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Stress Corrosion Cracking Detection of Sensitized Stainless Steel 304 in Chloride Media by Using Electrochemical Impedance Spectroscopy (EIS)

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Abstract
Electrochemical impedance spectroscopy (EIS) was used to detect stress corrosion cracking (SCC) in stainless steel 304 alloy exposed to an aqueous environment at 120 °C. Stainless steel 304 alloy as u-bend was tested in the solution that contains 40 weight percent of magnesium chloride. U-bended samples were prepared according to ASTM G30. EIS measurements were always performed simultaneously on u-bend samples under stress and non-stress conditions. The results indicate that changes in phase shift versus time could be related to the stress corrosion cracking process. Stress corrosion cracking is detectable at a frequency of 23.95 Hz. EIS measurement can be used for SCC monitoring in u-bend samples. Finally, analysis of the fracture surface by using metallographic and SEM techniques confirmed the EIS results.

Key words: Stress Corrosion Cracking, Stainless Steel 304, U-bend, Monitoring, EIS

Introduction
Stress corrosion cracking (SCC) is a well-known corrosion process which can cause failures of structures and their components. Several works have studied the SCC on stainless steel 304 by different methods. Some recent works have used electrochemical techniques such as electrochemical impedance spectroscopy to investigate SCC phenomenon on non-stressed samples. Bosch used EIS technique for studying strain rate tensile (SSRT) test of SS304 specimen in a solution of 5 mol/l H_2SO_4 and 0.1 mol/l NaCl at room temperature. They measured the phase shift in a particular frequency range during the tests and correlate crack initiation to changes in this phase shift [1]. Also, Li-juan investigated the stress corrosion cracking of type 40Cr steel alloy in acidified chloride solution (pH=1) [2].

Impedance measurements show that a change in shift phase can be related to the stress corrosion cracking process and this implies that EIS can be used to detect stress corrosion cracks [2]. Wang et al. also studied the samples of stainless steel 304 sensitized by electrochemical noise in BWR simulated media [3]. Additionally, Luo studied the electrochemical noise produced during SCC phenomenon in stainless steel 304 in 42% boiling magnesium chloride and during the SCC of brass in acetone solution under invariable loads; he concluded that noise signals of SCC included fast loss and slow retrieval of the potential [4].

Moreover, Leban investigated the electrochemical noise produced during the SCC of stainless steel 304 in hot magnesium chloride under slow strain condition and concluded that the common properties of electrochemical-noise-producing SCC vary depending on corrosion system like metal, sensitivity rate, and the type of corroding media [5].

Capcis group played an important role in SCC studies. They used u-shaped samples of manganese-carbon steel in a 4 molar sodium nitride solution at 80 °C. In this case, current and potential oscillations were repeated periodically [6].

Watanabe and Kondo studied the intergranular SCC process on stainless steel with different sensitivities in the aqueous solution of sodium thiosulphate and indicated that SCC occurred in the samples with intermediate sensitivity and distinct changes in the current noise and electrochemical potential were seen [7].

Cotiss studied the stainless steel 304 in a thiosulphate solution and indicated that there were two properties

occurred in the oscillation of electrochemical currents during SCC, namely immediate leaps in the current, and a change in basic current [8]. In addition, there are several works that have investigated SCC phenomena [9-15]. In this work, EIS measurements were performed on u-bend samples. Phase shifts at particular frequencies obtained from the EIS measurements showed a clear deference between the stressed and non-stressed specimens. It seems possible to use EIS for monitoring stress corrosion cracking.

