

Corrosion Behaviour of 2205 Duplex Stainless Steel in Oilfield Production Fluid Containing Sulphate-reducing Bacteria

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The corrosion behaviour of 2205 duplex stainless steel (DSS) in sulphate reducing-bacteria (SRB)-free and SRB-containing oil-field production fluid are performed via electrochemical techniques, microscopic imaging, and X-ray photoelectron spectroscopy (XPS). The results show that the corrosion morphology of 2205 DSS in oil field production fluid is pitting corrosion, and the pit becomes deeper in case of bacteria. The corrosion mechanism of 2205 DSS varies depending on the SRB growth stage. Corrosion is inhibited in the steady growth stage, but it is greatly accelerated during the other stages. Observed results of XPS demonstrate that the passivation film obtained in the presence of SRB comprises sulphides of Cr and Fe. The sulphide-containing passivation film is more easily penetrable by aggressive anion and the local corrosion is accelerated compared to the sulphide-free passivation film.

Keywords: 2205 Duplex stainless steel; sulphate reducing-bacteria; growth stage; microbiological corrosion; vulcanization

1. INTRODUCTION

The microbiologically influenced corrosion (MIC) phenomenon can be commonly observed in a variety of natural environments, such as soil and marine ones, and is a major cause of failure of engineering materials[1–5]. Corrosion caused by various microorganisms is believed to account for approximately 20% of all metal- and building-material-corrosion damage[6], and the sulphate-reducing bacteria (SRB) that grow under anaerobic environments are considered one of the most destructive strains[7, 8].

SRB is an anaerobic microorganism, which is widely found in soil, sea, river, underground pipelines, oil and gas Wells and other oxygen deficit environments. SRB can reduce sulfate to hydrogen sulfide by using the hydrogen generated by corrosion cells, thus accelerating corrosion [9]. More than 77% of the corrosion occurred in oil Wells are caused by SRB, and mostly the morphology

of the corrosion is pitting. Biofilm would be formed on the metal surface when the medium containing SRB, and the main component of the biofilm is extracellular polymer (EPS). [10] With the change of environment and microbial metabolism, the corrosiveness of biofilm to metal also changes, which may protect metal or accelerate metal corrosion [11-13].

Previous studies showing that at low concentrations, EPS can be adsorbed on the surface of carbon steel to inhibit cathode reactions, and thus, delay corrosion. On the other hand, formation of EPS-Fe²⁺ complexes at high EPS concentrations promotes anodic dissolution of the matrix material, which in turn, accelerates corrosion [14, 15]. Traditionally, SRB-promoted corrosion of carbon steel has been explained based on cathode depolarization, concentration cell, metabolic product, and under-film corrosion mechanisms [15]. Beech [16] observed that FeS₂ and FeS coexisted along with SRB on the specimen surface exposed in seawater, thereby demonstrating the metal surface as being seriously damaged. Sosa et al. [17] demonstrated that the product of carbon steel corrosion in natural seawater possessed a double-layered structure. The outer layer consisted of corrosion products or biofilm performed a protection function. On the other hand, the inner layer comprised Fe₂O₃ film that was porous and permeable to the aggressive medium. Castaneda [18] studied the effect of SRB on the corrosion of carbon steel and demonstrated that biofilm heterogeneity tends to accelerate electrochemical reactions, which in turn results in accelerated corrosion.

The current research indicates that the destructive effect of SRB on the metal passivating film is caused by factors different from those described above. Sun [19] observed that the pitting corrosion of 2507 duplex stainless steel is mainly caused by the synergy between the effects of SRB-iron-oxidase metabolic activity and Cl⁻. Dec [20] studied the effect of *D. desulfurization* strain on biofilm formation and microbial corrosion of 2205 DSS and found that the sulphidation of passive film affected the nature of cathodic behaviour of steel and helped to impede micro pit growth. Antony [21–23] investigated the Corrosion of 2205DSS in chloride medium containing sulfate-reducing bacteria. It was indicated that the attack was initiated at the grain boundaries and slowly encroached into austenite grains. The attack was preferentially in the ferrite phase of HAZ of the weldment, whereas it was restricted to the austenite phase of the parent metal. The MIC behaviour was found to be influenced by the microstructural changes which occurred due to the thermal treatments. Liang [24] investigated the effects of SRB on the 2205 DSS in SRB-containing oil industry environments and revealed that the distribution of SRB on the surface of 2205 DSS was nonuniform.

At present, most researches concerning SRB-induced corrosion focus on the behaviour of carbon and common stainless steels maintained in contact with cooling water systems or under marine environments. Duplex stainless steel contains both austenitic (γ) and ferritic (α) phases, and therefore, it exhibits excellent weldability and toughness of austenitic stainless steels along with the high strength and stress-corrosion resistance of ferritic steels [25, 26]. This makes DSS highly suitable for use in oil-field environments. In the proposed study, the corrosion behaviour of 2205 DSS under SRB-free and SRB-containing oil-field environments was investigated via electrochemical techniques, microscopic imaging, and X-ray photoelectron spectroscopy (XPS), and the mechanism of 2205 DSS corrosion in both media was discussed. It is expected that this work will give an essential insight into the SRB growth cycle on the mechanism of passivation film degradation in detail.

2. EXPERIMENTAL

2.1 Materials

The specimens used in this work were cut from a plate of 2205 DSS with a chemical composition in wt.% of 0.02 C, 0.16N, 0.68Si, 1.2Mn, 22 Cr, 5.42 Ni, 0.002S, 0.18P, and the balance was Fe. Specimens used in immersion and electrochemical measurement were processed into dimensions of 40×10×3 mm and 10×10×3 mm, respectively. The electrochemical samples were welded with copper wire and sealed with epoxy resin to obtain a working area of 10 × 10 mm. The samples were sequentially grinded by a series of SiC emery papers (# 80~2000) and further mirror-polished down to 1/4 μm using diamond paste. Then, the samples were degreased using acetone and ethanol. Microstructural characterization of 2205 DSS etched by aqua-regia (37 wt% HCl and 67 wt% HNO₃, 3:1 v/v) demonstrated the presence of ferritic (α) and austenitic phases (γ) in a ratio of approximately 1:1 (Figure 1: dark regions represent the α phase while light-coloured regions denote the γ phase).

