Effects of chitosan inhibitor on the electrochemical corrosion behavior of 2205 duplex stainless steel

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Abstract: The effects of chitosan inhibitor on the corrosion behavior of 2205 duplex stainless steel were studied by electrochemical measurements, immersion tests, and stereology microscopy. The influences of immersion time, temperature, and chitosan concentration on the corrosion inhibition performance of chitosan were investigated. The optimum parameters of water-soluble chitosan on the corrosion inhibition performance of 2205 duplex stainless steel were also determined. The water-soluble chitosan showed excellent corrosion inhibition performance on the 2205 duplex stainless steel. Polarization curves demonstrated that chitosan acted as a mixed-type inhibitor. When the stainless steel specimen was immersed in the 0.2 g/L chitosan solution for 4 h, a dense and uniform adsorption film covered the sample surface and the inhibition efficiency (IE) reached its maximum value. Moreover, temperature was found to strongly influence the corrosion inhibition of chitosan; the inhibition efficiency gradually decreased with increasing temperature. The 2205 duplex stainless steel specimen immersed in 0.4 g/L water-soluble chitosan at 30°C displayed the best corrosion inhibition among the investigated specimens. Moreover, chitosan decreased the corrosion rate of the 2205 duplex stainless steel in an FeCl₃ solution.

Keywords: inhibitor; chitosan; stainless steel; corrosion behavior; electrochemistry

1. Introduction

Because of their excellent mechanical properties and corrosion resistance characteristics [1–2], the 2205 duplex stainless steels have been widely applied in numerous fields in recent years, including the shipbuilding, off-shore oilfield, chemical, paper and pulp, petrochemical, desalination, and oil and gas industries [3–5]. Moreover, because of their high corrosion resistance and durability, duplex stainless steels are also attracting increasing interest for use in various biomedical applications [6–7]. However, even a small amount of metal species released from 2205 duplex stainless steel due to corrosion (electrochemical dissolution or chemical dissolution) may pose a potential health risk [8].

Adding a corrosion inhibitor is a simple, low cost, and adaptable anticorrosion method to improve the corrosion resistance or stability of 2205 duplex stainless steel. Natural, low-toxicity, and environmentally friendly corrosion inhibi-

tors such as chitosan are urgently needed. El-Haddad [9] studied the effect and inhibition mechanism of chitosan on the corrosion behavior of Cu in 0.5 mol/L HCl. Chitosan was found to essentially act as a mixed-type inhibitor and to exhibit good inhibition efficiency for Cu in 0.5 mol/L HCl solution. Moreover, the adsorption of chitosan onto the specimen surface from solution followed the Langmuir adsorption isotherm model. Sangeetha *et al.* [10] reported the corrosion inhibition performance of synthesized *O*-fumaryl-chitosan (OFC) for mild steel in 1 mol/L HCl. Their results suggested that the inhibition efficiency increased with increasing concentration of addition inhibitor, reaching a maximum of 94.1% at 500×10^{-6} OFC. Wang *et al.* [11] prepared a chitosan-based low-pH-sensitive intelligent corrosion inhibitor by loading a pH-sensitive hydrogel with benzotriazole (BTA). The results from electrochemical tests and immersion experiments indicated that the intelligent inhibitor provided a rapid response and effectively inhibited the corrosion of

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copper for an extended time period. Fayyad *et al.* [12] prepared an anticorrosion nanocomposite coating that consisted of chitosan (green matrix), oleic acid, and graphene oxide (nanofiller). The corrosion resistance of this nanocomposite coating was compared with that of a pure chitosan coating by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP). El-Mahdy *et al.* [13] synthesized new ionic liquids using chitosan through amidation and quaternization reactions with oleic acid and *p*-toluene sulfonic acid, respectively. The potentiodynamic polarization data revealed that the prepared ionic liquid reduced both dissolution and hydrogen evolution corrosion reactions. EIS was used to elucidate the characteristics of the charge-transfer process of the steel corrosion. Langmuir isotherms were found to properly fit the adsorption of the prepared polymeric ionic liquid over the steel surfaces. Sangeetha *et al.* [14] studied the corrosion mitigation of *N*-(2-hydroxy-3-trimethyl ammonium) propyl chitosan chloride (HTACC) as an inhibitor on mild steel. Their polarization studies revealed that HTACC acted as both an anodic and a cathodic inhibitor. EIS studies confirmed that the inhibition occurred through adsorption of HTACC onto the metal surface. The extent of inhibition exhibited a nega-

tive trend with increasing temperature. However, research on the corrosion inhibition mechanism of chitosan for duplex stainless steels has been insufficient.