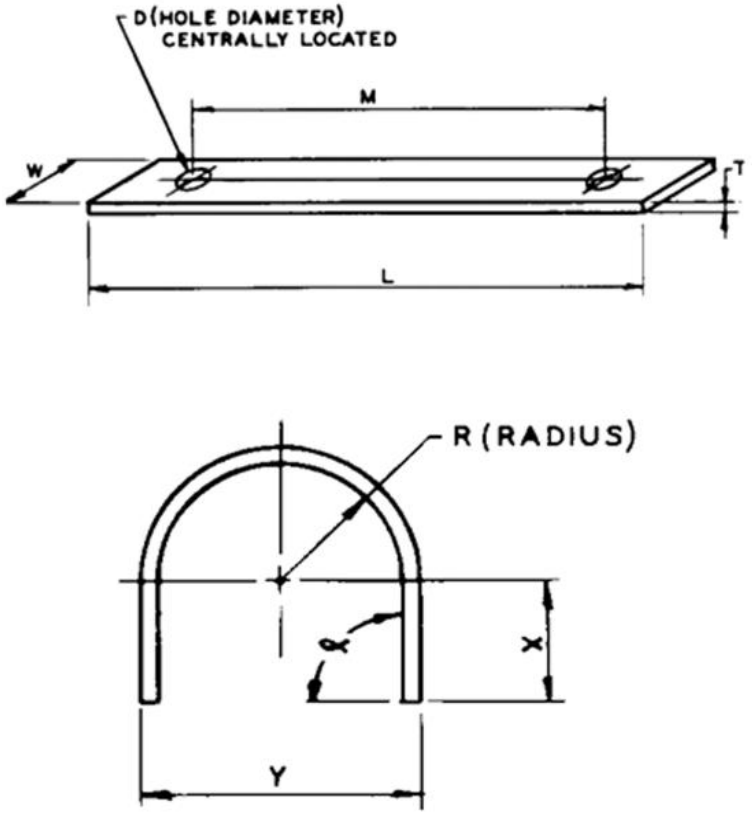
Experimental

U-bend specimens with the dimensions shown in Fig. 1 were experimented for tests according to ASTM G30. The chemical composition (mass fraction given in percent) of the 304 steel was given in Table 1.

Specimens were initially annealed at 700 °C for 1 hour. The working surface of the specimen was polished to 500 grit using standard grinding paper and then was degreased with acetone and distilled water before the u-bend tests. The test was performed using a 40% magnesium chloride solution with a pH of 4.5 at 120 °C. The electrochemical impedance spectroscopy (EIS) by the potentiostat/galvanostat model 273A EG and G and Solartron SI (high frequency response analyzer) was used. The impedance measurements were carried out at the rest potential (RP) with an amplitude of 5mV AC potential in the frequency range of 10 mHz to 100 kHz. The cell consisted of the sample used as the working electrode (WE), a platinum as the reference electrode (RE), and counter electrode (CE). The morphology of the fractured specimens was examined through optical microscopy and scanning electron microscope (SEM). EIS curves were simulated by Z-view software.

Results and Discussion

SS 304 specimens were annealed at 700 °C for 1 hour for sensitization. The optical microscopy and scanning electron microscopy (SEM) images of sensitized SS 304 are presented in Figures 2 and 3 respectively. As can be seen, the formation of chromium carbides is evidence for the sensitization of the SS 304 alloy.



Sample	L, mm	M, mm	W, mm	T, mm	D, mm	X, mm	Y, mm	R, mm	radÞ ,
b (Based on ASTM (G30	100	90	9	3.0	7	25	38	16	1.57

Figure 1- U-bend specimens with dimensions based on ASTM G30. Sample b was used in this study