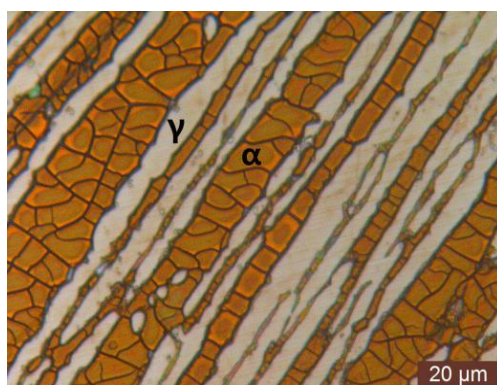


Figure 1. Microstructure of 2205 DSS.

2.2 Solutions and Bacterial Culturing

The SRB used in this work were extracted from oilfield production fluid collected from Liaohe oilfield in Liaoning, China. The SRB were cultivated in the nutrient medium recommended by China General Microbiological Culture Collection Center (CGMCC). The medium was composed medium A (0.5 gL⁻¹ K₂HPO₄, 0.5 gL⁻¹ Na₂SO₄, 1 gL⁻¹ NH₄Cl, 0.1 gL⁻¹ CaCl₂, 2 gL⁻¹ MgSO₄·7H₂O, 1 gL⁻¹ yeast, and 3 mL sodium lactate (55 vol%)) and medium B (0.1 gL⁻¹ ascorbic acid, 0.1 gL⁻¹ sodium hydrosulphite, and 0.1 gL⁻¹ (NH₄)₂Fe(SO₄)₂·6H₂O). The pH of medium A was adjusted to 7.2 using 4 vol% NaOH solution; subsequently, medium B was sterilized for 15-min in an autoclave at 121 °C; medium B, on the other hand, was UV sterilized in a cylindrical filter using UV light.

The experimental solution—the oilfield extract—contained 1.5 gL⁻¹ KCl, 2.2 gL⁻¹ NaHCO₃, 0.16 gL⁻¹ NaCl, 0.07 gL⁻¹ CaCl₂, 0.13 gL⁻¹ MgCl₂·6H₂O, 0.25 gL⁻¹ Na₂CO₃, 0.01 gL⁻¹ Na₂SO₄ (pH 8.7). This solution was used as the sterile medium. Considering the fact that SRB are anaerobic microbes,

the above solution was deoxygenated via a 60-min purging operation using nitrogen prior to sterilization. The bacteria were inoculated into the mixed solution consisting of the experimental solution (the oilfield extract solution) and culture medium in a known proportion (1:50). After bacterial inoculation, the mixed solutions were incubated in a biochemical incubator at 30 ± 2 °C.

2.3 Growth Curve for SRB

Considering that the study focused on the effect of SRB growth cycle on the corrosion behaviour of 2205 DSS, rather than the number of bacteria, turbidimetry was adopted to measure the growth curve of SRB[27, 28]. The bacteria medium was extracted, and the extract absorbance (Abs) was continuously measured for 14 days by using a spectrophotometer (UV-2550).

2.4 Observation of SEM

All samples were exposed into the bacteria and sterile media for 4, 7, 10, and 14 days. After soaking, samples exposed to the SRB-containing medium were fixed with 5 vol% glutaraldehyde solution for 2 h and dehydrated in ethanol (30, 50, 80, and 100 vol%) for 30 min to maintain biofilm integrity[29]. The prepared samples were all sputter-coated with gold, and then analyzed with a scanning electron microscope (SEM, SU-8010) and energy-dispersive X-ray spectroscopy (EDS, Q500MW).

2.5 X-ray Photoelectron Spectroscopy (XPS) Analysis

The elemental composition of the 2205-DSS surface soaked for 14 days (as described above) was determined using an X-ray photoelectron spectrometer (ThermoFisher Scientific). The X-ray excitation source (Al K) was calibrated using the C 1s signal at 284.8 eV, as a standard. An Ar-ion beam was utilized to etch each sample prior to the test to remove air contamination from its surface. Survey spectra were recorded, and high-resolution Fe $2p$, Cr $2p$, Ni $2p$, and S $2p$ spectra were subsequently acquired. A peak-fitting software (XPS Peak 4.1) was used for performing data calculations.

2.6 Electrochemical Experiments

The electrochemical measurements were made in a conventional three electrode electrochemical cell coupled with a potentiostat (EG&G-2273). The electrochemical cells were composed of 2205 DSS as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum plate as the counter electrode. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves measurements were carried out simultaneously under both biotic and abiotic conditions 4, 7, 10, and 14 days. All EIS measurements were carried over a

frequency range of 10^5 – 10^{-2} Hz with an AC amplitude of 10 mV. Polarization curves were recorded by scanning from -1.0 V to a current density of 10^{-2} A cm^{-2} at a scanning rate of 1 mV s^{-1} .

3. RESULTS

3.1 Growth Curve of SRB

Figure 2 depicts the curve for SRB growth in the oilfield water, thereby demonstrating that the growth process can be divided into four stages. The first stage, between days 1–4 was expressed as the viscous phase. In the second stage (days 5–7, logarithmic growth), active SRB increased rapidly. The stationary growth is attained at the end of day 7, The number of active SRB remained high during this stage. After day 10, the growth process reach decline phase, during which the number of SRB present decreased rapidly.

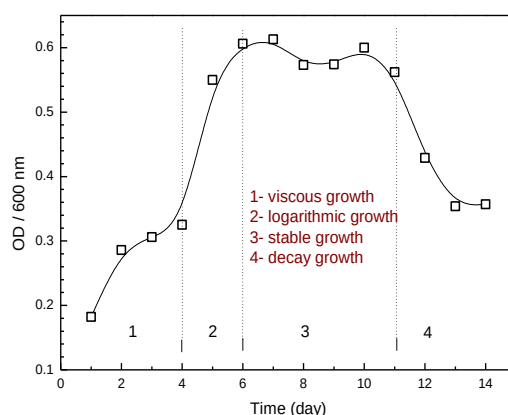


Figure 2. Growth curve of SRB in oilfield production fluid.

3.2 SEM and EDS Analyses

Figures 3 and 4 show SEM images of 2205 DSS immersed in SRB-containing and SRB-free media, respectively. The figures reveal that in the former case, corrosion pits has been formed on day 4 (Figure 3a), and these become the more pronounced after day 7 (Figure 3b). At day 10 (Figure 3c), the number of bacterial cells adsorbed on the surface increased significantly, and SRB began to cluster at the interface, leading to the accumulation of bacterial metabolic by-products such as EPS with the increase of exposure time. These EPS quickly adhere to the surface of the steel and form a dense biofilm on the surface of the steel. At the end of 14 days, the corrosion was seriously, with more deep corrosion pits (Figure 3d). In the case of the SRB-free media, sample-surface corrosion was also occurred in the sterile medium.

