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CREVICE CORROSION STUDY OF SAF 3207 HD IN 6% $FeCl_3$ SOLUTION USING POLARIZATION, WEIGHT LOSS, AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY METHODS

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ABSTRACT

Hyperduplex Stainless Steel 3207 (SAF 3207 HD) is one of the materials used in the oil and gas industry, especially for umbilical, which is a system to connect cables or instrumental setups between control platforms and wellhead station. It is used in deep water containing high chloride ion (Cl^-), so it needs high tensile strength and must be a highly corrosion-resistant material. In this research, several corrosion resistance tests were conducted on 3207 hyperduplex stainless steel such as polarization and weight loss testing. Roughness surface tests were carried out to observe alterations to the surface caused by underwater corrosion. SAF 3207 HD can form a passive layer due to an environmental reaction; to observe this phenomenon, an EIS test was conducted at the interface of the material. The weight loss test was conducted on a particular sample, in accordance with ASTM G48-97 method B. The corrosion test was carried out at temperatures of 60–90°C (at 5°C intervals) in 6% $FeCl_3$ solution. The results show that SAF 3207 HD has good crevice corrosion resistance, although crevices were not seen below temperatures of 70°C, which is known as critical crevice temperature. At this temperature, the corrosion rate reached 10.032 mm/year and the crevice depth was 1.034 μm. This means that the operating temperature of the umbilical can be increased up to 70°C.

Keywords: Corrosion; Crevice; EIS ; Hyperduplex stainless steel; Polarization

1. INTRODUCTION

Crevice corrosion is one of the local corrosions that is often encountered in the oil and gas industry. It occurs in metal with a geometrical gap or one that is on the surface layer, where the solution can be restrained. The gap could be between two different metals, or between metal and other materials. Crevice corrosion can occur in metals with good corrosion resistance, such as stainless steel, in hidden areas, causing sudden failure during service. Crevices are usually found in material connections such as welding, lap joints, and bolting.

There has been little research so far into SAF 3207 HD as it is a relatively new material. Previous research into corrosion resistance seen in SAF 3207 HD has been conducted by Chai et al. (2009). They measured critical pitting and crevice corrosion (CPT and CCT) by an MTI-2 crevice former for 24 hours, obtaining a critical crevice temperature of ≥ 75°C.

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2. METHODOLOGY

The specimen used in this research was SAF 3207 HD, with chemical composition as listed in Table 1. All corrosion testing was conducted in the same solution, namely, 6% $FeCl_3$ solution, referred to as ASTM G48,under temperatures ranging from 60–90°C at intervals of 5°C. The specimen's surface was polished by several grades of emery papers (600−1200 grade).

Table 1 Chemical composition of SAF 3207 HD

C	Si	Mn	Cr	Ni	Mo	N	Cu
< 0.03	0.25	0.82	31.38	7.07	3.50	0.48	0.21

2.1. Weight Loss Test and Surface Roughness Test

The sample's dimensions for weight loss tests were 5×1.94×0.35 cm. Before the crevice test, the specimen was assessed for its initial weight and the final weight after the test. The corrosion rate was calculated with the following equation:

$$mpy = \frac{Kx\ w}{DAT} \tag{1}$$

where,

K : constant (87.6)
w : weight loss specimen (mg)
D : specimen density (7.79 gr/cm^3)
A : surface area exposure (4.9 cm^2)
T : immersion time (72 hours)

The geometry of the specimen was measured referred to as ASTM G 48-method B, as shown in Figure 1. Two TFE-fluorocarbon blocks were securely attached to the test specimen SAF 3207 HD with rubber bands, before immersing it in 6% $FeCl_3$ solution for 72 hours.

A surface roughness test was conducted to observe the depth of crevice corrosion, at temperatures of 70°C, 80°C, and 90°C.