Table 1- The chemical composition (mass fraction %) of SS 304

Cr	Ni	Si	Mn	Fe
18.3	8.06	0.41	1.21	Balance

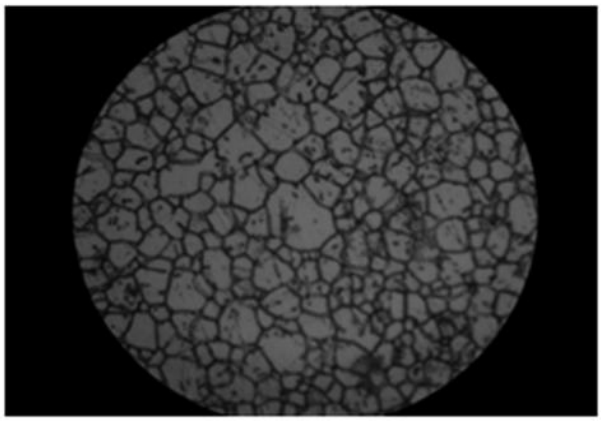


Figure 2- Optical microscope image of the sensitized sample of SS 304

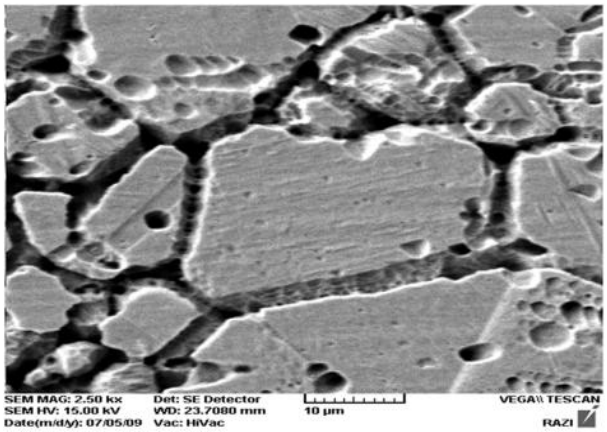
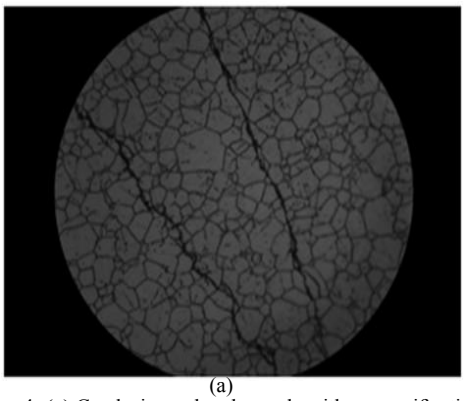


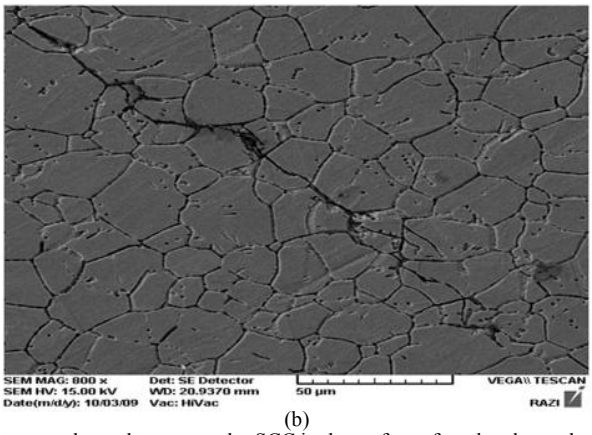
Figure 3- SEM image of the sensitized sample of SS 304

The samples were immersed in the solution of 40% magnesium chloride at 120 °C. Intergranular and transgranular SCC were observed after 137 hours of immersion. Cracks and intergranular and transgranular SCC damages on the surface of the samples are shown in Figure 4. The images were taken by optical microscopy and SEM respectively. The u-bend samples with the area of 1200 mm 2 and the blank sample (unsensitized) were joined to the set through the water proof wire and tested at different times by electrochemical impedance spectroscopy.