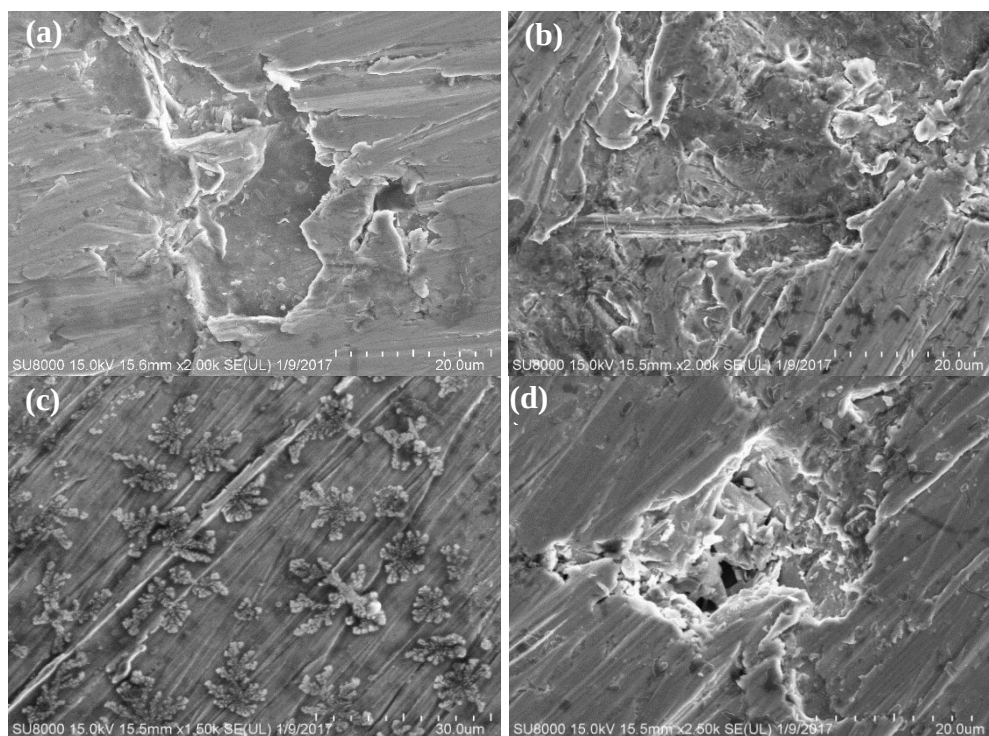


Figure 3. SEM of 2205 DSS immersed in SRB-containing oilfield production fluid, (a) 4 days, (b) 7, days , (c) 10 days , (d) 14 days.

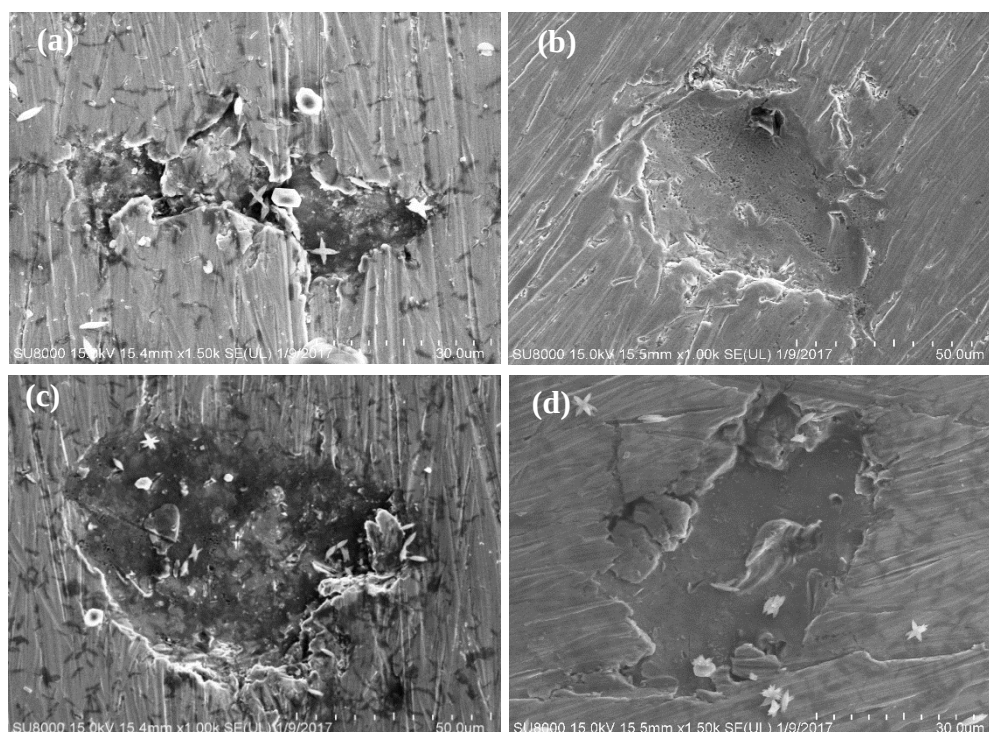


Figure 4. SEM of 2205 DSS immersed in SRB-free oilfield production fluid, (a) 4 days, (b) 7, days , (c) 10 days , (d) 14 days.

Compared to the case of the SRB-containing medium, however, corrosion pits on specimens were observed to be shallower and the samples immersed for 10 and 14 days demonstrated severe corrosion (Figures 4c and 4d).

Table 1 summarizes the results of EDS analysis of 2205 DSS samples immersed in SRB-free and SRB-containing media. The results demonstrate that in the latter case, the corrosion products mainly contain oxides and sulphides owing to the SRB-promoted reduction of SO_4^{2-} to S^{2-} . Maximum S content is observed on day 10, beyond which, it subsequently declines. In the sterile medium, the formation of S-containing products can be explained by the presence of this element either within the solution or as a chemical composition of 2205 DSS; however, concentrations of these products are much smaller compared to those observed in the bacteria medium. Additionally, small amounts of O and C elements are observed in the corresponding EDS spectrum.

Table 1. EDS results for 2205exposed in sterile solution (at%).