In the present paper, the effects of chitosan on the corrosion inhibition behavior of 2205 stainless steel were studied by electrochemical techniques and immersion tests. A stereological microscope was used to observe the microstructures of the duplex stainless steel. Moreover, the optimum parameters of water-soluble chitosan on the corrosion inhibition performance of 2205 duplex stainless steel were determined.

2. Experimental

2.1. Materials

The composition of the 2205 duplex stainless steel used in the experiments is shown in Table 1. To observe the microstructures of the duplex stainless steel, a specimen was polished using abrasive silicon carbide papers (400[#], 800[#], 1200[#], and 2000[#]) and mirror finished with 1- μ m polishing pastes; it was then subjected to ultrasonic cleaning in alcohol for 5 min and dried in cold air. The polished specimen was eroded with aqua regia, and the microstructures were observed by stereology microscopy.

Table 1. Composition of 2205 duplex stainless steel

wt%

C	Si	Mn	P	S	Cr	Ni	N	Mo	Fe
0.014	0.39	1.39	0.023	0.001	22.39	5.68	0.17	3.13	Balance

2.2. Electrochemical tests

Stainless steel specimens with dimensions of 10 mm $\times$ 10 mm $\times$ 5 mm were used in electrochemical analyses. Copper wires were welded to the samples, which were subsequently embedded in epoxy resin. Before the electrochemical tests, all the specimens were subjected to polishing and mirror finishing.

Electrochemical tests were performed in a conventional three-electrode system using a model VMP3 electrochemical system (EG&G Princeton Applied Research). A Pt plate and a saturated calomel electrode were used as the counter electrode and the reference electrode, respectively. Polarization measurements were conducted from -0.5 V vs. open-circuit potential toward the anodic direction; the scan rate was 0.1667 mV/s. All electrochemical tests were conducted under a constant controlled temperature in a thermostated water-bath cauldron. The electrolytes used in the electrochemical measurements were 3.5wt% NaCl solutions, which were prepared from analytical-grade reagent and deionized water.

To observe the morphology of pits, the specimens were first cleaned with deionized water and dried with cold air after the polarization tests. The specimens were then treated with erosion

solution and again cleaned with alcohol and deionized water.

2.3. Immersion tests

As is well known, 2205 duplex stainless steel exhibits good corrosion resistance but suffers from pitting corrosion in specific environmental media under certain temperature and pH conditions [15–16]. In the present work, to further characterize the corrosion inhibition performance of chitosan for 2205 duplex stainless steel, immersion tests in FeCl₃ were performed in accordance with standard GB/T 10125–1997; carboxylated chitosan ((C₆H₁₁NO₄)_n) was used. The specimens, whose dimensions were 25 mm $\times$ 50 mm $\times$ 2 mm, were polished according to standard GB/T248.1. The immersion test specimens were divided into two groups: group-A specimens were immersed in 6wt% FeCl₃ solution; group-B specimens were immersed in 6wt% FeCl₃ + 0.2 g/L chitosan solution. To determine the mass loss, the specimens were subsequently subjected to chemical etching according to standard GB/T 16545–1996 and were then cleaned with alcohol and deionized water. Before and after the immersion tests, the specimens were weighed on the same balance. The

micromorphology of the specimens after the immersion tests was observed by scanning electron microscopy (SEM, FEI Quanta250).

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the microstructures of the 2205 duplex stainless steel. It mainly consists of ferrite and austenite phases, where the striped black parts are austenite and the white parts are the ferrite matrix. The calculation results of the two phase contents (area fraction) analyzed using the ImageTool software show that the microstructures are composed of 48.6% ferrite phase and 51.4% austenite, which satisfies the requirements specified in standard ASTM A240/A240M-01.

Fig. 1. Microstructures of the 2205 duplex stainless steel.

3.2. Effects of immersion time on corrosion inhibition performance

To characterize the corrosion inhibition of water-soluble chitosan for 2205 duplex stainless steel, immersion tests were carried out. In these experiments, the specimens were immersed in a 0.2 g/L water-soluble chitosan solution for various times and subsequently subjected to a polarization test in 3.5wt% NaCl solution. The polarization results for the specimens exposed to water-soluble chitosan for various times are shown in Fig. 2. The inset of Fig. 2 is an enlarged view of the red-boxed area. To obtain the parameters related to the corrosion process, the polarization curves were fitted

using the EC-Lab software; the fitted results are shown in Table 2. The inhibition efficiency (IE) was calculated as

$$IE = \left(1 - \frac{i_{\text{corr}}}{i_0} \right) \times 100\% \quad (1)$$

where i_{corr} represents the corrosion current density of specimens exposed in chitosan solution for different times (2, 4, 6, and 8 h) and i_0 is the corrosion current density of the blank specimen (0 h).

