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We study a rhodamine-based fluorescent compound (FD2) as corrosion indicator for T91 steel in 3% NaCl solution. FD2 has a desirable property of “turn-on” fluorescence emission via forming a complex with Fe$^{3+}$ ions. The varying of fluorescence intensity is linked to that of weight-loss of T91 steel. Early attack on T91 steel was detected using fluorescence microscopy. This nondestructive method of initial corrosion detection can be used during maintenance before serious damage happens.

1. Introduction

T91 alloy is widely used as tube material for heater or super-heater in the thermal power equipment because of its excellent creep resistance. Metal corrosion is one of the major damage reasons influencing the structural integrity of equipment. Usually, corrosion is a dissolving of metal caused by an electrochemical reaction, involving the electron loss and ionization of metal. For iron-based alloy corroding in water solution, the anodic reactions can be represented as

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e \quad (1)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}^+ + \text{H}^+ \quad (2)$$

$$3\text{Fe(OH)}^+ + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 5\text{H}^+ + 2e \quad (3)$$

The cathodic reaction in a near neutral solution involves reduction of the dissolved oxygen according to

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \quad (4)$$

The cathodic reaction in the acidic solution is as follows

$$\text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2\text{H}_2\text{O} \quad (5)$$

$$2\text{H}^+ + 2e \rightarrow \text{H}_2 \uparrow \quad (6)$$

Metal loses electron at the anode and ionization leads to corrosion dissolution. At the cathode, electrons are captured and damage such as hydrogen embitterment can occur. Detection of corrosion at its earliest stages is essential to avoid critical engineering failures, which will reduce maintenance costs and improve the safety of the electric generating units. Several nondestructive techniques are implemented to detect corrosion, including ultrasonic testing, eddy current, and electrochemical approaches [1, 2]. Early corrosion detection by fluorescent compounds receives scientific interests due to their nondestructive and sensitive properties [3, 4]. People believe that probes with a fluorescence enhancement signal are much more efficient for early corrosion detection [5, 6]. Studies have mainly employed either fluorescent dye added in the solution itself or nonfluorescent agents in the solution that form fluorescers and emit fluorescence after corrosion electrochemical reaction at interfaces. Most studies have examined initiation of localized corrosion based on pH sensitive dyes for aluminium alloys [7, 8]. However, so far there are relatively few reports on the fluorescent detection of general corrosion and pitting corrosion for iron and steel [9, 10]. As for steel substrates, the ferric ion is well known as fluorescence quencher owing to its paramagnetic nature [11].

In this paper, a rhodamine-based compound (FD2) is designed to detect T91 steel corrosion. Figure 1 shows the proposed FD2-Fe$^{3+}$ bonding structure. Fluorescence enhanced method is established to check T91 steel corrosion. The polarization curves are used to study the electrochemical property of T91 steel with and without FD2 in 3% NaCl solution.
2. Experimental Section

2.1. Materials. The used steel specimens were from T91 alloy with the following composition (wt%): C 0.08–0.12; Si 0.20–0.50; Mn 0.30–0.60; Cr 9–12; Mo 0.085–1.05; V 0.18–0.25; P ≤0.02; S ≤0.01; Ni ≤0.40 and Fe balance. FD2 was facilely synthesized from rhodamine 6G and diethylenetriamine according to the procedure reported in [7]. All other reagents were of analytical grade and employed as received.

2.2. Fluorescence Spectra. The fluorescence emission of FD2 in the presence of different metal ions was examined using a Shimadzu RF-5301 fluorescence spectrophotometer. The excitation wavelength is 510 nm. The scan range was set from 520 nm to 640 nm for emission spectra. FeCl₃, FeSO₄, Zn(NO₃)₂, BaCl₂, Al(NO₃)₃, CuSO₄, Na₂SiO₄, and MnSO₄ were used as the sources of metal cations.

2.3. Weight-Loss Tests. Weight-loss test was carried out in a thermostat water bath (30°C). The suspended coupons with the size of 40 mm × 10 mm × 0.5 mm were abraded with emery paper (01#, 04#, and 06#) and washed and degreased with alcohol. These coupons were then fully immersed in the 250 mL 3% NaCl solution containing 0.1 μM FD2. After different immersion time, the corrosion solution was sent for fluorescence analysis. The coupons were rinsed with water and erased with a plastic brush, then dried with hot air, and weighed to determine the weight loss.

2.4. Optical and Fluorescence Images. T91 steel specimens were removed at different immersion time and rinsed with enough deionized water to get rid of the physically adsorbed FD2. The specimens were investigated with an Olympus SZX7 Stereo Fluorescence Microscope. A mercury vapor lamp with excitation between 460 and 550 nm in combination with a 515 nm filter was used. The optical and the fluorescence microscopic examination were compared to determine the corrosion detection effect.