Condition	Time (d)	Fe	Cr	C	O	Mn	S	Ni
With SRB	4	34.74	15.11	20.81	22.97	1.96	1.08	2.92
	7	57.01	18.24	12.07	4.22	20.8	1.30	4.61
	10	53.20	16.14	11.32	8.29	1.94	1.45	4.48
	14	54.15	18.49	14.76	4.49	1.86	1.31	4.40
Without SRB	4	35.84	12.65	32.05	14.21	1.33	0.83	2.70
	7	49.43	18.96	18.30	6.02	2.36	0.75	3.50
	10	39.74	12.78	33.78	7.97	1.58	0.73	3.11
	14	35.29	12.94	76.53	15.05	1.58	0.64	3.82

3.3 Electrochemical Characterization E_{corr}

Figure 5 demonstrates that E_{corr} values for 2205 DSS immersed in the SRB-free medium significantly exceeded those corresponding to the SRB-containing medium. In the former case, the initial E_{corr} value of -202 mV increased to -100 mV on day 7, beyond which, it became more negative and equalled -144 mV on day 10 before finally attaining a value of -110 mV. Huang studied the corrosion potential data of 38 metallic materials immersed in seawater and found that E_{corr} of the stainless steel that had high passivation capability moved nobly with time and the time for E_{corr} to become stable was longer [30]. In the bacterial medium, the corresponding E_{corr} value appeared an initial decrease to attain a minimum of -411 mV. Then, it became positive and equalled -397 mV on day 12 remaining stable.

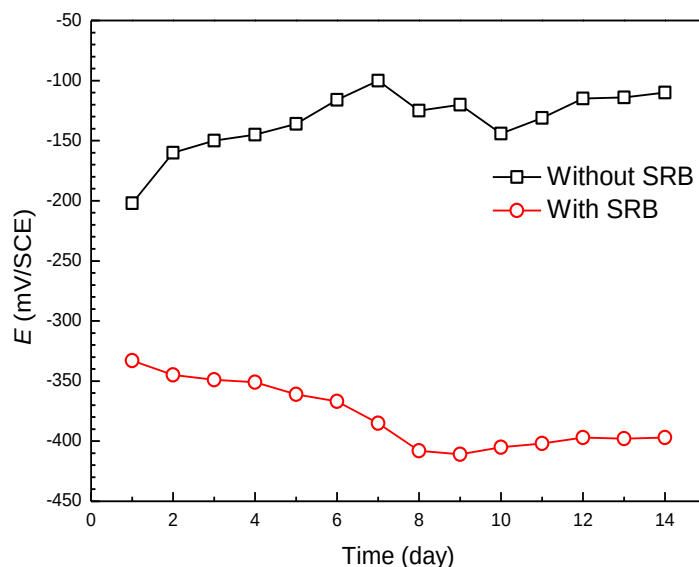


Figure 5. E_{corr} of 2205 DSS immersed in oilfield production fluid..

3.4 EIS Results

Figures 6 and 7 depict EIS test results obtained for 2205 DSS immersed in SRB-containing and SRB-free media, respectively. The high frequency part of the loops is shown to be coincident, whereas the low frequency part deviates more significantly. High frequency impedance spectroscopy reflects the combination information of the electrode surface, and low frequency impedance spectroscopy reflects the information of the electrode reaction. The sizes of radii of the capacitive loops at lower frequencies represent the polarization resistance and present a certain regularity with time: the larger the size of the low frequency loops' radii, the higher the corrosion resistance of the metal.

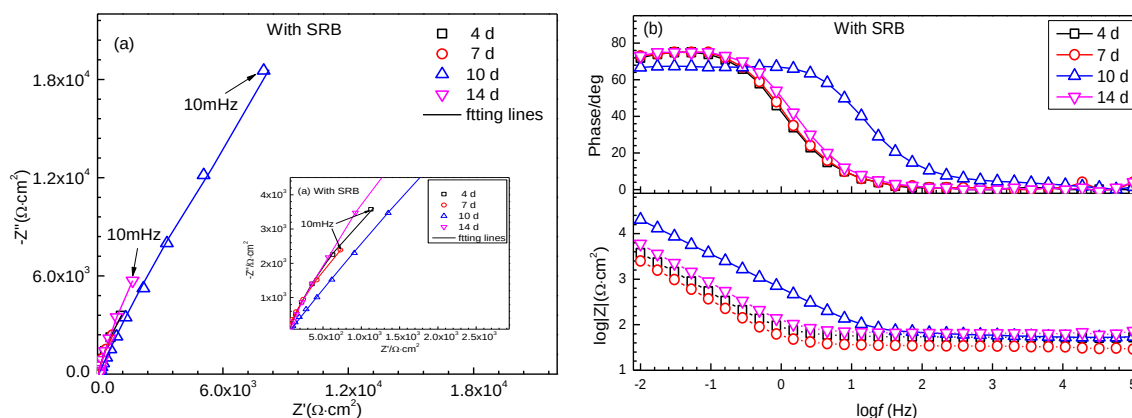


Figure 6. EIS results for 2205 DSS immersed in SRB-containing oilfield production fluid

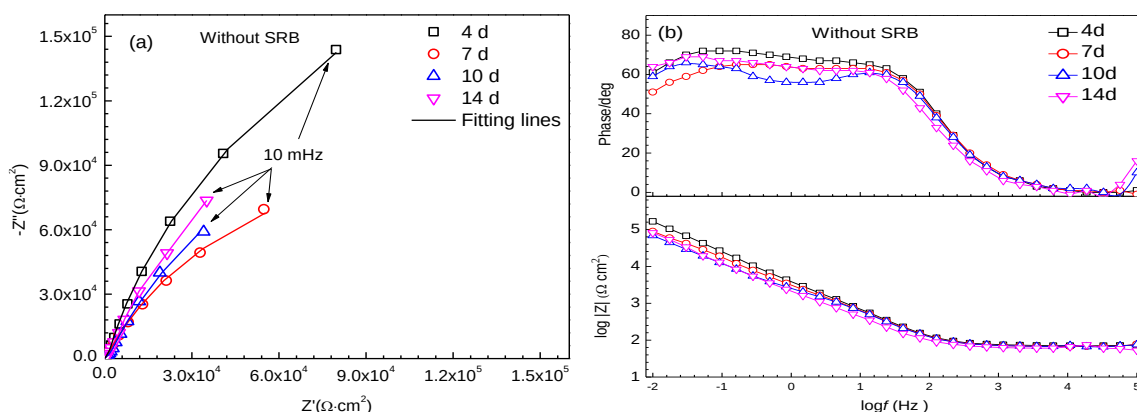


Figure 7. EIS results for 2205 DSS immersed in SRB-free oilfield production fluid .

