A novel mathematical method is presented to determine equivalent circuit modeling based on electrochemical impedance spectroscopy (EIS) data, and to investigate the corrosion behavior of corrosion resistant steel for cargo oil tank (COT) in NaCl acid solution. First, the corrosion rate is calculated by weight loss method, it indicates superior corrosion resistance. Next, the transfer function of system is obtained by the electrochemical impedance spectroscopy (EIS) data, and determines proper time constants for equivalent circuit to fit experimental results. Finally, the results of EIS are in agreement with accelerated corrosion measurements by the fitting errors and relating to known physical parameters, which indicate the novel mathematical method is very effective.

**Keywords:** corrosion resistant steel; corrosion behavior; electrochemical impedance spectroscopy (EIS); equivalent circuit modeling; transfer function

**1. INTRODUCTION**

With the broaden applications of corrosion resistant steel in industrial and military field, more corrosion resistant steels have been developed to reduce the following problem in economic issues, environmental pollution, secure questions, and so on. The oil tanker is an important tool for ocean transportation of crude oil. There is a certain amount of chloride ion, hydrogen ion and sulphide when the tank is filled with crude oil, so the service environment of cargo oil tanks (COT) steel is more complex, the special condition determines the life of COT steel, even leading to massive oil leakage.
and some accidents, which not only cause economic losses, but also bring on serious destruction of marine environment. So the development of COT steel has very important research significance and practical value.

The corrosion resistant problems of some alloy steels have been studied, and have obtained some achievements, mainly for atmospheric corrosion [1-4], marine corrosion [5-8] and the corrosion for other special environments [9-12]. However, very few studies on the corrosion behavior of COT steel have been reported [13-15]. Now, word-wide there is increasing attention being given to reliable methods for corrosion rate problems. Weigh loss measurement is currently the most direct and reliable method but time consuming and information limited. So the corrosion resistance of alloy steel has been investigated by simulated and accelerated corrosion tests. Electrochemical measurement is a powerful tool for researching corrosion process, has obtained some results by equivalent circuit [16-20], and corrosion of COT steel/NaCl system has been poorly studied using the electrochemical impedance spectroscopy [13-14], and the common used an equivalent electrical includes two time constants. There are main reasons for the scarcity of corrosion studies carried out using the EIS method: the absence of a stable steady-state and scientific basis for selecting the reasonable time constant. Researchers have used some methods to analyze the impedance data and to estimate curve fitting uncertainties [21-22]. To our knowledge, no studies have been reported in the literature concerning the stability of impedance data for COT steel corrosion by consideration of its transfer function. This work forms part of an effort to cover this gap.

In this paper, the corrosion behavior for a new type of corrosion resistant steel for COT is studied in NaCl acid solution. Firstly, the weight loss is got to calculate corrosion rate. Then the electrochemical impedance spectroscopy (EIS) dates are obtained, the transfer function of system is established, on the basis of the stability theory of system, the stability condition is that all the roots of the characteristic equation characterizing the system have negative real parts, further test the stability and choose proper time constant to fit experimental results by equivalent circuit method. Finally, it is found that the results of EIS are in agreement with accelerated corrosion measurements.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials

The chemical composition (mass fraction, %) is C=0.085, Si=0.24, Mn=1.36, P=0.006, S=0.002, Al=0.04, Cr=0.23, Cu=0.16, W=0.21, Mo=0.21, Sn=0.1, Ni=0.11, Nb=0.012, and Fe to balance. The sample is obtained by rolling process parameters, including final rolling temperature for 840°C, final cooling temperature for 617°C and cooling rate for 15.2°C/s. The mechanical performance is also tested. The yield strength and tensile strength at room temperature is 437MPa and 612MPa, respectively, the yield ratio is 0.71 and the elongation is 20%. The impact energy is 195 Joules at -20°C and 172 Joules at -40°C. The mechanical properties for corrosion resistant steel can meet the requirement of DH36 steel, which indicate the designing of TMCP process is feasible.
2.2 Accelerated corrosion measurements