(a)

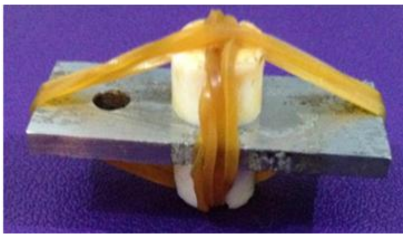

(b)

Figure 1 (a) Specimens of SAF 3207 HD; (b) Specimen of crevice corrosion test

2.2. Polarization and Electrochemical Impedance Spectroscopy (EIS) Test Methods

The surface area of the specimen that was exposed in the polarization test was 1.94 cm^2 (1cm×1.94cm). The linear polarization test was conducted with reference to the ASTM G5-82 standard, with a 0.01 mV/s scan rate and a -0.5 V to -1.5 V potential range vs the Ag/AgCl reference electrode. This test was conducted using the CMS 100 and Nova 1.10 programs.

An EIS test was conducted to study the interface behavior of SAF 3207 HD in 6% $FeCl_3$, using the same program.

2.3. Microstructure Examination

Microstructure examination was carried out as part of this study to identify the presence of local corrosion. Microstructures were examined based on ASTM E3-11, before and after corrosion testing by an Olympus AH optical microscope, which had been etched by KOH & Murakami reagent (10 g KOH, 10 g K_3FeCN_6, and 100 ml of water).

3. RESULTS

3.1. Weight Loss and Surface Roughness Testing

A visual observation of the specimen after weight loss testing confirmed the presence of crevice corrosion in the test environment.

Table 2 Weight loss of SAF 3207 HD in 6% $FeCl_3$ solution after 72 hours of immersion

Solution temp. (°C)	W_o (gram)	W_f (gram)	Weight loss (mg)	Corr. evaluation (mm/year)
60	25.5748	25.5421	49	0.790
65	25.8672	25.8138	80	1.290
70	26.1978	25.5748	623	10.032
80	25.7891	24.8483	941	15.150
90	26.1005	23.9778	2123	34.181

It can be seen in Figure 2 that the higher the temperature of the solution that was introduced, the more numerous and wider were the points of corrosion, which are indicated by black points. From the surface roughness test of the specimen after weight loss testing, the depth of the crevice as a result of the corrosion process could be measured. Table 3 shows the measurement results.

(a) (b) (c) (d) (e)

Figure 2 Visual observation of SAF 3207 HD after weight loss in 6% $FeCl_3$ with solution temperature of: (a) 60°C; (b) 65°C; (c) 70°C; (d) 80°C; and (e) 90°C for 72 hours

Table 3 Crevice corrosion depth obtained from surface roughness testing

Solution temperature (°C)	Corrosion depth$_{av}$ (μm)
70	1.034
80	1.774
90	2.101

3.2. Polarization Measurement Result

The polarization behavior of SAF 3207 HD was studied in relation to the nature and concentration of the solutions. Figure 3 shows a typical linear sweep potentio-dynamic trace for SAF 3207 HD in 6% $FeCl_3$ solution under different temperatures.

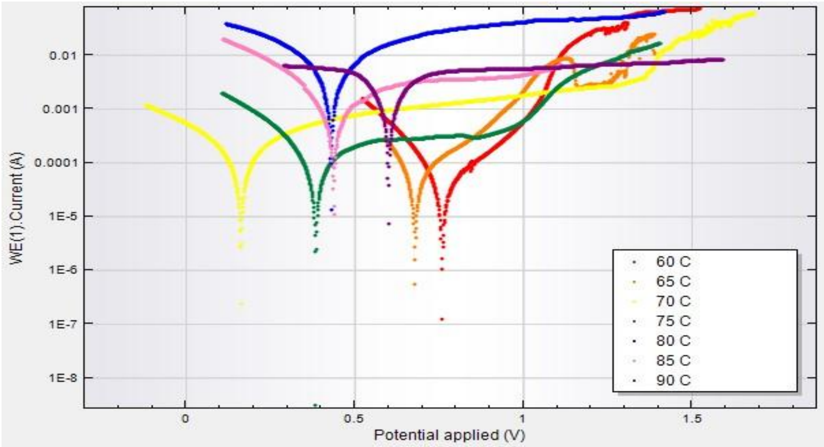


Figure 3 Polarization curve of linear polarization testing of SAF 3207 HD at various temperatures in 6% $FeCl_3$ solution

Data for the E_{corr} and I_{corr} values obtained in this polarization testing show the corrosion rate, and are listed in Table 4.

