from further entering the surface of a substrate; therefore, corrosion products improved the corrosion resistance of HAZQ235.

Figure 8(h) depicts the corrosion morphology of BMQ235. Although corrosion occurred on ferrite, the corroded surface was relatively flat, meaning that corrosion was shallow. Additionally, there were fewer corrosion products (highlighted with a white elliptical area), which were mainly located on the pearlite. The morphology characterization data show that BMQ235 had the better corrosion resistance. The reason is that the area proportion of pearlite in BMQ235 was low (15.6%), so the cathode reaction area was small when corrosion occurred, and its galvanic corrosion effect was weak. In addition, the formation of corrosion products at pearlite inhibited the further dissolution of EF between the pearlite lamellae, which decreased the corrosion rate and endowed BMQ235 with better corrosion resistance. Compared with TMAZQ235 and HAZQ235, BMQ235 had the lowest area proportion of pearlite and the best corrosion resistance. Finally, HAZQ235 had the corrosion resistance characteristics between the above two zones. In addition, according to the micromorphology of pearlite in the three zones and the electrochemical corrosion results, the interlamellar spacing and distribution uniformity of pearlite did not obviously affect the corrosion resistance.

To quantitatively compare the corrosion degree of micro-zones in the joint, a laser confocal scanning microscope was used to determine their roughness characteristics by finding the corresponding RMS values. The results are shown in figure 9. The RMS value of each micro-zone varied in the order of BM304 < TMAZ304 < HAZ304 < SZQ235 < SZ304 < BMQ235 < HAZQ235 < TMAZQ235. Therefore, the corrosion resistance of the micro-zones followed a sequence of BM304 > TMAZ304 > HAZ304 > SZQ235 > SZ304 > BMQ235 > HAZQ235 > TMAZQ235, which is consistent with the corrosion morphology characterization.

3.2.4. Corrosion products

In this section, Raman spectroscopy was used to characterize the corrosion products in each micro-zone on the sample’s surface, and the results are shown in figure 10. Because the surface Raman spectra of BM304, RS304, and SZ304 were similar, we only tested and analyzed the corrosion products inside and outside BM304 pits on the SS304 side. In the Raman spectrum of the outer region of the BM304 pit (figure 10(a)), the peaks of α-FeOOH, γ-Fe2O3, Cr2O3, and FeCrO4 were at 248 cm⁻¹, 378 cm⁻¹ [35], 530 cm⁻¹, and 680 cm⁻¹, respectively [51, 52]. The presence of Cr oxide in the Raman spectrum indicates that the external area of the BM304 pit was passivated, which is consistent with the corrosion morphology data. The peaks at 1340 cm⁻¹ and 1590 cm⁻¹ are the D and G bands of carbon atoms [53], which represent disordered carbon and graphitized carbon, respectively. Generally, the relative intensity ratio (I_D/I_G) is used to express the crystallinity of carbon materials, where a smaller ratio represents fewer defects in the carbon material and a higher graphitization degree [54]. The I_D/I_G ratio in the Raman spectrum of the outer region of the BM304 pit was relatively high (0.84), indicating that there were fewer carbon defects in the outer region and that the hexagonal crystal structure was retained [55]. In the Raman spectrum of the interior of the BM304 pits (figure 10(b)), there were two oxide peaks with a weak intensity, associated with γ-Fe2O3 (378 cm⁻¹) and FeCrO4 (680 cm⁻¹) [52]. The I_D/I_G ratio in the spectrum (0.86)
exceeded that of the pit exterior. These results indicate that more C defects were present inside the pit than outside and that corrosion was more obvious.

In the Raman spectrum of SZQ235 on the Q235 steel side (figure 10(c)), the peaks at 212, 271, and 583 cm\(^{-1}\) were attributed to \(\alpha\)-Fe\(_2\)O\(_3\), and the weak peak at 378 cm\(^{-1}\) was assigned to \(\gamma\)-Fe\(_2\)O\(_3\) \([35]\), whereas \(I_D/I_G\) was 0.85. According to the Raman spectra of TMAZQ235, HAZQ235, and BMQ235 (figures 10(d)–(f)), the corrosion products in ASQ235 mainly included \(\alpha\)-Fe\(_2\)O\(_3\), \(\alpha\)-FeOOH, and \(\gamma\)-FeOOH. The peaks of \(\alpha\)-Fe\(_2\)O\(_3\) appeared at 280, 293, 473, and 589 cm\(^{-1}\); those of \(\alpha\)-FeOOH were at 217, 390, and 480 cm\(^{-1}\); that of \(\gamma\)-FeOOH was at 657 cm\(^{-1}\) \([35]\). Within the Raman shift range of 100–700 cm\(^{-1}\), TMAZQ235 showed strong characteristic peaks, revealing the formation of abundant corrosion products. The Raman peaks of HAZQ235 and BMQ235 were relatively weak, indicating few corrosion products. Moreover, the \(I_D/I_G\) values of the three zones were 1.18, 0.88, and 0.86, respectively, meaning that the largest amount of carbon defects and the most serious corrosion occurred in TMAZQ235. The corrosion degrees of HAZQ235 and BMQ235 decreased successively, which is consistent with the corrosion morphology results.