The accelerated corrosion experiments are carried out using rectangular form (length=6cm, width=2.5cm, thickness=0.5cm), and then drilled hole for suspension. The longitudinal direction of samples is parallel to rolling direction of steels. Prior to testing, the samples are ground with a series of SiC waterproof abrasive papers (200, 600, 800, 1500 and 2000), and washed with acetone and ethanol ultrasonic, then dried in the air. The measurements are performed in 10% (mass fraction) NaCl solution, the pH value of the solution is adjusted to 0.85 using concentrated hydrochloric acid, the temperature is controlled at about 30°C by electro-thermostatic water bath heating. The immersion time is 72 hours, time interval is 24 hours, after each immersing period, the samples are withdrawn, carefully washed with acetone and ethanol ultrasonic, dried in the air and then weighted using an analytical balance (precision±0.1mg). Five parallel samples are used to perform each immersion experiment to ensure reproducibility, and the mean weights losses are reported. Such conditions are used to simulate inner bottom plate of COT.

2.3 Electrochemical impedance spectroscopy measurements

The electrochemical measurements are performed using a PATSTAT2273 electrochemical workstation. A conventional three-electrode cell is used. It contains the platinum electrode as the auxiliary electrode, the saturated calomel electrode (SCE) as the reference electrode, which is connected to the NaCl acid solution via a Luggin capillary and a salt bridge, and the steel sample as the working electrode. The steel samples are cut into 1×1×1cm dimensions, only 1cm² is exposed to air, and other sides are coated with an insulating material. The samples are ground with a series of SiC waterproof abrasive papers from 200# to 2000#, washed with acetone and ethanol ultrasonic, and then dried in the air. In electrochemical experiment, all the conditions are the same as accelerated corrosion experiments.

The EIS experiments are measured in a frequency range of 100 KHz to 0.1 Hz. EIS involves the imposition of a 5mV amplitude sine-wave. In order to obtain a stable open-circuit potential, the electrodes are kept in electrolyte for 60min. The EIS results are analyzed using Zsimpwin software and fitted using its appropriate equivalent circuits.

2.4 Mathematical modeling determination and stability analysis

First of all, the transfer function of electrochemical impedance spectroscopy is established based on the electrochemical experimental dates and control theory knowledge. And then the roots distributions of system characteristic equation are analyzed by MATLAB software, if all roots have negative real parts, the system will be stable, or else, the system will be not stable. Finally, the time constants of system are determined and selecting a suitable equivalent circuit, to analyze the corrosion behavior of corrosion resistant steel.
3. RESULTS AND DISCUSSION

3.1 Accelerated corrosion measurements

The annual average corrosion rate is calculated according to the following equation [13].

\[ v = \frac{365 \times 24 \times W \times 10}{S \times 72 \times \rho} \]  

(1)

where \( v \) is the annual average corrosion rate, mm/a; \( W \) is the weight loss, g; \( S \) is the total surface area of sample, cm\(^2\); \( \rho \) is the density of experiment steel, g/cm\(^3\).

According to the experiment results, the annual average corrosion rate of test steel is 0.201 mm/a. The accepted criterion for corrosion resistant steel of COT is \( v \leq 1 \) mm/a, according to IMO MSC 87/26/Add.1 Annex 3 MSC. 289(87)[23]. The corrosion rate of test steel is about 1/5 of the accepted criterion. It shows that the developed steel has superior corrosion resistance.

The weight loss as a function of time is shown in Figure 1. We can see that the weight loss is also varied for corrosion resistant steel under different immersion time. The slope of test steel is relatively bigger between 24 hours and 48 hours. In the latter period, the slope will become smaller, and it is probable to the protective film is formed during the period.

![Figure 1. Weight loss of test steel vs. immersion time](image)

3.2 Electrochemical impedance spectroscopy (EIS)

In order to clarify the corrosion process, the electrochemical impedance spectroscopy (EIS) characteristic curves of test steel in 10% NaCl acid solution for different immersion time are displayed in Figure 2 and Figure 3.
Figure 2. Nyquist plots of test steel for different immersion time

Figure 3. Bode plots of test steel for different immersion time (a) The amplitude-frequency characteristic curve (b) The phase-frequency characteristic curve
As can be seen from Figure 2, the arcs in low frequency are not incomplete, which diameters increase with immersion time and the arcs mostly become into the straight lines. The low frequency part of Nyquist plot, below 0.409 Hz, appearing a large degree of scattering, obviously without the definition of a clear relaxation process, and for this reason these results have not been considered in Figure 2.

