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Study of methionine as green corrosion inhibitor for TWIP steel in neutral chloride solution

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Abstract

The influence of Methionine (MTI) on corrosion behavior of Twinning induced plastic (TWIP) steel in 3.5wt.% NaCl solutions was investigated using electrochemical techniques, scanning electron microscopy (SEM), white light interferometer (WLI) analyses and Raman spectra. With increasing inhibitor concentration, the corrosion inhibition rate first increased and then decreased, and the maximum inhibitor efficiency was found to be 30 mg l\(^{-1}\). MTI was acting as a mixed-type inhibitor. The inhibition effect of MTI could also be evaluated by SEM and WLI results, and the trend was the same as that obtained by electrochemistry. At the same time, Raman spectra results showed that MTI was adsorbed on the surface of the steel.

1. Introduction

As the most commonly used structural materials, corrosion of metal will cause huge economic losses and major safety hazards. One simple and practical way to protect metals from corrosion is adding inhibitors in their service environment [1–3]. Several kinds of corrosion inhibitors have been developed, including synthetic corrosion inhibitors, inorganic inhibitors, plants extracts, amino acids and so on. However, the wild application of traditional inorganic inhibitors and organic inhibitors was hindered by the risk of polluting water and even the whole environment. The demand for environment-friendly corrosion inhibitors to replace traditional corrosion inhibitors has become a global issue [4]. Amino acids are considered to be green corrosion inhibitors for their properties such as nontoxic, biodegradable. They are also relatively cheap corrosion inhibitors which can be plenty supplied by hydrolysis of proteins [5]. Amino acids adsorb on metal/solution interface, thus hindered the corrosion solution access to metal surface, the process of which could affected by the chemical structure of the inhibitor molecular, the surface charge of metal, the type of corrosion solution and most important of the interaction between inhibitors and the metal surfaces [6]. Although predecessors have done a lot of work to create favorable conditions for amino acids’ application development, still some researchers were investigating the inhibition performance of amino acids on corrosion of metals [7–9]. The scope of application is still to be expanded and the mechanism of corrosion inhibition needs further study and exploration.

E Oguzie and co-workers [10] reported the successful application of methionine (MTI) as a corrosion inhibitor for a mild steel specimen in sulfuric acid solution and pointed out that MTI inhibited the corrosion reaction by adsorption onto the metal/solution interface. Li Chen et al. investigated a novel glycine derivative by weight loss measurements and electrochemical tests which was found to be an excellent corrosion inhibitor for N80 carbon steel in saline solution [11]. Xiuhong Li and co-workers reported that Met as a corrosion inhibitor for copper-nickel has 65% corrosion inhibition efficiency at 40 ppm through a set of electrochemical tests, SEM and other methods [12]. Xingwen Zheng et al. studied the corrosion performance of mild steel in acidic solutions with the L-lysine using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), Quantum chemical calculation and found that L-lysine played different role in HCl solution and H\(_2\)SO\(_4\) solution. L-lysine behave as a mixed-type inhibitor in HCl solution with mostly cathodic action, while more like a modest cathodic inhibitor in...
0.5 M H₂SO₄ solution [13]. Sehiety’s group studied the corrosion performance of low alloy steel in acid media with Tryptophan (Trp) as inhibitor and proved that Trp is suit for low alloy steel’s inhibition in acid solution [14]. They subsequently investigated inhibitory properties of Cystine for low alloy steel in acid solutions [15]. Bobina et al. reported inhibition performance of L-histidine for carbon steel in acetic acid/sodium acetate solution by weight loss measurements and energy dispersive x-ray analysis [16]. Mobin and co-workers found L-Cysteine shows good inhibition performance for mild steel in 1 M HCl solution, the inhibition efficiency increased with the increasing of concentration and decreasing of service environment temperature [17]. Therefore, amino acids are considered as promising environment-friendly corrosion inhibitors.

High-manganese twinning-induced plasticity (TWIP) steels are recently developed novel material with attributes including excellent strength, ductility and special strain hardening which are of great interest to car industry and petroleum industry [18]. For the applications of TWIP steel in structures and components exposed to seawater, the primary problem is corrosion resistance which needs to be solved at first [19]. However, the high proportion of manganese in TWIP steels along with high dissolution rate makes them hardly form a stable passive film in chloride and acidic solutions [20]. Therefore, the first problem should be noticed regarding to its anti-corrosion behavior, which become the most concern in engineering applications.

