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Short Communication

Comparative Study on Electrochemical Corrosion Behavior of B500SD Carbon Steel and 2205 Duplex Stainless Steel Exposed to Concrete Pore Solution Containing Chloride Ions

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In this work, a comparative study was done on electrochemical corrosion behavior of B500SD carbon steel and 2205 duplex stainless steel rebars immersed into concrete pore solution containing chloride ions. An electrochemical impedance spectroscopy (EIS) analysis was conducted to consider the corrosion resistance of steel rebars in various environmental conditions such as pH, temperature and chloride ion concentration. The EIS results exhibit that the double-layer capacitance value decreased as pH-value gradually increased, which indicates that the size of passive film was enhanced, causing an improvement of the protective ability. Corrosion resistance of both steel rebars was increased by a temperature drop from 45 °C to 20 °C. The electrochemical findings reveal that 2205 duplex stainless steel exhibits a higher corrosion resistance and higher impedance with a higher durability in different conditions than B500SD carbon steel rebar which can be associated with the existence of Cr noble metal in stainless steel composition.

Keywords: Electrochemical corrosion behavior; 2205 duplex stainless steel; B500SD carbon steel; Concrete pore solution; Electrochemical impedance spectroscopy

1. INTRODUCTION

Durability and corrosion resistance are the main issues of steel reinforced concrete structure, as the need to maintain the same mechanical properties throughout the lifetime of the reinforced concrete structure is crucial [1-3]. Reinforced concrete structures are not only subject to applied loads, but they are also affected in some cases, such as marine structures and bridges, by an aggressive corrosion environment [4, 5].

Various kinds of steel are used in reinforced concrete structures, such as carbon steel, lowcarbon steel, stainless steel, duplex stainless steel and so on [6]. One of the major methods for corrosion resistance in aggressive media is the formation of passive layer on steel surface [7, 8]. However, the passive film is not stable once the duplex stainless steel comes in contact with simulated concrete solution and a new procedure of passivation happens [9]. Many studies on stainless steel have reported appropriate corrosion resistance in an environment containing chloride ions [10]. Carbon steel rebar outperforms plain concrete structures in terms of compressive, bending, and tensile strength [11]. But the structure may be damaged via the corrosion of carbon steel when the passive later on the steelsurface is broken [12]. Among the serious factors, the corrosion process by chloride ions plays an important role, mostly in the marine environment [13-15]. High corrosion resistance of stainless steel rebars has been considered for changing carbon steel reinforced concrete, probably as another valid way to prevent the reinforcing steelcorrosion [16, 17].

However, it is widely acknowledged that a respectable passive effect has a major impact on the corrosion resistance of various types of steel rebars [18]. There has been no research on the impact of passive film on corrosion resistance in various types of steel rebars under various environmental conditions such as pH, temperature, and Cl concentration. Therefore, electrochemical impedance spectroscopy was used to investigate the influence of pH, temperature, and chloride content of the corrosive environment on the corrosion resistance of B500SD carbon steel and 2205 duplex stainless steels in a concrete pore solution containing chloride ions.

2. EXPERIMENTAL

Different kinds of steel rebars 25 cm long and 1.2 cm in diameter were utilized for investigation of corrosion behavior. Prior to the experiment, the surface of all rebars were washed with acetone and distilled water and then dried in air. The tips of the steel rebars were coated with an epoxy resin. B500SD carbon steel and 2205 duplex stainless steel rebars were used to study the corrosion behavior. Table 1 indicates the chemical compositions of steel rebars which were applied in this study.

| Table 1. | Chemical | composition | of steel | rebars (| (wt%) |
|----------|----------|-------------|----------|----------|-------|
|----------|----------|-------------|----------|----------|-------|

| Steel rebars | Fe | Ni | Si | С | Mn | Cr | Р | S |
|-----------------------|-----------|------|------|------|------|------|-------|-------|
| B500SD carbon steel | Remainder | 0.13 | 0.22 | 0.23 | 0.78 | 0.13 | 0.007 | 0.022 |
| 2205 duplex stainless | Remainder | 5.2 | 0.8 | 0.02 | 1.9 | 22.3 | 0.026 | 0.02 |
| steel | | | | | | | | |

The concrete pore solution (CPS) was prepared with a mixture of $0.3 \text{ M Ca}(\text{OH})_2$, 0.5 M KOH and 0.2 M NaOH. The pH-value of the CPS was adjusted by the addition of different amounts of NaHCO₃ in 10, 11, 12 and 13 and calibrated by a pH-meter.