2.5. Electrochemical Measurements. Electrochemical measurements were performed in a conventional three-electrode cell connected to a computer-controlled electrochemical workstation (Solartron 1287 Electrochemical Interface coupled with a 1260 Impedance/Gain-Phase Analyzer). Zplot and CorrWare software packages were used for the electrochemical analysis. The electrochemical cell was open to the air and the test solution was not stirred or deaerated. T91 working electrodes (WE) were sealed with epoxy resin so that only the circular cross section (0.5 cm²) was exposed. Saturated calomel electrode (SCE) was used as reference electrode; the counter electrode was a platinum electrode. EIS measurements were done at the open-circuit potential in the frequency range from 0.02 Hz to 100 kHz. A sine wave with 5 mV amplitude was used to perturb the system. Polarization studies were carried out at a scan rate of 0.5 mVs⁻¹. All potentials were presented in mV (SCE).

3. Results and Discussion

3.1. Fluorescence Emissions of FD2 in Aqueous Solution. FD2 was a pale pink solid and its molecular structure was supported by IR analysis. The peak at 1583 cm⁻¹ is caused by C–N and δN–H. The bands around 3473 cm⁻¹ can be assigned to N–H. Although FD2 is a derivative of rhodamine 6G, it is nearly colorless in 3% NaCl solution, suggesting that the spirocyclic forms exist mainly. Figure 2(a) shows the fluorescence emission of 0.1 μM FD2 in the presence of different amounts of Fe³⁺ ions in 3% NaCl solution. FD2 presented no fluorescence signal without Fe³⁺ ions. When Fe³⁺ ions were introduced to the solution, the characteristic fluorescence emission at 550 nm was observed. Besides, the fluorescence intensity improved significantly with the increase of Fe³⁺ concentration. During steel corrosion, other alloy elements may also dissolve into cations. The fluorescence enhancement effects of FD2 by other metal ions were given in Figure 2(b). Obviously, other ions, such as Ba²⁺, Cu²⁺, Mn²⁺, Zn²⁺ and SiO₄²⁻, were unable to arouse a
distinct fluorescence response, while Al$^{3+}$ and Fe$^{2+}$ ions have tiny fluorescence response compared with Fe$^{3+}$ ions. The distinct discrimination between Fe$^{3+}$ and other ions provided an opportunity for FD2 to detect Fe$^{3+}$ in aqueous system containing some coexisting ions, showing that FD2 has a very practical corrosion detection effect.

The relationship between fluorescence intensity and Fe$^{3+}$ concentration was presented in Figure 3. It is indicated that the enhanced extents of the fluorescence were in good proportion to the Fe$^{3+}$ concentrations from 30 $\mu$M to 250 $\mu$M. It shows FD2 can be used to monitor the concentration of Fe$^{3+}$ in the neutral water solution to some extent.

The effect of pH on the fluorescence intensity of FD2 in the water solution is shown in Figure 4.

From Figure 4, we can see that the fluorescence intensity of FD2 increased gradually with the decrease of pH values. Fluorescence emission of FD2 increased sharply in the presence of 200 $\mu$M Fe$^{3+}$ ions. Fluorescence intensity has the similar variation tendency with the change of pH values for FD2 with and without Fe$^{3+}$ ions. This shows FD2 has a reorganization of Fe$^{3+}$ ions in a wide pH range.

3.2. FD2 as a Corrosion Indicator for T91 Steel. In order to examine the correlation between fluorescence emission and T91 steel corrosion, the weight-loss of T91 steel in 3%NaCl solution was tested. The fluorescence spectra of the test solution were determined at the same time. The relationship between weight-loss ($\Delta W$) and fluorescence intensities ($I_F$) is shown in Figure 5. It is clear the values of $\Delta W$ and $I_F$ follow similar variation trends.
After T91 steel specimens were immersed in 3% NaCl solution, and Fe\(^{3+}\) ions from corrosion dissolution lead to enhance the fluorescence emission of FD2. The fluorescence intensity varies periodically with the weight-loss of T91 steel specimens. More weight-loss of steel has, the higher concentration of the dissolved Fe\(^{3+}\) ions is, and the stronger fluorescence emission exists. Thus, FD2 can be used for corrosion detection of T91 steel in aqueous solution. However, as shown in Figure 3, the quantitative determination for Fe\(^{3+}\) ions by FD2 during corrosion process still needs further study.