In the bacterial medium, the radius of the EIS loop reached the maximum on day 10 while its corresponding lowest value was observed on day 7. All curves are composed of a single capacitive arc, indicating that the reaction is controlled only by electrochemical reaction. In the Phase- $\lg f$ diagram, the curves basically overlap except on day 10. The peak-wide on day 10 indicated existence of a dual structure on the metal surface. In the sterile medium, the $|Z|$ - $\lg f$ curve demonstrated only little change over the fourteen days. The largest impedance radius of the capacitive loop was observed on day 4 with the corresponding minimum being observed on day 10. In the Phase- $\lg f$ diagram, all samples immersed for different times demonstrated peaks in the middle- and low-frequency regions with a wide range of crests, which could be attributed to the superposition of two time constants.

EIS spectra were fitted using the equivalent circuit depicted in Figure 8, wherein R_s , R_f , and R_{ct} , respectively, denote solution, passivation film and biofilm, and charge-transfer resistance, and CPE denotes the double-layer constant phase-angle element. CPE_f and CPE_{dl} denote biofilm or corrosion products film and electric double-layer capacitors, respectively. The ZsimpWin software was used to fit the data; the fitting results are summarized in Table 2. Here the total resistance R_p is defined as the sum of the resistors. Figure 9 depicts R_p curve obtained upon immersion of 2205 DSS in SRB-free and SRB-containing media for different times. As depicted in Figure 9, R_p values obtained for the SRB-containing medium were observed to be significantly lower compared to those corresponding to the sterile medium, thereby indicating the former medium to be more corrosive.

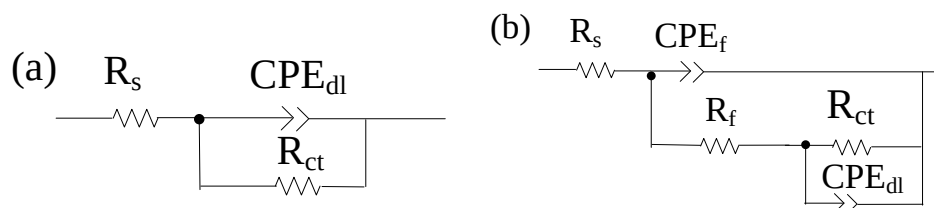


Figure 8. Equivalent circuit diagram of impedance diagram of 2205 DSS in electrochemical test.

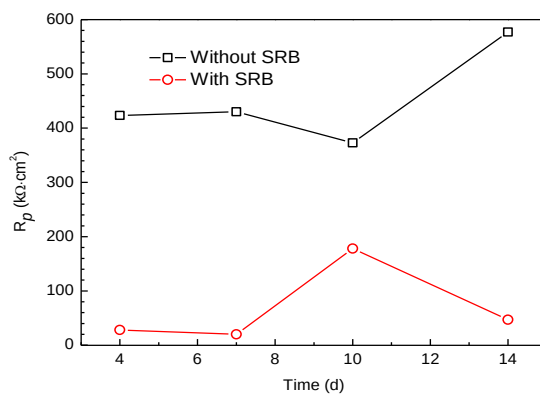


Figure 9. R_p for 2205 DSS immersed in oilfield production fluid.

Table 2. EIS fitting results for 2205DSS exposed in oilfield production fluid

Condition	Time/ (d)	$R_s/$ ($\Omega \cdot \text{cm}^2$)	$CPE_f/$ ($\text{F} \cdot \text{cm}^{-2}$)	n_1	$R_f/$ ($\Omega \cdot \text{cm}^2$)	$CPE_d/$ ($\text{F} \cdot \text{cm}^{-2}$)	n_2	$R_{ct}/$ ($\Omega \cdot \text{cm}^2$)
Without SRB	4	62.1	7.1×10^{-5}	0.8	3410	5.0×10^{-5}	0.8	4.2×10^5
	7	68.0	7.2×10^{-5}	0.7	0.6	7.0×10^{-6}	1.0	4.3×10^5
	10	68.6	4.4×10^{-5}	0.9	2890	8.5×10^{-5}	0.8	3.7×10^5
	14	70.4	4.8×10^{-5}	0.8	1.7×10^4	1.2×10^{-5}	1.0	5.6×10^5
With SRB	4	53.3	--	--	--	3.0×10^{-3}	0.9	2.8×10^4
	7	33.3	--	--	--	4.5×10^{-3}	0.9	2.0×10^4
	10	53.0	4.0×10^{-4}	0.78	1.7×10^5	1.2×10^{-5}	0.9	5.75
	14	65.7	--	--	--	1.9×10^{-3}	0.89	4.7×10^4

3.5 Polarization Curves

Figure 10 depicts polarization curves obtained for 2205 DSS immersed in SRB-containing and SRB-free media while Table 3 describes corresponding fitting results. Also noteworthy, is the marked difference between polarization curves obtained under presence and absence of SRB. As depicted in Figure 10(a), the anode polarization curves showed activation behavior when the potential below 0.05 V and a current peak value at 0.05 V was observed. Then, polarization curves entered activation-passivation transition range, and it reached stable passivation zone at 0.2 V. SRB metabolism demonstrated little effect on initiating passive potential, passivation potential and over passivation potential. However, compared with the 4th day and the 7th day, the initiating passive current at the 10th day and the 14th day decreased significantly. Figure 10(b) reveals that the immersion time has little to no effect on the polarization behaviour of 2205 DSS, showing its better corrosion resistance in

the sterile medium. Moreover, the activation-passivation transition potential for the sterile medium showed disappeared compared to those corresponding to the SRB-containing medium. This indicates that the current peak corresponding to the activation -passivation transition potential is caused by the corrosion products formed by SRB.

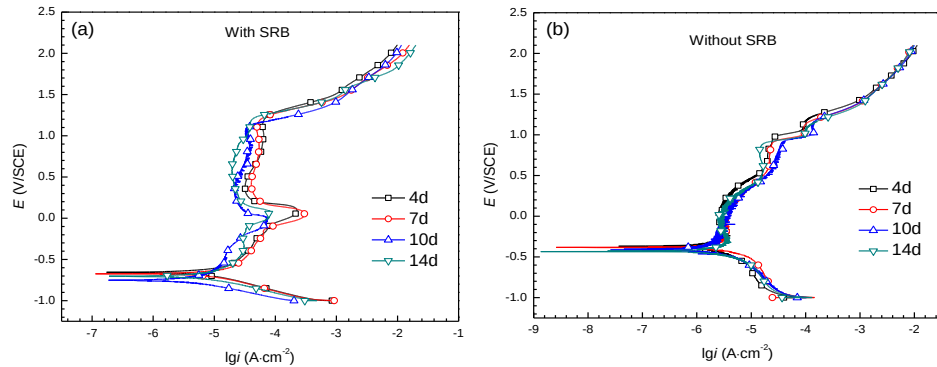


Figure 10. Polarization curves for 2205 DSS exposed to oilfield production fluid, (a) with SRB, (b) without SRB.