The electrochemical impedance spectroscopy (EIS) was done via a three-electrode electrochemical cells with steel rebars, a saturated calomel electrode and a Pt wire as working, reference and counter electrodes, respectively. The rebars were immersed into CPS with different NaCl content (0, 1, 2, 3 and 4 wt%). Four environment temperatures, 20, 25, 35 and 45 °C, were carefully

chosen as seasonal changes of temperature in the CPS environment. A scanning electron microscope (SEM) was used to evaluate the rebar surface morphologies.

3. RESULTS AND DISCUSSION

The EIS assessment was used to consider the pH value effect on the corrosion behavior of steel rebars with passive layer creation in the CPS environment. As indicated in Figure 1, when the pH-value increases, the arc radius rises in both steel rebars that shows the improvement of the corrosion resistance in steel rebars.



Figure 1. Nyquist and bode diagrams of (a) and (b) B500SD carbon steel and (c) and (d) 2205 duplex stainless steel rebarsin CPS containing 1 wt% chloride ions with various pH-value after one week exposure time at 20 °C



Figure 2. The equivalent circuit model

Figure 2 reveals an equivalent circuit used to fit the EIS of both B500SD carbon steel and 2205 duplex stainless steel rebars in CPS.

At higher frequencies, C_f and R_f present a capacitive behavior of shaped passive layer and resistance due to the ionic paths through the oxide film, respectively. At the second-time constant, C_{dl} and R_{ct} show the double-layer capacitance in the interfaces and the charge-transfer resistance.

| Steel rebars | pН | $R_s (\Omega cm^2)$ | $C_f(\mu F cm^{-2})$ | $R_f(k\Omega cm^2)$ | $C_{dl}(\mu Fcm^{-2})$ | $R_{ct}(k\Omega cm^2)$ |
|-----------------|----|---------------------|----------------------|---------------------|------------------------|------------------------|
| B500SD carbon | 10 | 28 | 3.1 | 2.1 | 4.3 | 2.7 |
| steel | 11 | 27 | 2.9 | 2.6 | 3.5 | 3.3 |
| | 12 | 25 | 2.2 | 3.2 | 2.8 | 3.8 |
| | 13 | 30 | 1.37 | 4.71 | 1.92 | 5.45 |
| 2205 duplex | 10 | 32 | 1.1 | 5.0 | 1.7 | 5.6 |
| stainless steel | 11 | 35 | 0.9 | 5.4 | 1.2 | 6.8 |
| | 12 | 36 | 0.6 | 7.3 | 0.8 | 8.1 |
| | 13 | 33 | 0.31 | 7.93 | 0.55 | 9.21 |

Table 2. Electrochemical parameters attained from a fitted equivalent circuit.

Table 2 exhibits electrochemical parameters attained from a fitted equivalent circuit.

The passive film thickness may be determined by the following equation [19]:

$$D = \frac{\varepsilon \varepsilon_0 A}{C_{dl}}$$

Where *D* represents the passive layer thickness. ε (12 for Fe₂O₃) and ε_0 (8.85×10⁻¹²F/m) are the dielectric constant and vacuum permittivity, respectively. *C*_{dl}and *A* show capacitance and an effective area.

(1)

As revealed in table 2, the value of C_{dl} falls as the pH-value increases, which shows that the passive layer thickness was improved and the causing protective capacity was increased when the pH-value of CPS was slowly increased.