Based on immersion tests, crack initiation was started after 137 hours of immersion; the u-bend samples were examined before cracking and during crack propagation. Impedance diagrams obtained for various durations are shown as Bode phase in Figure 5. According to Figure 5, it is clear that impedance decreases with increasing immersion time and crack initiation. Total impedance increased after 118 hours of immersion at a frequency of 0.01 Hz. As EIS curves show, the amount of impedance at a frequency of 0.01 Hz decreased to 2774.7 ohm during cracking. EIS curves were simulated by Z-view software for determining equivalent circuits. It seems that there must be a minimum time constant in the equivalent circuit. The analysis of EIS curves has been shown in Table 2. R_s, CPE, and Rp are solution resistance, constant phase element, and polarization resistance respectively; Z_{crack} impedance also stands for produced initiation and propagation crack. The equivalent circuit obtained from simulated EIS curves is shown in Figure 6. It is clear from Table 2 that Rp decreases with crack formation. Therefore, it would cause a gradual increase in the corrosion rate of the material. In addition, because value "n" is lower than 1, double layer shows deviation from capacitance behavior. Rp values obtained from the simulation of EIS curves are shown in Figure 7. As can be seen, Rp shows a sudden decrease after 142 hours of immersion in Figure 8. It seems that crack initiation would cause a sudden decrease in the value of Rp. The effect of surface area was investigated by decreasing the immersion area from 1200 mm^2 to 600 mm^2. The results revealed that impedance cracking ($Z_{cracking}$) decreased by decreasing surface area; in addition, time cracking was constant and about 142 hours. It is obvious that the equivalent circuit is like Figure 6. The analysis of EIS curves for a surface area of 600 mm^2 has been shown in Table 3. It seems that the double layer behavior is becoming close to capacitance by increasing n.

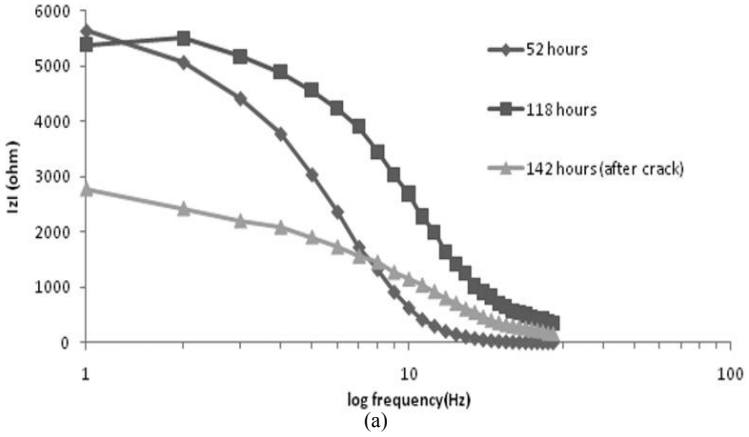


(a)



(b)

Figure 4- (a) Cracks in a u-bend sample with a magnification of 200, **(b)** Intergranular and transgranular SCC in the surface of a u-bend sample measured by SEM microscopy



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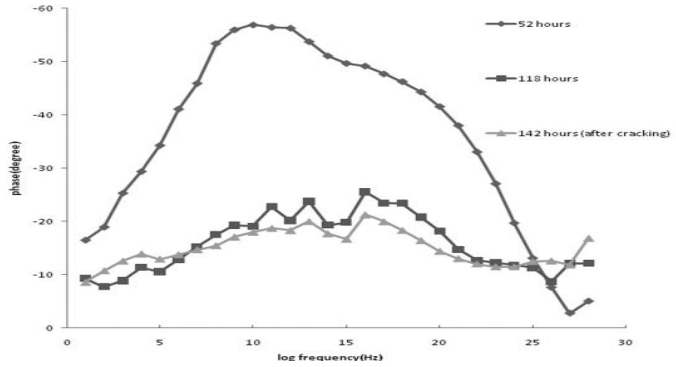
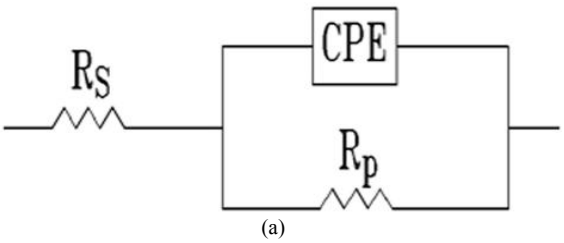