Table 3. Polarization curve fitting results.

Condition	Time (d)	$I_p(\mu A cm^{-2})$	$E_{corr}(mV)$	Passivation interval(mV)
With SRB	4	4.295	-656	219~1226
	7	4.645	-665	196~1185
	10	2.317	-741	840~1109
	14	3.828	-703	196~1217
Without SRB	4	1.396	-393	-234~974
	7	1.221	-384	-303~936
	10	1.753	-403	-311~887
	14	1.109	-441	-268~855

3.6 XPS Results

Figure 11 depicts XPS survey spectra of the stable passivation film obtained for 2205 DSS exposed in the bacterial and sterile medium. The observed spectra demonstrate that in both cases, signals corresponding to Fe, Cr, C, and O are stronger compared to those of Ni and Mn. Figure 12

depicts XPS fits of Fe 2p_{3/2}, Cr 2p_{3/2}, Ni 2p_{3/2}, and S 2p_{3/2} peaks observed for the stable passivation film of 2205 DSS in the SRB-containing medium. Notably, the Fe 2p_{3/2} signal observed in the SRB-containing medium could be de-convoluted into two peaks with binding energies of 708.2 and 706.3 eV corresponding to Fe₃O₄ and FeS₂, respectively[31, 32]. Similarly, the Cr 2p_{3/2} peak can be de-convoluted into signals with binding energies of 575.8 and 573.5 eV, which are ascribed to Cr₂S₃ and Cr, respectively [33]. Likewise, the Ni 2p_{3/2} signal can be de-convoluted into peaks centred at 852.3 and 845.1 eV ascribed to Ni [29] and NiO [31], respectively. The S 2p_{3/2} signal was de-convoluted into three peaks with binding energies of 161.4, 160.1, and 159.2 eV ascribed to FeS, Na₂S, and NiS, respectively[33]. Figure 13 depicts XPS fits of Fe 2p_{3/2}, Cr 2p_{3/2}, Ni 2p_{3/2}, and S 2p_{3/2} peaks observed for the stable passivation film of DSS 2205 immersed in the SRB-free medium, revealing that the Fe 2p_{3/2} signal could be de-convoluted into two peaks with binding energies of 708.9 (FeO) and 706.1 (Fe) eV[24]. Moreover, the Cr 2p_{3/2} signal was de-convoluted into peaks centred at 576.1 (Cr₂O₃) and 573.3 (Cr) eV[33, 34]. Lastly, the Ni 2p_{3/2} signal was de-convoluted into peaks centred at 852.3 and 845.0 eV were ascribed to Ni [29] and NiO [31], respectively.

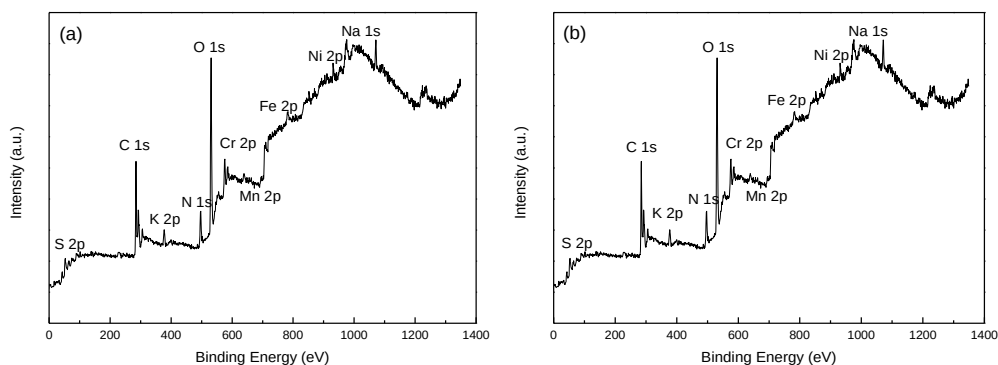
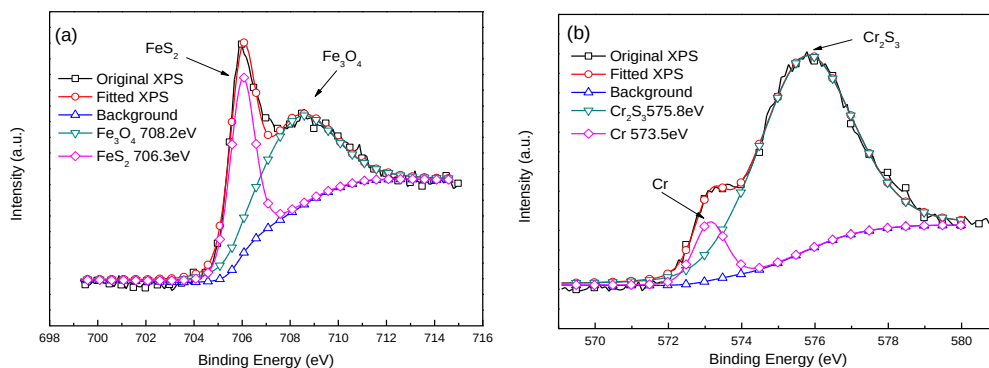


Figure 11. Full XPS spectrum of 2205 DSS immersed in (a) SRB-containing and (b) SRB-free oilfield production fluids for 14 days.



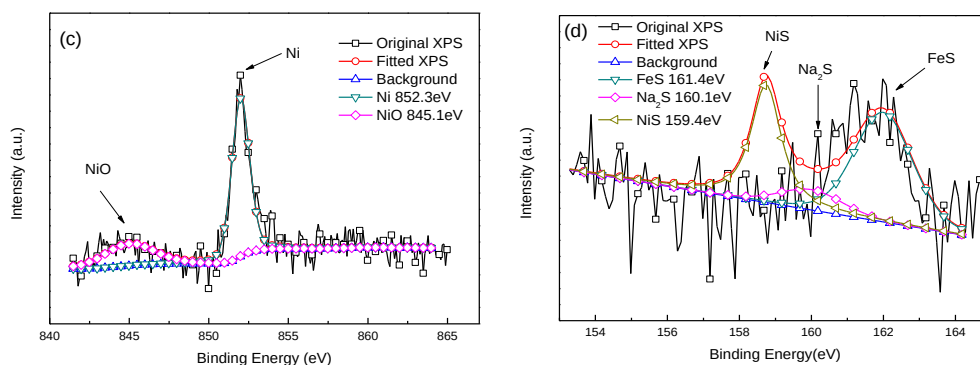


Figure 12. High-resolution XPS spectroscopy of passivation film of 2205 DSS immersed in SRB-containing oilfield production fluid for 14 days.