Table 4 Corrosion rate value of SAF 3207 HD as a result of polarization testing in 6% $FeCl_3$ solution at various temperatures

Solution temp. (°C)	E_{corr} (mV)	i_{corr} (μA)	Corr. Rate (mm/year)
60	759.01	37.61	0.085
65	678.08	90.74	0.205
70	162.27	352.60	2.156
75	383.91	101.23	0.228
80	429.36	6742.00	15.206
85	437.14	1769.20	3.990
90	599.53	4480.50	10.106

3.3. Electrochemical Impedance Spectroscopy

Figure 4 shows a Nyquist plot of the results of the SAF 3207 HD EIS test. Table 5 shows the EIS test results, describing some parameter values of the EIS method, while Table 6 shows the models of the circuit's electrical equivalent in front of surface specimens during the corrosion test.

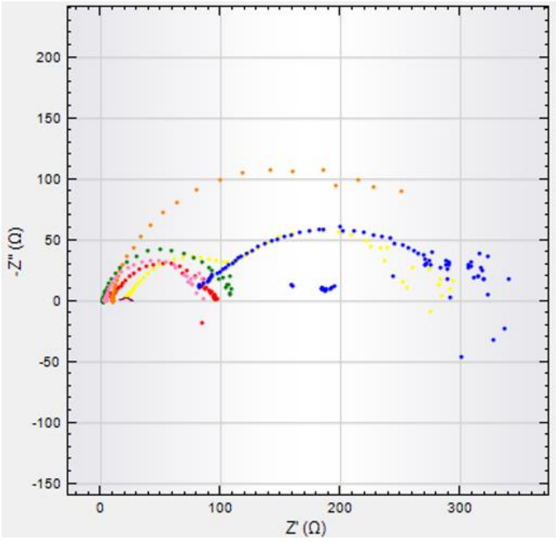


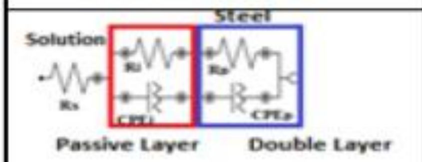
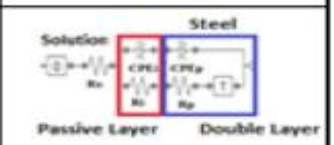
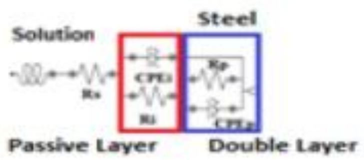
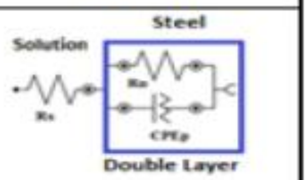
Figure 4 Nyquist plot of EIS result from HDSS 3207 testing with $FeCl_3$solution (red = 60°C, orange = 65°C, yellow = 70°C, green = 75°C, blue = 80°C, indigo = 85°C, violet = 90°C)

Table 5 EIS of SAF 3207 HDin 6% $FeCl_3$ solution testing results

Solution temp. (^oC)	R_i (Ω)	R_p (Ω)	CPE_i (μF)	N	CPE_p (μF)	N
60	141	87	0.0004	1	60.8	0.7
65	218	234	0.0879	1.05	1570	0.9
70	181	115	577	0.787	59	0.7
75	-648	756	252	0.943	18.6	0.3
80	0.68	211	610	0.732	24.4	0.9
85	-	80.3	-	-	1020	0.9
90	14.4	4.41	6090	0.197	278	0.8

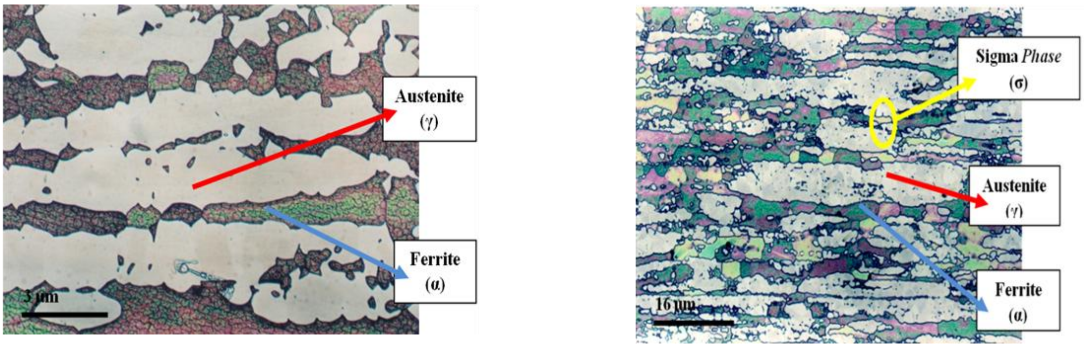
Notes: Ri: Passive film resistance, Rp: EDL resistance, CPEi: Passive film conductance, CPEp: EDL conductance