Bode plots are shown in Figure 3. It is seen that the impedance modulus of test steel will gradually decline with the increase of immersion time, which shows that the sample did not appear serious corrosion phenomenon. And the impedance modulus of test steel is biggest for the immersion 24 hours, and the smallest one is immersed for 72 hours in the low frequency range. For bare steel sample, it does not appear the local corrosion on the surface, but also does not have the corrosion film, so the impedance modulus takes between 24 hours and 72 hours.

Based on above analysis, the transfer function is applied to analyze the stability of the electrochemical system, can be defined as [24]

\[ Z(s) = \frac{U(s)}{I(s)} \]  

(1)

Where \( U(s) \) is the Laplace transform of voltage, \( I(s) \) is the Laplace transform of current, \( s \) is the Laplace operator [25]. The frequency domain transfer function is obtained by substituting \( s \) for \( j\omega \) in the transfer function of the system. The equation (1) will also be written as

\[ Z(j\omega) = Z^\prime(\omega) + jZ^\prime\prime(\omega) \]  

(2)

\[ \phi(\omega) = \arctan \frac{Z^\prime(\omega)}{Z^\prime\prime(\omega)} \]  

(3)

Where \( Z^\prime(\omega) \) and \( Z^\prime\prime(\omega) \) are the frequency-dependence real and imaginary parts of impedance, respectively. \( \phi(\omega) \) is the phase angle.

Using the method of automatic control theory, taking \( L(\omega) = 20\log_{10}|Z(j\omega)| \), dB. The amplitude-frequency characteristic curve is given for Figure 4.

Figure 4. The amplitude-frequency characteristic curve for test steel
From Figure 4 and Figure 3(b), it is seen that the lines are similar in shape for different corrosion time. So we choose the line type for immersing 24 hours to study the corrosion properties based on equivalent circuit method, and the Bode plot is shown in Figure 5.

**Figure 5.** Bode plots of test steel for immersion 24h (a) The amplitude-frequency characteristic curve (b) The phase-frequency characteristic curve

The transfer function \( Z(j\omega) \) for a system is written, in its general form as

\[
Z(j\omega) = \frac{K \prod_{s=1}^{m} (j\tau_s \omega + 1)}{(j\omega)^{\delta} \prod_{i=1}^{p} (jT_i \omega + 1)}
\]  \quad (4)

Where \( K, \tau_s, \lambda, T_i \) is real.

We have
\[
L(\omega) = 20\log |Z(j\omega)| = 20\log K + \sum_{\mu=1}^{n} 20\log \left(\frac{1}{\tau_i\omega} + 1 - \lambda 20\log \omega - \sum_{\nu=1}^{m} 20\log \left(\frac{T_i\omega}{\mu\delta}\right)^2 + 1\right) \quad (5)
\]

\[
\phi(\omega) = -\lambda \times 90 + \sum_{\mu=1}^{m} \arctan r_i\omega - \sum_{\nu=1}^{n} \arctan T_i\omega \quad (6)
\]

The scope of the curve is about -20dB/dec in low frequency band from figure (5a). \(\omega = 0.409\), \(L(\omega) = 41.677\), \(\phi = -40^\circ\). With the increase the frequency, the phase angle will decrease, so we can get \(\lambda = 0\). The equation (5) will be approximate rewritten for the following form.

\[
L(\omega) = 20\log |Z(j\omega)| = 20\log K + 20\log \left(\frac{1}{\tau_i\omega} + 1 - \sum_{\nu=1}^{m} 20\log \left(\frac{T_i\omega}{\mu\delta}\right)^2 + 1\right) \quad (7)
\]

Base on the results of Bode plots, it is seen that there is an inertia link and a differential part in low frequency band. And the about most negative phase value \(\phi = -50^\circ\) is provided in \(\omega = 2\) Hz. So we first consider the low frequency characteristic which is important for the stability of the system. The frequency domain transfer function is given.

\[
Z(j\omega) = K \frac{\frac{1}{\tau_i\omega} + 1}{\frac{1}{T_i\omega} + 1} \quad (8)
\]

We have

\[
L(\omega) = 20\log |Z(j\omega)| = 20\log K + 20\log \left(\frac{1}{\tau_i\omega} + 1 - \sum_{\nu=1}^{m} 20\log \left(\frac{T_i\omega}{\mu\delta}\right)^2 + 1\right) \quad (9)
\]

\[
\phi(\omega) = \arctan \tau_i\omega - \arctan T_i\omega \quad (10)
\]