Polarization resistance (R_p) is recognized as a predictable indicator to explore the corrosion resistance of steel rebars in the corrosive environment [20]. The higher R_p value indicates greater value of corrosion resistance for both steel rebars. According to table 2, the 2205 duplex stainless steel reveals a greater value of R_p than B500SD carbon steel at the same pH-value which may be related to the formation of passive film, presenting a higher amount of Cr into the duplex stainless steel structure helped to form stable passive films. As shown in figures 1b and 1d, the rise in absolute impedance was found in Bode plots with ph value for both steels, which confirmed improvement in efficiencies with increasing pH value by forming a passive layer on the steel surface.



Figure 3. The EIS and bode diagrams of (a) and (b) B500SD carbon steel and (c) and (d) 2205 duplex stainless steel rebars immersed in CPS containing 1wt% chloride ions at various temperatures after one week immersion time

However, previous researchers had studied temperature effect on corrosion behavior of steel rebars. There is still disagreement about the EIS results of steel rebar in CPS at different ambient temperatures.

| Table 3. EIS parameters obta | ined from eq | uvalent | circuit | model |
|-------------------------------------|--------------|---------|---------|-------|
|-------------------------------------|--------------|---------|---------|-------|

| Steel rebars | Temperature | $R_s(\Omega \ cm^2)$ | $C_f(\mu F \text{ cm}^{-2})$ | $R_f(k\Omega \ cm^2)$ | $C_{dl}(\mu F \text{ cm}^{-2})$ | $R_{ct}(k\Omega \ cm^2)$ |
|-----------------|-------------|----------------------|------------------------------|-----------------------|---------------------------------|--------------------------|
| B500SD | 20 °C | 30 | 1.37 | 4.71 | 1.92 | 5.45 |
| carbon steel | 25 °C | 33 | 1.64 | 3.65 | 2.25 | 4.34 |
| | 35 °C | 37 | 2.86 | 2.54 | 3.57 | 3.11 |
| | 45 °C | 36 | 3.52 | 1.81 | 4.21 | 2.43 |
| 2205 duplex | 20 °C | 33 | 0.31 | 7.93 | 0.55 | 9.21 |
| stainless steel | 25 °C | 38 | 0.63 | 5.93 | 0.93 | 6.79 |
| | 35 °C | 35 | 0.84 | 4.57 | 1.23 | 5.22 |
| | 45 °C | 34 | 1.18 | 2.99 | 1.64 | 3.76 |

Figure 3 exhibits the Nyquist and bode plots of the B500SD carbon steel and 2205 duplex stainless steel rebars immersed in CPS containing 1wt% chloride ions at various temperatures. Nyquist diagrams typically indicate a capacitive loop which its diameter falls as the temperature rises, which may be related to more dissolution of steel rebars. The EIS results reveal resistance between the working electrodes (both rebars) and the electrolyte solution (CPS) at the high-frequency. Moreover, at

the low-frequency, it may be associated with the charge-transfer resistance in the corrosion process [21].

Table 3 shows the EIS parameters obtained by the fitted circuit model used in this work. As shown in table 3, the R_{ct} values of both rebars are considerably reduced, as the temperature rises in the CPS, which indicates that the environment temperature has improved the corrosion behavior of both steel rebars.

Furthermore, Table 3 displays that R_f slowly reduced by increasing the environment temperature for both B500SD carbon steel and 2205 duplex stainless steel, which reveals that non-protective corrosion and porous products were increased on the surface of steel rebars. These findings are according to the best-fit result for C_{dl} which was slowly increased at 45 °C in the CPS, signifying that corrosion may occur on the surface of steel rebars. Besides, the Rct of the 2205 duplex stainless steel was greater than that of B500SD carbon steel rebar which shows higher corrosion resistance of duplex stainless steel rebar in CPS. It can be associated with the existence of Cr noble metal in stainless steel composition. 2205 duplex stainless steel rebar is produced by the addition of Cr element which result in the creation of passive oxide, a thin and chemically stable layer [22]. Furthermore, the decrease of absolute impedance was found in Bode plots with an increase in temperature for both steels (Figs. 3b and 3d), which confirmed an increase of corrosion by increasing temperature due to more dissolution of steel bars.