Table 6 Models of circuit's electrical equivalent in EIS testing results

Solution Temperature of 60°, 70°, 80°, and 90°C	Solution Temperature of 65°C
	
Solution Temperature of 75°C	Solution Temperature of 85°C
	

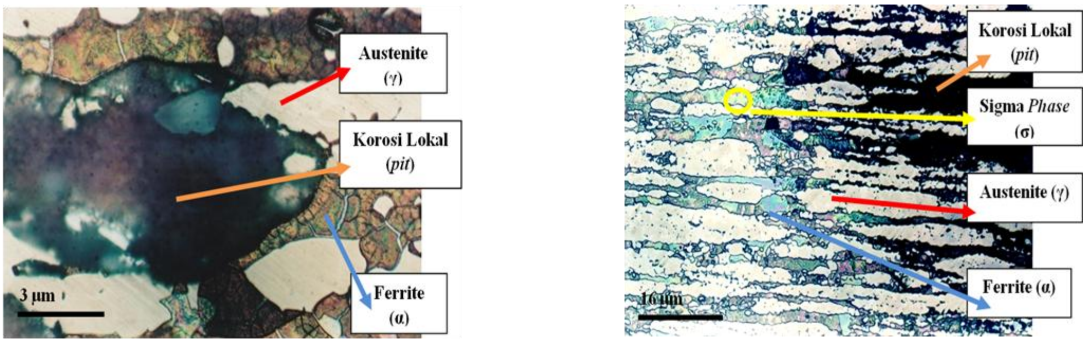
3.4. Microstructure Observation

Figures 5 and 6 show the results of the optical microstructure examination, before and after corrosion testing.



(a) (b)

Figure 5 Microstructures of SAF 3207 HD *before* corrosion testing, using: (a) KOH reagent etching; (b) Murakami reagent etching



(a) (b)

Figure 6 Microstructures of SAF 3207 HD *after* corrosion testing, using: (a) KOHetching; (b) Murakami reagent etching

4. DISCUSSION

4.1. Result of Corrosion Rate Measurement by Weight Loss Testing

Weight loss testing was conducted to determine the corrosion resistance of specimens, as measured by the value of corrosion rate. The data provided in Table 2 is summarized by the curve in Figure 7. This shows that the weight loss incurred at 60°C and 65°C was not a result of crevice corrosion. Figures 2a and 2b also verify whether the corrosion product, which showed as a small hole, occurred outside the crevice area.

At 70°C and 80°C, the weight loss of the material increased to 623 and 941 mg. As a result, the corrosion rate grew to 10.032 mm/year and 15.1250 mm/year. This increasing corrosion rate expresses the broken passive layer which was formed in the surface of the specimen.

As supported by visual observation at 70°C and 80°C (Figures 2c and 2d) and depth of crevice for the same temperatures (Table 4), 1.034 µm and 1.774 µm, 70°C temperature is the critical crevice temperature (CCT) for 3207 hyperduplex stainless steel.