From the analysis of phase-frequency characteristic curve in low frequency band, we can see that system is first affected inertia link, and then the differential part, having \(T_i > \tau_i\). Then we will obtain time constant \(T_i\) and \(\tau_i\). First, according to maximum principle, we have

\[
\frac{d\phi(\omega)}{d\omega} = 0 \quad (11)
\]

\[
\omega_m = \sqrt{\frac{1}{T_i} - \frac{1}{\tau_i}} \quad (12)
\]

\[
\phi_m = -\arcsin \left(\frac{T_i}{\tau_i}\right) - 1 \quad (13)
\]

So we choose \(\phi_m = -50^\circ\), having

\[
\frac{T_i}{\tau_i} \approx 8 \quad (14)
\]

\[
\omega_m = \sqrt{\frac{1}{T_i} - \frac{1}{\tau_i}} \approx 2 \quad (15)
\]

We get approximate value \(T_i = \frac{1}{0.6}, \tau_i = \frac{1}{6}\).

Then we will research the transfer function of middle frequency. Due to the phase-frequency curve is not quickly reached \(\phi(\omega) = 0^\circ\) around 100 Hz, which indicates this system have an inertial link, but the angle is also slowly rising, there are a differential link at the same time.

\[
Z(j\omega) = K \frac{(j\tau_i\omega + 1)(jT_i\omega + 1)}{(jT_i\omega + 1)(jT_i\omega + 1)} \quad (16)
\]
Where \( T_1 > \tau_1 > T_2 > \tau_2 \).

Based on above model, the K value can be obtained through generation into the special points B (2.223, 33.614). It is because the K value is affected by the low frequency. So let’s plug the special points B into the equation (8). We approximate have

\[
33.614 = 20\log K + 20\log \sqrt{\frac{2.223^2}{6}} + 1 - 20\log \left(\frac{2.223^2}{0.7}\right) + 1 \quad (17)
\]

Getting \( K = 141 \).

Then we research the amplitude-frequency characteristic curve, the scope is about -20dB/dec before about 700HZ, and will be 0 dB/dec, combining with the phase-frequency characteristic, it shows there is an inertial links and a differential parts.

\[
Z(j\omega) = K \frac{(j\omega_1^2 + 1)(j\omega + 1)}{(j\omega_1^2 + 1)(j\omega + 1)(j\omega_2^2 + 1)} \quad (18)
\]

Where \( T_1 > \tau_1 > T_2 > \tau_2 > T_3 > \tau_3 \). \( T_3 \) and \( \tau_3 \) should be selected at around 700 HZ. So choosing \( T_3 = 1/500, \tau_3 = 1/900 \).

\[ \text{Bode Diagram} \]

**Figure 6.** Bode plots of test steel for immersion time of 24h

Base on the stable value of high frequency, the value can be obtained through generation into the special points C (828.643, 12.987), at the same time, the time constant for \( T_1 \) and \( \tau_1 \) is neglected, but considering the two parts will generate the decrease of amplitude, so we choose \( \omega = 828, L(\omega) = 15 \).

We will substitute the special value into the equation (17).

\[
15 = 20\log 141 + 20\log \left(\frac{828}{6}\right) + 20\log (828\tau_1) - 20\log \left(\frac{828}{0.7}\right) - 20\log (828T_3) \quad (19)
\]
Getting $\tau_2/T_2 = 0.32$. And choosing $T_2 = 1/18$, $\tau_2 = 1/55$.

Finally, the transfer function of system is obtained as follows.

$$Z(s) = \frac{0.0004747s^3 + 0.4562s^2 + 26.22s + 141}{0.0001587s^3 + 0.08233s^2 + 1.486s + 1}$$

(20)

Then we use MATLAB to program, get the eigenvalues of dynamic system. $\lambda = -500.0785$, -17.9990, -0.7001. And all the roots of the characteristic equation possess a negative real part. And the Bode plot for the transfer function is given for Figure 6.

Based on the above analysis, we can see that the curve shape for Figure 6 is about the same to the obtained experimental curve, which shows the studied method is feasible. And we can also know that the dynamic system is stable by eigenvalues. As can be seen from the phase frequency characteristic curve and transfer function, the alloy steel are tested in acid solution, it is likely to appear three time constants. So an equivalent circuit mode is given to fit the impedance data for analyzing the corrosion process in Figure 7, and the corresponding fitting curves are shown in Figure 8.