The results in Fig. 2 and Table 2 indicate that E_{corr} slightly decreases with increasing immersion time in the chitosan solution. This behavior is mainly due to the complex reaction between the reactive functional groups of chitosan and metal ions in solution. Usually, a compact adsorption film will form on and cover the surface of a steel specimen through Langmuir adsorption [10,17–18]. However, in the present case, the complex reaction suppresses the formation of an adsorption film on the surface. The absolute value of the cathodic Tafel slope of the polarization curves (β_c) changes only slightly as a function of immersion time; by contrast, the value of the anodic Tafel slope of the polarization curves (β_a) first decreases and then increases with increasing immersion time, which indicates that the chitosan acts as a mixed-type inhibitor for 2205 duplex stainless steel in 3.5wt% NaCl solution. Previously published results [19–20] also show that chitosan is a mixed-type inhibitor for carbon steel.

Fig. 2. Polarization curves of specimens after immersion in the 0.2 g/L water-soluble chitosan solution for various times.

Table 2. Fitted results of the polarization curves in Fig. 2

Immersion time / h	$E_{\text{corr}} / \text{mV}$	E_p / mV	$(E_p - E_{\text{corr}}) / \text{mV}$	$\beta_a / (\text{mV} \cdot \text{dec}^{-1})$	$\beta_c / (\text{mV} \cdot \text{dec}^{-1})$	$i_{\text{corr}} / (\mu\text{A} \cdot \text{cm}^{-2})$	IE / %
0	-217.8	1.046	218.9	261.1	156.1	1.138	0
2	-269.6	1.062	257.6	224.1	151.8	0.632	44.46
4	-266.7	1.012	267.7	193.3	150.2	0.427	62.47
6	-275.2	1.052	276.3	263.6	153.9	0.731	35.76
8	-242.7	1.082	243.7	347.6	157.8	0.77	32.33

Note: E_{corr} , E_p , and i_{corr} represent the corrosion potential, pitting potential, and corrosion current density, respectively; β_a and β_c are the anodic and cathodic Tafel slopes of polarization curves, respectively; IE is the inhibition efficiency.

Compared with the blank specimen (0 h), the specimens with chitosan inhibitor exhibit a smaller corrosion current density, a greater pitting potential, and a wider anodic passivation zone, which demonstrates the excellent inhibition effect of chitosan on 2205 stainless steel. Moreover, the IE progressively increases with increasing immersion time in the 0.2 g/L chitosan solution. However, when the immersion time is longer than 4 h, the IE decreases. This behavior is attributable to damage to the adsorption film created by the complex reaction between the reactive groups of chitosan and metal ions.

After the polarization tests, the morphologies of pits on the specimens' surfaces were observed, as shown in Fig. 3. A large number of small pitting sites exist at the junctures of the two phases. However, the number of pits is substantially lower on the surfaces of specimens previously immersed in 0.2 g/L chitosan solution for 2 h. This result further demon-

strates the outstanding corrosion inhibition by the chitosan inhibitor for the 2205 duplex stainless steel.

3.3. Effects of temperature on corrosion inhibition performance

Fig. 4 shows the polarization curves of 2205 duplex stainless steel at different temperatures in 3.5wt% NaCl solution. The small plots in Fig. 4 are the polarization curves of specimens immersed for 2 h in 0.2 g/L chitosan solution at different temperatures. All of the curves show the same behavior, which indicates that the electrochemical reaction mechanism under different temperature conditions is the same. That is, the anodic process is the dissolution reaction of the metal electrode and the cathode reaction is the depolarization process of oxygen. Moreover, the corrosion current density gradually increases and the corrosion potential decreases with increasing temperature.

Fig. 3. Morphologies of the pits after polarization measurements: (a) blank specimen (0 h); (b) after immersion in 0.2 g/L chitosan solution for 2 h.

Fig. 4. Polarization curves of the 2205 stainless steel at different temperatures in 3.5wt% NaCl solution.

The polarization curves in Fig. 4 were fitted; the results are shown in Table 3. The chitosan exhibits the best corrosion inhibition efficiency at 30°C. Under other temperature conditions, the chitosan still inhibits corrosion of the 2205 duplex stainless steel but the IE value gradually decreases with increasing temperature. Because of the higher kinetic energy of molecules at higher temperatures, adsorption is

difficult; the desorption effect of the corrosion inhibitor is enhanced at higher temperatures, which affects the formation of the stable and compact film layer. A comparison of the polarization curve of the specimen immersed for 2 h with that of the blank specimen (0 h) reveals that parameters β_a and β_c change. Thus, the chitosan solution still exhibits a mixed-type inhibition behavior at different temperatures.