(b)

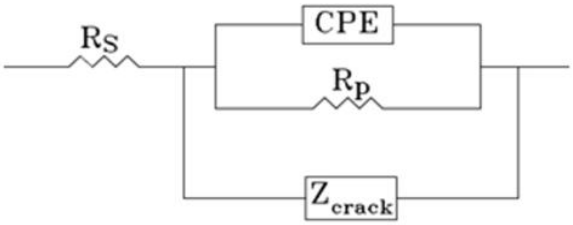
Figure 5- Bode plots of u-bend samples (surface area = 1200 mm^2) at different immersion times; **(a)** Bode, **(b)** Bode phase

Table 2- Calculated equivalent parameters (surface area =1200 mm^2)

Immersion time (hours)	$R_{s\ (ohm.cm^2)}$	CPE*10^{-4} (Ω^{-1} cm^{-2} s^n)	n	$R_{p\ (ohm.cm^2)}$	$Z_{crack\ (ohm.cm^2)}$
52	10.6	2.4058	0.64803	7320	-
118	313.5	682.1968	0.39152	6633	-
(after crack)142	111.8	3.3117	0.29716	949.99	4252



(a)



(b)

Figure 6- (a) Equivalent circuit before cracking; **(b)** Equivalent circuit for a u-bend specimen after cracking

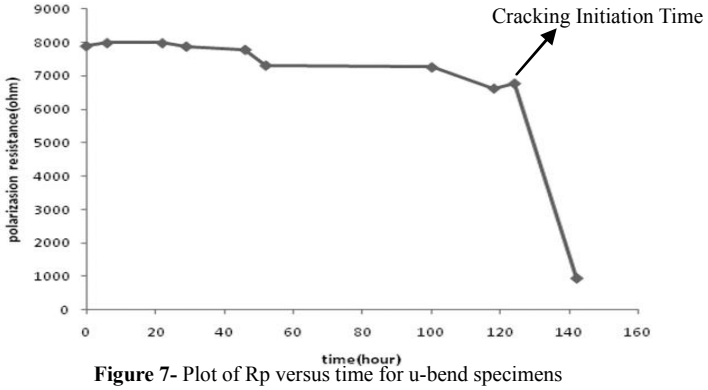


Figure 7- Plot of Rp versus time for u-bend specimens

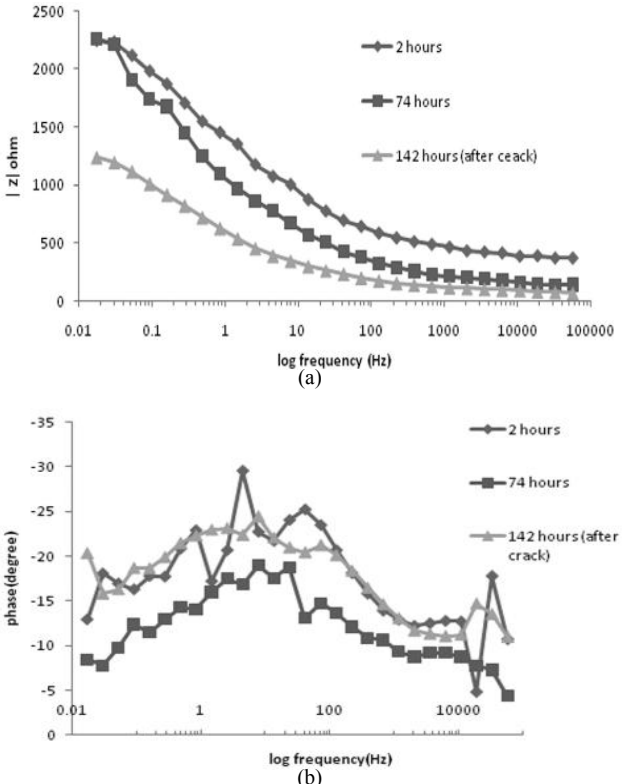


Figure 8- Bode plots of u-bend samples (surface area = 600 mm^2) at different immersion times; **(a)** Bode, **(b)** Bode phase