The traditional process for corrosion resistant steel is analyzed by the equivalent circuit with two time constants, as shown in Figure (7a)[13,18]. However, based on the above analysis, three time constants of the equivalent circuit are researched in this paper, as shown in Figure (7b). The fitting results can reflect the trend of different capacitive arc, and three time parameter is significantly better than two parameters, but it is not very ideal. So CPE replace the electric double layer capacitance C in Figure (7c), CPE is the constant phase element with an impedance given by $Z = \frac{1}{Y_0(j\omega)^n}$, where $Y_0$ is a general admittance function equal to the capacitance $C$, $j$ is the complex operator with $j = (-1)^{1/2}$, $\omega = 2\pi f$ is the angular frequency, $n$ is the exponent, which is an adjustable parameter that lies between 0 and 1. It is found that the fitting effect is very well both low frequency and high frequency area. So CPE instead of capacitance C can well.
Figure 7. Equivalent circuits for test steel: (a) Two time constants (b) Three time constants (c) Three time constants with CPE
Figure 8. Measured and fitted results of Nyquist plots for corrosion resistant steel (a) Two time constants (b) Three time constants (c) Three time constants with CPE

The dates are obtained from the equivalent circuits, which is listed in Table 1. The fitting error is very small.

Table 1. Parameters of equivalent circuit at different immersion time

<table>
<thead>
<tr>
<th>Time(hour)</th>
<th>R_s(Ω·cm²)</th>
<th>Y_01(S·sec^n/cm²)</th>
<th>n_1</th>
<th>R_ct(Ω·cm²)</th>
<th>Fitting error</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.483</td>
<td>0.003953</td>
<td>0.571</td>
<td>81.82</td>
<td>9.27*10^-4</td>
</tr>
<tr>
<td>48</td>
<td>3.418</td>
<td>0.01085</td>
<td>0.5019</td>
<td>26.14</td>
<td>5.12*10^-4</td>
</tr>
<tr>
<td>72</td>
<td>3.486</td>
<td>0.0003385</td>
<td>0.7915</td>
<td>254.5</td>
<td>3.01*10^-4</td>
</tr>
</tbody>
</table>

Based on the above results, the R_s value changes a little, the average value is about 3.4, the electrolyte resistance is almost the same, which will indicate each test system is in a state of relative stability.

With the increasing of immersion time, the value of Y_01 will fluctuate, it may be that the corrosion products leave the surface of the electrode, and get into the solution. The more obvious the fluctuation of Y_01, and the more serious the samples surfaces are corrode.

The dense layer of test steel is generated during the corrosion process, and kept a steady state, at this time the dispersion effect is the largest, n1 come up to its minimum value, it show the inner protective film become unstable and even burst for immersion 48 hours. Instead, the n1 value of test steel becomes big after immersion 72 hours, dispersion effect will be smaller which show that inner protective film may be damaged [12].

Rct is inversely proportional to corrosion rate, the decrease of R_ct shows that the corrosion behavior of test steel substrate becomes more and more serious. With increasing immersion times, the value of R_ct will appear the trend of decreasing for test steel, it shows that corrosion product film is
damaged during this period, it may be appear serious corrosion. The reaction resistance $R_{ct}$ of test steel declines at the first time, this may be because the protective film has not appeared. When immersing 72 hours, the value will increase quickly and reach to the 254.5 $\Omega$, which indicate there is high resistance of CR15 steel, declining the corrosion rate [13,26]. The fluctuation of the $R_{ct}$ value may indicate constantly the generation and destruction of the corrosion film. The results of EIS analysis are in agreement with methods of accelerated corrosion experiments.

4. CONCLUSIONS

1) The test steel has superior corrosion resistance by accelerated corrosion measurements method, its average corrosion mass loss rate is only 0.201 mm/a, which is 1/5 of the accepted criterion according to IMO MSC 87/26/Add.1 Annex 3 MSC. 289(87).

2) Based on the dates of electrochemical impedance spectroscopy (EIS) characteristic, the transfer function of the system is established, and the stability analysis is carried out on the electrochemical system, which will be good for choosing proper three time constants of equivalent circuit modeling determination. The fitting results verify the effectiveness of the research method.

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