Figure 6 displays the optical and fluorescence images observed in 3% NaCl solution during the weight-loss test. At first, no significant corrosion was observed by the optical microscope after 2 h immersion. Meanwhile, a few bright red spots appear from the fluorescence images. The red spots were due to the formation of the FD2-Fe\(^{3+}\) complexes. With prolonging immersion time, some corrosion spots were observed from the optical images. Red bright spots increase and become larger from the fluorescence images. FD2 reports the onset of corrosion by red bright areas. Clearly, the response for corrosion was more visible for the fluorescence images than that for the optical images. It shows that FD2 acts as an initial corrosion indicator. This is critical to the timely maintenance of metal equipment before too much damage occurs.

### 3.3. Inhibition of FD2 on Steel Corrosion

A suitable corrosion indicator should not have any corrosive effect on the metal concerned. Figure 7 shows the impedance spectra of T91 steel in 3% NaCl solution after 1 h immersion with and without FD2. A capacitive loop was observed for the T91 steel electrode, suggesting that the corrosion of T91 steel is controlled by the charge transfer process. The equivalent circuit employed to analyze the impedance plots is inserted in Figure 7. In the circuits, \(R_s\) stands for the solution resistance, \(R_{ct}\) the charge-transfer resistance, and \(C_{dl}\) the double layer capacitance. The impedance parameters are given in Table 1. From Table 1, we can see that the presence of FD2 gives a larger \(R_{ct}\) value, showing that FD2 has no corrosion effect for T91 steel.

Figure 8 is the polarization curves of T91 steel in 3% NaCl solution after 1 h immersion. The polarization parameters are shown in Table 2. It is obvious that the anodic corrosion process of T91 steel was suppressed by FD2. The presence of FD2 shifts the corrosion potential in a positive direction and decreases the corrosion current density significantly. Thus, FD2 can be used as a corrosion indicator without any corrosion damage risks.

It was believed that the pitting corrosion of steel in halide-containing solution involves the following steps:

\[
Fe \rightarrow Fe^{2+} + 2e^{-} \tag{7}
\]

\[
Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \tag{8}
\]

\[
FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2Cl^- + 2H^+ \tag{9}
\]

\[
4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O_2^{2-} \tag{10}
\]

\[
Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{11}
\]

\[
Fe(OH)_3 \rightarrow \gamma-FeOOH + H_2O \tag{12}
\]

\[
2\gamma-FeOOH \rightarrow Fe_2O_3 + H_2O \tag{13}
\]

The initiation of pitting attacks by the aggressive Cl\(^-\) ions could be attributed to competitive adsorption between Cl\(^-\) ions and oxygenated species (OH\(^-\) and H\(_2\)O dipoles) at the active sites on oxide covered layer [12]. The adsorbed Cl\(^-\) ions can penetrate through the passive layer especially at its point defects and flaws with the assistance of a high electric field across the passive film to reach the base metal surface and accelerate the local anodic dissolution [13]. FD2 and the anodic dissolved Fe\(^{3+}\) ions have the following reaction:

\[
2FD + Fe^{3+} \rightarrow FD\ldots Fe^{3+} \ldots FD \tag{14}
\]

The formation of the complex on the film surface acts as barrier layers to diffusion of Cl\(^-\) anions from attacking the passive film. The complex of FD-Fe\(^{3+}\)-FD moves \(E_{corr}\) towards more positive potential and retards the anodic dissolution reaction effectively. It is reported that the iron-inhibitor complex formed on steel surface can be detected by fluorescence spectral analysis [14]. In the present study, Fe\(^{3+}\) ions produced from localized corrosion on T91 steel surface are monitored in-situ by FD2, whose fluorescence intensity has Fe\(^{3+}\)-enhanced features. The dissolution of the FD-Fe\(^{3+}\)-FD complex also leads to the improvement of the fluorescence emission in 3% NaCl solution.

### 4. Conclusions

The “turn-on” fluorescence emission via chelation between FD2 and Fe\(^{3+}\) ions can be used for corrosion detection of T91 steel in 3% NaCl solution. The fluorescence intensity in the test solution also varies periodically with the weight loss of T91 steel. The initiation of localized corrosion can be indicated by the bright red fluorescence spots on T91 steel.
Figure 6: Optical images (a) and fluorescence images (b) observed at different immersion times during weight-loss test.

Figure 7: Nyquist plots of T91 steel in 3% NaCl solution without and with 0.1 μM FD2.

Table 1: Electrochemical parameters for T91 steel in 3% NaCl solution.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$R_s$ (Ω·cm²)</th>
<th>$C_{dl}$ ($10^{-5}$ F·cm⁻²)</th>
<th>$R_{ct}$ (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8.876</td>
<td>13.66</td>
<td>267.1</td>
</tr>
<tr>
<td>0.1 μM FD2</td>
<td>6.764</td>
<td>12.97</td>
<td>347.0</td>
</tr>
</tbody>
</table>

FD2 provides a useful tool for early nondestruction corrosion detection of T91 steel based on its Fe³⁺-amplified fluorescence property.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


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