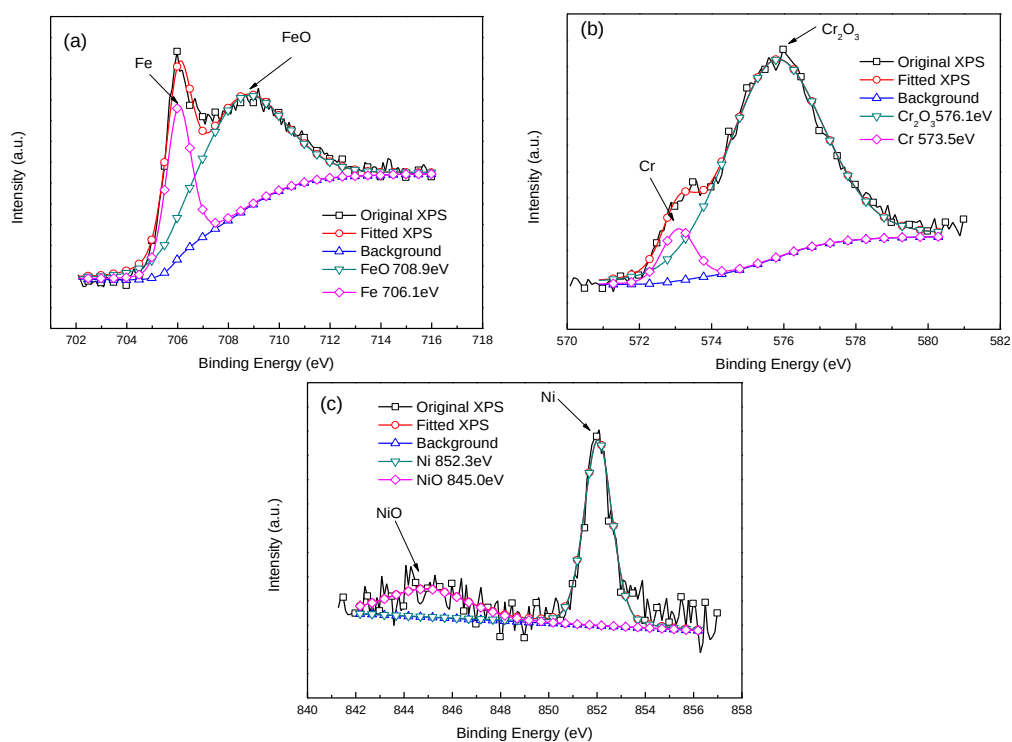


Figure 13. High-resolution XPS spectroscopy of passivation film of 2205 DSS immersed in SRB-free oilfield production fluid for 14 days.

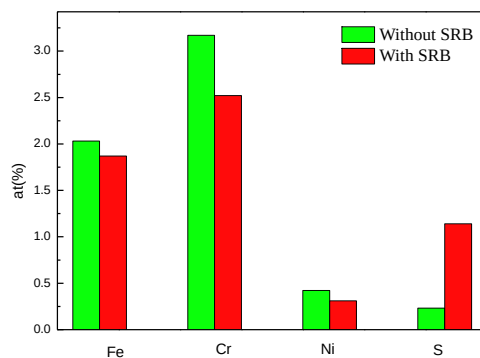


Figure 14. Main contents of 2205 passivation film with and without presence of SRB.

Figure 14 depicts the elemental composition of passivation films obtained for 2205 DSS in the absence and presence of SRB, thereby demonstrating that higher concentrations of Fe, Cr, Ni, and other contents were observed in the former case with the opposite being true for S.

4. DISSCUSSION

4.1 Effects of SRB metabolism on corrosion morphology

Observed results from SEM demonstrate that the corrosion morphology of 2205 DSS immersed in oilfield production fluid was dominated by pitting corrosion, and that the corrosion of samples immersed in the SRB-containing medium was worse compared to that of samples immersed in the sterile medium. Corrosion of the sample immersed into the sterile medium was observed to have weakened on day 14 owing to increased adherence of corrosion products to the steel surface. The biofilm has not been completely formed on the metal surface in the SRB-containing medium during the viscous-growth period. The corrosion pits were observed to appear on the sample surface in both bacterial and sterile media, since the aggressive anions, such as Cl^- , SO_4^{2-} , first reacted with the passivation film. During the logarithmic growth phase, surfaces of samples immersed in the SRB-containing medium were observed to be significantly more corroded compared to those immersed in the sterile medium. Because in the former case, most of SRB existed in the solution in the dissociated state, a large amount of O_4^{2-} was converted into S^{2-} . As a result, Fe^{2+} and Cr^{3+} entered the solution to form sulfide thereby promoting corrosion. During the stable growth phase, significant biofilm attachment was observed on the sample surface in the SRB-containing medium. This finding was ascribed to coverage of the SRB-exposed steel surface with a mostly EPS-comprising protective biofilm that prevented mass transfer across itself [35]. However, during the decay stage, the initially compact biofilm became loose and was eventually delaminated, thereby exposing the substrate to a solution containing a large amount of aggressive species and promoting corrosion [5]. Results of EDS analysis demonstrate that in the SRB-containing medium, Fe and S compounds were deposited on the steel surface, and the additional observation of C was ascribed to the deposition of organic matter produced owing to SRB metabolism [36].

4.2 Effects of SRB metabolism on the electrochemical behaviour of 2205 DSS

The E_{corr} value of 2205 DSS were dependent on the growth phase of SRB. During the viscous growth and logarithmic growth, E_{corr} was observed to become increasingly negative owing to the incomplete biofilm by SRB rapidly colonized and the electronegativity of its metabolites [37]. During the steady-growth stage, E_{corr} became more positive owing to gradually formation of a biofilm. The E_{corr} value gave information concerning the biofilm and sulphide layer, not the substrate instead. After commencement of the decay period, the value of E_{corr} remained stable owing to increased SRB mortality.

EIS results demonstrate that the presence of SRB greatly facilitates corrosion. In the SRB-containing medium, the capacitive-impedance-loop radii were observed to be broadly variable with

great dependence on the SRB growth period. During the logarithmic growth stage, the said radii values were observed to sharply decrease owing to quickly increase of the quantity of SRB, thereby resulting in a significant increase in S^{2-} that reacts with the Fe^{2+} in the solution. The largest radius was observed to correspond to the stable growth period, wherein biofilm and corrosion product film on the steel surface formation and gradual thickening. The above processes tend to alter the steel surface characters and reduce the corrosion rate [38]. The time constant in the low-frequency region in the Bode diagram must have originated owing to SRB biofilm formation [39]. Two time constants appeared during the period of stable growth representing the biofilm and corrosion-product film, respectively. Both films showed protective effect, with biofilm acting as barriers to prevent chemical transfer in the presence of biofilm, observed on day 10 during SEM imaging (Figure 3c).