Table 3. Fitted results of the polarization curves in Fig. 4

Temperature / °C	Immersion time / h	E_{corr} / mV	β_a / (mV·dec ⁻¹)	β_c / (mV·dec ⁻¹)	i_{corr} / (μA·cm ⁻²)	IE / %
30	0	-217.8	261.1	156.1	1.138	0
	2	-256.6	224.1	151.8	0.632	44.47
40	0	-377.2	359.0	207.1	8.289	0
	2	-407.4	513.2	222.1	5.785	30.21
50	0	-366.7	423.9	200.5	10.720	0
	2	-456.9	553.3	189.0	7.680	28.36
60	0	-373.5	228.1	180.1	10.980	0
	2	-464.4	292.6	101.1	8.588	21.79
70	0	-391.8	230.5	201.4	12.610	0
	2	-433.2	220.2	294.2	9.863	21.78

Note: An immersion time of 0 h represents the blank specimen.

3.4. Effects of the chitosan concentration on corrosion behavior

Fig. 5 shows the polarization curves of the specimens immersed for 2 h at 30°C in chitosan solutions with various concentrations. The corresponding fitted results are displayed in Table 4. With increasing chitosan concentration, E_{corr} shifts toward more negative potentials and E_p increases slightly. The E_p reaches its maximum value when the chitosan concentration is 0.4 g/L. Moreover, β_a reaches its maximum value at 0.8 g/L. This result implies that a high concentration of chitosan is beneficial to rapid adsorption onto the specimen surface and to the formation of a uniform and dense inhibition film. However, with increasing concentration, the complex reaction that occurs between the reactive groups of chitosan molecules and metal ions generated in the corrosion process is enhanced, which reduces the inhibition efficiency. Given the aforementioned results, the best corrosion inhibition performance is attained at a chitosan concentration of 0.4 g/L.

3.5. Immersion tests

Fig. 6 displays the corrosion rates of specimens in the immersion tests. The corrosion rates of the group-A specimens (6wt% FeCl₃) are consistently higher than those of

Fig. 5. Polarization curves of the specimens after immersion for 2 h at 30°C in chitosan solutions with various concentrations.

Table 4. Fitted results of the polarization curves in Fig. 5

Concentration / (g·L ⁻¹)	E_{corr} / mV	β_a / (mV·dec ⁻¹)	β_c / (mV·dec ⁻¹)	i_{corr} / (μA·cm ⁻²)	E_p / mV
0	-217.8	261.1	156.1	1.138	1.049
0.2	-256.6	224.1	151.8	0.632	1.076
0.4	-392.7	759.8	249.9	4.336	1.179
0.6	-454.9	1427.0	236.9	8.733	1.161
0.8	-488.3	2019.0	228.9	9.381	1.159

Fig. 6. Corrosion rates of the specimens in immersion tests.

the group-B specimens (6wt% FeCl₃ + 0.2 g/L chitosan solution), which implies that chitosan slows the corrosion rate of the 2205 duplex stainless steel. Moreover, the corrosion rates of the group-B specimens tend to decrease in the early stages of the experiment but increase after the specimens

have been immersed for 96 h. This behavior is attributed to the formation of a dense adsorption film onto the specimen surface at the initial stage, which may suppress the corrosion process of the specimens. However, with increasing immersion time, the adsorption film is also damaged by Cl⁻. Thus, the corrosion rate tends to increase at the end of the experiment. In this situation, pitting corrosion may occur on the specimen surface. To investigate this possibility, we observed the micromorphology of the specimens immersed for 120 h, and the results are shown in Fig. 7. Numerous pits are scattered on the surface of the group-A specimen, which demonstrates that the specimen immersed in FeCl₃ solution suffers from serious corrosion. The pit diameter is almost 10 μm. However, in the case of the surface of the group-B specimen, only slight corrosion is observed. Moreover, the pits are relatively small and few in number. These results suggest that the chitosan exhibits excellent corrosion inhibition performance on the 2205 duplex stainless steel.

Fig. 7. Micromorphology of the specimens after 120-h immersion tests: (a) group-A specimen immersed in an FeCl₃ solution; (b) group-B specimen immersed in an FeCl₃ + 0.2 g/L chitosan solution.

4. Conclusions

(1) In the 3.5wt% NaCl solution system, the water-soluble chitosan exhibited excellent corrosion inhibition performance for 2205 duplex stainless steel. Polarization curves suggest that chitosan acted as a mixed-type inhibitor. When the specimen was immersed in 0.2 g/L chitosan solution for 4 h, a dense and uniform adsorption film covered the sample surface and the IE reached its maximum value.

(2) Temperature strongly influences the corrosion inhibition of chitosan. The 2205 duplex stainless steel specimen immersed in 0.4 g/L water-soluble chitosan at 30°C displays the best corrosion inhibition. Moreover, chitosan can also decrease the corrosion rate of 2205 duplex stainless steel in FeCl₃ solution.

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