Figure 4. (a) EIS and (b) Bode diagrams of 2205 duplex stainless steel exposed to the CPS with different concentration of NaCl at 20 °C temperature after one week immersion time.

The Nyquist diagrams of 2205 duplex stainless steel exposed to the CPS with different concentration of NaCl at 20 °C temperature after one week's immersion time is shown in Figure 4. As shown, Nyquist plots typically show that as NaCl concentration increases, the diameter of capacitive loops decreases. It can be accredited to the corrosion behavior of chloride ions on the stainless steel surface. The best fitted parameters based on the used equivalent circuit indicated in figure 2 are summarized in Table 4. As shown, the R_{ct} value is meaningfully reduced from 10.42 k Ω to 4.41 k Ω , by the addition of NaCl in the CPS, revealing that the existence of chloride ions leads to better corrosion resistance on the stainless steel surface. Figure 4b shows that increasing the NaCl concentration in CPS decreased absolute impedance in Bode plots for both steels, confirming the formation of corrosion products and unprotected steel.

| NaCl concentration | $R_s(\Omega cm^2)$ | $C_f(\mu F cm^{-2})$ | $R_{f}(k\Omega cm^{2})$ | $C_{dl}(\mu F \text{ cm}^{-2})$ | $R_{ct}(k\Omega \ cm^2)$ |
|--------------------|--------------------|----------------------|-------------------------|---------------------------------|--------------------------|
| 0 wt% | 39 | 0.14 | 8.71 | 0.24 | 10.42 |
| 1 wt% | 33 | 0.31 | 7.93 | 0.55 | 9.21 |
| 2 wt% | 35 | 0.65 | 6.57 | 0.83 | 7.97 |
| 3 wt% | 38 | 0.97 | 5.42 | 1.26 | 6.23 |
| 4 wt% | 36 | 1.32 | 3.29 | 1.95 | 4.41 |

Table 4. The best fitted parameters based on the used equivalent circuit indicated in figure 2

Furthermore, table 4 exhibits that R_f slowly decreased by increasing the NaCl concentration in CPS which shows formation of corrosion products and unprotected steel rebar. These results are consistent with the C_{dl} values which were gradually increased up to 1.95 μ Fcm⁻² with 4wt% NaCl in the CPS, indicating that generalized corrosion can take place on the stainless steel surface [23].



Figure 5. FESEM images of (a) B500SD carbon steel and (b) 2205 duplex stainless steel rebars exposed to the CPS with 1wt% concentration of NaCl at 20 °C temperature after one week immersion time

The FESEM images of the B500SD carbon steel and 2205 duplex stainless steelrebars are indicated in Fig. 5. The 2205 duplex stainless steel surface was about uniform, without evidence of roughness and defects/pores and which may decrease the influence of corrosive ions and moisture on the steel surface from the CPS.

4. CONCLUSIONS

In this work, a comparative study was done on electrochemical corrosion behavior of B500SD carbon steel and 2205 duplex stainless steel rebars immersed into concrete pore solution containing

chloride ions. The EIS analysis was conducted to consider the corrosion resistance of steel rebars in various environmental conditions such as pH, temperature and chloride ion concentration. The EIS results exhibit that the double-layer capacitance value was decreased as pH-value gradually increased, which reveals that the size of passive film was enhanced, causing an improvement of the protective ability. Corrosion resistance of both steel rebars was increased by a temperature drop from 45 °C to 20 °C. The electrochemical findings reveal that 2205 duplex stainless steel exhibits a higher corrosion resistance and higher impedance with a higher durability in different conditions than B500SD carbon steel rebar which can be associated with the existence of Cr noble metal in stainless steel composition.

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