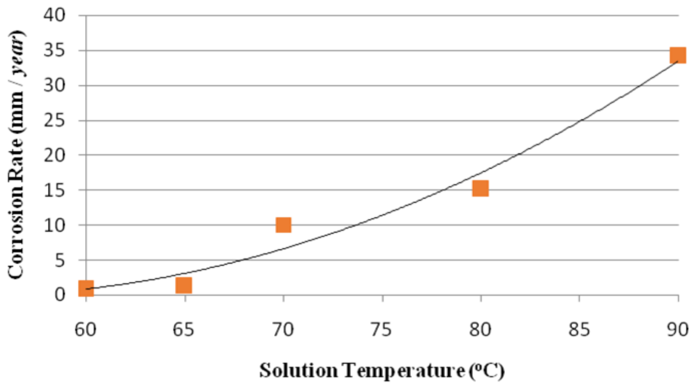


Figure 7 Graph of temperature solution effect on crevice corrosion rate of SAF 3207 HD in 6% $FeCl_3$ solution

4.2. Result of Corrosion Rate Measurement by Polarization Test

The behavior of each curve in Figure 3 shows the tendency of the specimen in active conditions or when oxidized (corroded), but in certain potentials the curve tends to be passive. This phenomenon occurred for all temperature testing conditions except 60°C.

The i_{corr} value increased in line with the solution testing temperature. This shows an enhancement of the corrosion rate; Fontana et al. (1991) stated that an increase in environmental temperature can exacerbate anodic dissolution in metal. The temperature parameter influences the cathodic reaction (Escrivà-Cerdán, 2003). The polarization curve for temperatures of 70°C to 75°C and 80°C to 85°C, shows the reduction of the corrosion current (i_{corr}) as 352.60 to 101.23 µA and 6742 to 1769.2 µA. This demonstrates a decline in the corrosion rate. The curve's behavior shows the formation of a passive layer. According to Escrivà-Cerdán (2012), rising temperature can improve the growth of the passive layer on the surface of the metal.

Jones (2012) provides a reference for the interpretation of Table 4, where in the corrosion rate in the range of 0.085–15.206 mm/year is classified, as well as a corrosion resistance specimen in the testing solution for the specimen at temperatures of 60°C, 65°C, and 75°C, and fair corrosion resistance for a specimen of SAF 3207 HD immersed at 70°C (2.156 mm/year).

4.3. Observation of Metal-Solution Interface Phenomenon with EIS Measurement

The result of the EIS test can be found in the Nyquist plot shown in Figure 4. This shows the influence of temperature on the semicircle curve of the Nyquist plot, which also automatically affects the value of impedance at each temperature. By increasing the temperature, the diameter of the curve decreases, which could represent a fall in material resistance due to increasing temperature. The interface phenomenon of metal solution is depicted with the electrical circuit equivalent model under EIS measurement. Table 5 shows that this model, as a result of fitting, becomes a measurable parameter such as R_p (polarization resistance), R_s (solution resistance), double layer capacitance, or constant phase element (Q), where the pure capacitor has the value N = 1. The EIS measurement shows that the range of N values are 0.3–0.9; this value fluctuates in line with the rising solution-testing temperature, showing a tendency to increase. This demonstrates that higher temperatures will cause irregularities or non-homogeneous surface metal due to the formation of a passive layer.

4.4. Microstructural Analysis of SAF 3207 HD before and after Corrosion

There was no difference in terms of the microstructure of SAF 3207 HD before and after corrosion testing (Figures 5a and 6a). It contains austenite (48.5%) and ferrite (51.5%) phases. The local corrosion of SAF 3207 HD steel mostly occurred in the ferrite phase, while in fact it should happen in the austenite phase. Austenite has a lower Pitting Resistant Equivalent (PRE) number than ferrite; however, it can be formed due to the presence of a sigma phase (Figure 5b). As can be seen from Figure 6b, local corrosion first occurs in the sigma phase. Sigma phase precipitation will consume Cr, Mo, and Ni in order to form a stable intermetallic. It will also cause the oxide layer to fail to form. The formation of the sigma phase is common in the fabrication process of duplex stainless steel.

5. CONCLUSION

The corrosion resistance of SAF 3207 HD in 6%$FeCl_3$ solution below the temperature of 70°C is excellent, whereas it is not recommended to use SAF 3207 HD at a temperature higher than 80°C.

The critical crevice temperature of SAF 3207 HD in 6% $FeCl_3$ solution is 70°C. The deepest crevice depth was obtained from testing at a solution temperature of 90°C (2.101 μm).

Crevices tend to form in the ferrite phase of SAF 3207 HD, due to the presence of the sigma phase. However, the sigma phase is produced by the fabrication process of the steel, not by any treatment done in this study.

6. ACKNOWLEDGEMENT

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