### 3.3. Corrosion mechanism of the SZ mixed zone

Figure 11 displays a schematic diagram of the potential polarization corrosion process within the SZ mixed zone of the FSW joint in 3.5 wt% NaCl solution. The left side of the SZ mixed zone was SZ304, whose composition was a mixture of PF, pearlite, and \(\gamma\) with a river-like morphology (figure 4(a)). On the right side, there was SZQ235, containing a mixture of PF, B, and \(\gamma\) (figure 4(c)). Because \(\gamma\) is electrochemically more stable than B, PF, and
pearlite, the potential of the former one was more positive, making it difficult to corrode. Thus, when $\gamma$ was the cathode, while PF, pearlite, and B were the anodes, galvanic pairs formed (figure 11(a)). On the left side, due to the non-uniform mixing of the components, there was a large potential difference, and the cathodic reaction area was large, so that PF and EF in the pearlite were corroded preferentially. The corrosion was serious, and $\gamma$ and Fe$_3$C remained after corrosion. On the right side, B and PF were preferentially corroded in turn. Shallow surface corrosion pits were mainly formed by the PF corrosion, and honeycomb cracks emerged due to the corrosion of B (figure 11(b)). Upon prolonging the corrosion time, the Fe$^{2+}$ content increased, and corrosion products such as a little iron oxides were formed (figure 11(c)) according to the reaction equations below $[47, 56, 57]$:  

Anodic reaction: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$  

Cathodic reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$  

$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2$  

$4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3$
Here, equations (2) and (3) exhibit the dissolution of steel and reduction of oxygen. Equations (4)–(6) show the formation of iron oxide, while those (7) and (8) indicate the appearance of hydroxyl-containing compounds. A higher concentration of Cl\(^{-}\) promoted the emergence of FeOOH \([56]\). The formations of iron(III) oxide (Fe\(_2\)O\(_3\)) and iron oxyhydroxide (FeOOH) are consistent with the Raman spectroscopy data.

4. Conclusions

1. Dissimilar steel FSW joints composed of 304 stainless steel and Q235 low carbon steels were divided into five macro-zones, namely BM\(_{304}\), RS\(_{304}\), SZ, AS\(_{Q235}\), and BM\(_{Q235}\). Among them, RS\(_{304}\), SZ, and AS\(_{Q235}\) each included a pair of micro-zones, videlicet HAZ\(_{304}\) and TMAZ\(_{304}\), SZ\(_{304}\) and SZ\(_{Q235}\), TMAZ\(_{Q235}\) and HAZ\(_{Q235}\), respectively. The microstructures in the BM\(_{304}\), HAZ\(_{304}\), and TMAZ\(_{304}\) were mainly presented by \(\gamma\) phase. SZ\(_{304}\) was mainly composed of \(\gamma\), PF, and pearlite, and those in SZ\(_{Q235}\) were mainly a mixture of \(\gamma\), PF, and B. TMAZ\(_{Q235}\) comprised PF and pearlite, while HAZ\(_{Q235}\) and BM\(_{Q235}\) were formed by ferrite and pearlite.

2. The open-circuit potentials, potentiodynamic polarization curves, and electrochemical impedance spectra of the joint’s macro-zones showed that the corrosion resistance of the joints followed a sequence of BM\(_{304}\) > RS\(_{304}\) > SZ > BM\(_{Q235}\) > AS\(_{Q235}\). The characterization results on the corrosion morphology of the joint’s micro-zones were consistent with the laser confocal scanning microscopy data, and the corrosion resistance varied in the following order: BM\(_{304}\) > TMAZ\(_{304}\) > HAZ\(_{304}\) > SZ\(_{Q235}\) > SZ\(_{304}\) > BM\(_{Q235}\) > BM\(_{Q235}\) > HAZ\(_{Q235}\) > TMAZ\(_{Q235}\).

3. The corrosion mechanisms of BM\(_{304}\), HAZ\(_{304}\), and TMAZ\(_{304}\) were referred to pitting corrosion, while those of SZ\(_{304}\) and SZ\(_{Q235}\) corresponded to galvanic corrosion between mixed structures. Meanwhile, the corrosion of TMAZ\(_{Q235}\) was mainly the galvanic corrosion of PF and pearlite, while the corrosion of HAZ\(_{Q235}\) and

4Fe(OH)\(_2\) + O\(_2\) → 2Fe\(_2\)O\(_3\) + 4H\(_2\)O \hspace{1cm} (6)

Fe(OH)\(_2\) + \(\frac{1}{4}\)O\(_2\) → FeOOH + \(\frac{1}{2}\)H\(_2\)O \hspace{1cm} (7)

Fe(OH)\(_3\) → FeOOH + H\(_2\)O \hspace{1cm} (8)

Figure 11. Schematic diagram of the potential polarization corrosion process through the SZ mixed zone in 3.5 wt% NaCl solution.
BM$_{2325}$ was predominately the dissolution of ferrite and weak galvanic corrosion of ferrite and pearlite. The corrosion products inside and outside the BM$_{304}$ pit included $\gamma$-Fe$_2$O$_3$, FeCr$_2$O$_4$, and Cr$_2$O$_3$, while those of SZ$_{4233}$, TMAZ$_{4233}$, HAZ$_{4233}$, and BM$_{4233}$ were mainly $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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