Table 3- Calculated equivalent parameters (surface area = 600 mm^2)

Immersion time (hours)	$R_{s\,(ohm.cm^2)}$	CPE*10^{-4} (Ω^{-1} cm^{-2} s^n)	n	$R_{p\,(ohm.cm^2)}$	$Z_{crack\,(ohm.cm^2)}$
2	107.6	4.2297	0.33749	3680	-
74	327.9	3.1097	0.34413	2727	-
(after cracking) 142	125	2.706	0.4296	813	3826

As can be seen in Table 3, Rp suddenly decreases after 142 days of immersion. Comparing the EIS curves of a blank specimen (plate-non stressed) with those of the u-bended sample with the same time of immersion indicated that the total impedance at low frequency is lower in blank specimen than the u-bend specimen. The equivalent circuit of blank specimen is from type of Randels model the analysis of which has been given in Table 4. The phase angle versus time plot of the stressed and non-stressed specimen were derived in the range of 1 to 100 Hz. It was found that the phase angles had different heights for the stressed and non stressed specimens at a frequency of 23.95 Hz. The phase angle-time plots are shown for each set of two specimens in Figure 9. As shown, phase angle shows a sudden increase after 124 hours of immersion. According to the immersion tests and optical microscopy and SEM images, 124 hours of immersion is almost the time for crack initiation. Therefore, SCC phenomena can be monitored by electrochemical impedance spectroscopy at a frequency of 23.95 Hz.

Conclusion

EIS technique can be used to monitor and detect SCC phenomena in SS 304 u-bend specimens exposed to a 40% solution at 120 °C. The SCC behavior in SS304 u-bended samples in a solution of 40% $MgCl_2$ was successfully investigated by electrochemical impedance spectroscopy, surface analysis, and metallographic. The results showed that changes in phase shift versus time could be related to the stress corrosion cracking process, which was detectable at a frequency of 23.95Hz using EIS. So, the time of SCC phenomena is predictable in SS 304 u-bended samples by EIS measurements. The analysis of the fracture surface by using metallographic and SEM techniques also confirmed the EIS results.

Table 4- Calculated equivalent parameters for blank samples after 142 hours of immersion (surface area = 1200 mm^2)

$R_{s(ohm.cm^2)}$	1.475
$R_{p(ohm.cm^2)}$	2842
CPE($\Omega^{-1}cm^{-2}s^n$)*10^{-4}	3.6013
n	0.66294

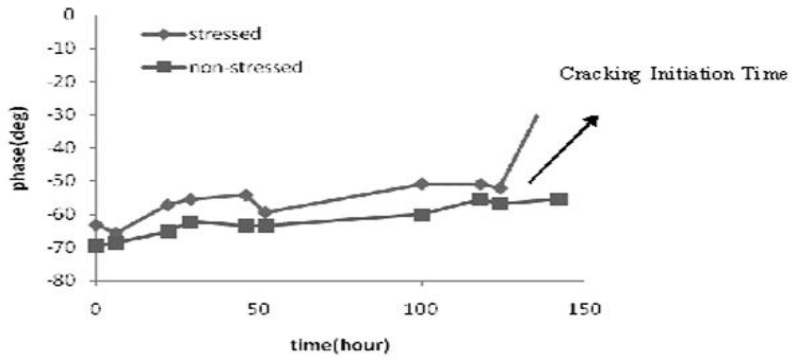


Figure 9- Phase-time plot of the stressed and non-stressed specimens at a frequency of 23.95 Hz

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