In this paper, MTI, one of the amino acids, was used as inhibitors for TWIP steel in 3.5 wt.% NaCl solution. Relevant electrochemical parameters were measured, so as to optimize the optimal concentration of the inhibitor in 3.5 wt.% NaCl media. The surface morphology of TWIP steel samples without and with (MTI) was observed using white light interferometer (WLI) and scanning electron microscopy (SEM). Meanwhile, the corrosion inhibition mechanism of MTI on TWIP steel in saline solution was preliminarily discussed in order to provide theoretical reference for industrial application.

2. Experimental

2.1. Materials and solutions

All chemicals, Methionine (MTI) (Sigma adrich, 98%), ethanol (98%) and deionized water (CSR-1–100 (II), R > 10MΩ·cm⁻¹), were used as bought with no further purification. The molecular structure of MTI was shown in figure 1.

The material used in this study was Twinning induced plastic (TWIP) steel with a composition (in wt. %) of 0.6% C, 0.3% Si, 18.0% Mn, 1.5% Al, and the remainder iron (Fe).

TWIP steel samples were immersed in a 3.5 wt.% NaCl solution with different concentration of MTI (15 mg l⁻¹, 30 mg l⁻¹, 45 mg l⁻¹, 60 mg l⁻¹, 75 mg l⁻¹).

2.2. Electrochemical tests

2.2.1. Potentiodynamic polarization measurements

The electrochemical measurements (Princeton, parstatmc PMC, multi-channel electrochemical workstation) were conducted in a conventional three electrodes electrochemical cell in 3.5 wt.% NaCl, without and with the MTI in the concentration gradient. NaCl and MTI were weighed with an Analytical balance instrument to match the reaction solution. A sheet with size 1 × 1 cm² TWIP steel was welded in a wire from one side as an working electrode. To control the exposed area of TWIP steel, the working electrode was fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin to make the uncovered area to 1 cm². 4 × 4 cm² platinum foil was applied as the counter electrode and Ag(s)/AgCl(s)/Sat. KCl) was applied as the reference electrode. The working electrodes were wet-polished with silicon carbide abrasive paper (100, 400, 800, 1500, and 2000), rinsed with deionized water, and then dried in warm air. Before all electrochemical tests, the working electrode was immersed in the corrosion solution for 150 min to establish a steady state of open-circuit potential. Then potentiodynamic polarization curves could be observed at 1 mV · s⁻¹ scan rate from −0.25 V to +0.25 V (versus Ag/AgCl)
relative to the corrosion potential. The final data were collected using Versastudio software. And the data were used to draw the picture with Origin software.

2.2.2. Electrochemical impedance spectroscopy (EIS)
The impedance measurements were performed using a signal with amplitude of 10 mV in the frequency range from $10^5$ Hz to $10^{-2}$ Hz. The spectra were recorded under open circuit conditions after 150 min exposure in the test solution. All electrochemical assays were performed at room temperature ($23 \pm 2^\circ C$) in the absence of agitation. The EIS data were collected using Versastudio software and fitted with Zsimpwin software.

2.3. SEM measurement
The electrode surfaces of TWIP steel were analyzed by Scanning electron microscope (Qutanta FEG 450 Sield Emission environmental scanning electron microscope) after immersion in test solutions at $23 \pm 2^\circ C$ for 150 min.

2.4. White light interferometer (WLI) measurement
TWIP steel samples were immersed in the experimental solution at $23 \pm 2^\circ C$ for 150 min. After taking out from experimental solution, the corrosion products on the surface of samples were first cleaned by solution ($\text{HCl} + \text{Hexamethylene tetramine (HMT)}$) to remove corrosion products. Then, the surface morphology of the samples was characterized with a White light interferometer (WLI) (Bruker, GT-K).

2.5. Raman spectroscopy
Raman spectroscopy (WITec, alpha R300, confocal Raman spectrometer) was used to collect spectra of TWIP steel samples after soaking in MTI solution. Then the spectra were analyzed to characterize the corrosion products and corrosion inhibition mechanism of MTI.