In addition, as seen from Table 3, the current density in the SRB-containing medium was observed to be greater compared to that in the sterile medium, thereby indicating that the metabolic activity of SRB promotes corrosion. The corrosion resistance of 2205 DSS varied significantly during different SRB growth stages, its lowest value being recorded during the logarithmic growth period. According to SEM results, in this stage, although the bacterial proliferated in large numbers, most of SRB existed in the solution in the dissociated state, and there was a few on the metal surface. As a result, Fe^{2+} and Cr^{3+} entered the solution to form sulfide and the corrosion rate increases. Conversely, as the biofilms prevented Fe^{2+} and Cr^{3+} from entering solution and hindered H^+ reduction, corrosion was less likely to occur during the stable growth period.

4.3 XPS analysis

Observed results of XPS peak fitting indicate that in the sterile medium, the passivation film mainly comprises Fe, Cr, Ni, and their oxides, whereas in the SRB-containing medium, the film mainly comprised sulphides of Fe, Cr, and other simple substances owing to the effect of S^{2-} infiltration. In the former case, although main components of the passivation-film outer layer include easy-to-dissolve FeO and NiO, the presence of Cr_2O_3 plays a vital role in determining the stability of the passivation film, because Cr^{3+} is poorly soluble in water and has high stability causing it to additionally act as a skeletal component to stabilize the inner layer of the passivation film[40]. Cr_2O_3 , therefore, forms a denser film hardly affected by complex adsorption, complexation, and dissolution, thereby providing good protection against corrosion in agreement with the observed results of electrochemical characterization obtained for the sterile medium. In the SRB-containing medium, S^{2-} infiltration changes the composition of the passivating film to FeS, FeS_2 , Cr_2S_3 , and NiS, thereby resulting in the activation-passivation transition potential in the anodic polarization curves. Chen [41] believed that the passivation film with sulphide is more easily penetrable by SO_4^{2-} and Cl^- compared to the sulphide-free passivation film. The decrease in Fe, Cr, and Ni content and increase in that of S demonstrates that the corrosion resistance of 2205 DSS in the SRB-containing medium is deteriorated by vulcanization.

4.4 Corrosion Mechanism 2205 DSS in the Oilfield Production Fluid Containing SRB

Electrochemical and SEM results showed that the corrosion mechanism of 2205 DSS is different at each growth stage of SRB. In the viscosity growth stage, SRB is basically free in the solution and has no direct reaction with the surface of the steel. At this time, only the weak spots on the passivation film are attacked by the corrosive ions in the oilfield produced water, resulting in the corrosion being slight. In the logarithmic growth stage, SRB existed in the solution in dissociation state and SO_4^{2-} was converted into S^{2-} . As a result, metal ions entered the solution to form sulfide and 2205DSS corrosion rate increased. In the stable growth stage, corrosion is slowed down by the presence of a compact biofilm and sulphide layer on the metal surface. However, the passivation film, thus, transforms into a sulphide film, namely S^{2-} infiltration changes the composition of the passivating film to FeS , FeS_2 , Cr_2S_3 , and NiS , thereby resulting in release of oxygen from oxide. In the decay stage, the vulcanization of oxide layer makes it easy for the corrosive anions to permeate, leading to the breakdown of the passivation film. In additions, the biofilm and corrosion-product layer began to delaminate or even drop off with increasing of mass metabolic byproducts, thereby the local corrosion is accelerated. The corrosion mechanism of 2205 DSS in different growth stages of SRB is depicted in Figure 15.

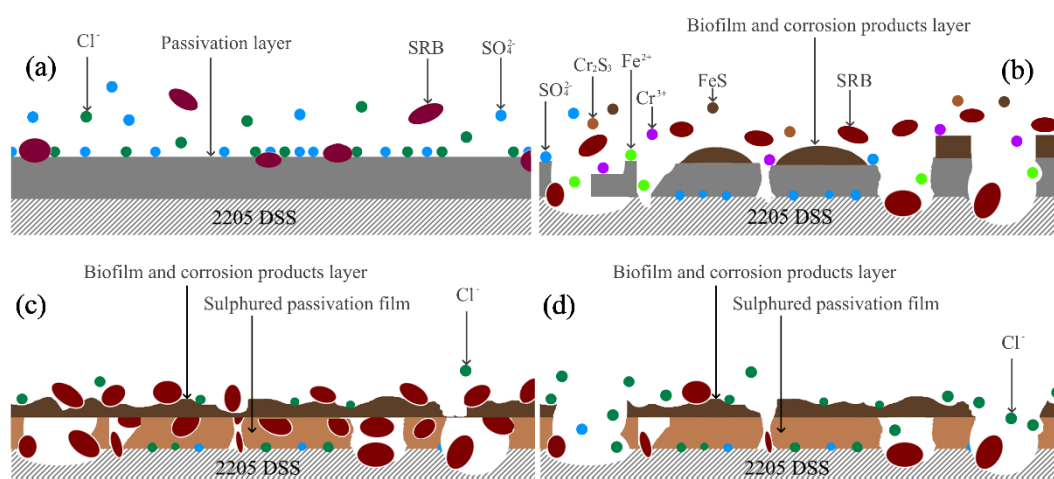


Figure 15. Corrosion mechanism of 2205 DSS during different SRB growth periods—(a) viscous growth;(b)logarithmic growth; (c)stable growth; (d)decay.

5. CONCLUSIONS

The corrosion morphology of 2205 DSS in oilfield water-injection systems is pitting corrosion, and the pit become deeper in case of bacteria. Self-passivation performance of 2205DSS degenerated under presence of SRB. The current peak corresponding to the activation -passivation transition potential is caused by the corrosion products formed by SRB. Corrosion rate significantly increased during the logarithmic growth phase, SRB existed in the solution in dissociation state and SO_4^{2-} was converted into S^{2-} . As a result, metal ions entered the solution to form sulfide and 2205DSS. Corrosion

is inhibited during the steady growth phase of SRB, however, the corrosion resistance of 2205 DSS in the bacteria medium is deteriorated by SRB vulcanization. The sulphide-containing passivation film is more easily penetrable by aggressive anion and the local corrosion is accelerated compared to the sulphide-free passivation film.

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