3. Results and discussion

3.1. Electrochemical measurements
3.1.1. Potentiodynamic polarization measurements
Polarization measurements were applied to compare the difference of the anodic and cathodic partial reactions of the corrosion process with and without MTI. The potentiodynamic polarization curves of TWIP steel in saline solution (3.5 wt.% NaCl) without and with different concentrations of MTI are shown in figure 2. The values of corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), cathodic and anodic Tafel slopes ($\beta_c$ and $\beta_a$) were determined by tafel extrapolation method. The inhibition efficiency ($\eta$) can be calculated using equation (1) [21].

![Figure 2. Polarization curves of TWIP steel in 3.5 wt.% NaCl with different concentrations of MTI.](image)
the curve, meanwhile, the corrosion potential (inhibitor is a mixed type inhibitor is considered as an anodic or cathodic type inhibitor, while the difference less than 85 mV indicates the $I_{corr}$)

where $I_{corr}$ and $I_{corr}$(inh) are the corrosion current densities of TWIP steel electrodes in the uninhibited and inhibited solutions, respectively.

Figure 2 shows that the introduction of MTI into 3.5 wt.% NaCl affects both the anodic and cathodic parts of the curve, meanwhile, the corrosion potential ($E_{corr}$) shifted slightly. This indicates that MTI acts as a mixed-type inhibitor. Figure 2 also shows that the corrosion current density ($I_{corr}$) decreased along with the addition of MTI which demonstrates an inhibiting effect. In addition, the adding of MTI did not cause significant change in the anodic and cathodic Tafel slopes, indicating that the MTI inhibitor adsorbs on the metal/solution interface and slows down corrosion reaction by blocking the active sites without changing the cathodic and anodic reaction mechanisms [10].

The values of inhibition efficiency together with different electrochemical parameters obtained from figure 2 were summarized in table 1. As displayed in table 1, The positive value of $\eta$ suggests the addition of MTI retarded the rate of corrosion reactions. The inhibition efficiency increased with the MTI concentration from 28.35% (15 mg l$^{-1}$ MTI) to 58.84% (30 mg l$^{-1}$ MTI), then decreased to 8.6% as MTI concentration increased to 75 mg l$^{-1}$. Therefore the highest inhibition efficiency was achieved when the concentration of MTI is 30 mg l$^{-1}$.

The data in table 1 shows that increasing of MTI concentration causes the values of potential ($E_{corr}$) move toward negative potential while the values of corrosion current density declined. The changes of potential and corrosion current density indicate that MTI can inhibit the corrosion of TWIP steel. We can also observe that the corrosion potential values are around ($-13.663, -27.602, -35.666, -45.99, -58.524$ and $-68.338$ mV) for (3.5 wt.% NaCl + 15 mg l$^{-1}$ MTI, 3.5 wt.% NaCl + 30 mg l$^{-1}$ MTI, 3.5 wt.% NaCl + 45 mg l$^{-1}$ MTI, 3.5 wt.% NaCl + 60 mg l$^{-1}$ MTI, 3.5 wt.% NaCl + 75 mg l$^{-1}$ MTI), respectively. As discussed in literature, if the difference of $E_{corr}$ values between the blank solution and solutions with inhibitor is more than 85 mV, the inhibitor is considered as an anodic or cathodic type inhibitor, while the difference less than 85 mV indicates the inhibitor is a mixed type [22]. Therefore, MTI was a mixed corrosion inhibitor in this study. The slopes of cathodic ($\beta_c$) and anodic ($\beta_a$) in table 1 altered while the inhibitors added. The result indicates that this inhibitor plays a role as blocking agent that decline the available surface area. In other words, MTI declines the corrosion surface area of TWIP steel, and only leads to partial deactivation of metal surface [23].

3.1.2. EIS measurements

EIS experiments were applied to investigate the characteristics and kinetics of electrochemical processes occurring at the TWIP steel/NaCl solution interface in the saline solutions with MTI at different concentrations [24]. The impedance of the corrosion system gets a significant increase if inhibitors adsorb on the metal surface. Therefore, impedance measurements of the corrosion system could be utilized to evaluate the inhibition performance of an inhibitor. The effect of corrosion protection can be evaluated by comparing the impedance of the corrosion system with different concentrations of corrosion inhibitors [6]. Besides, double layer capacitance values can be collected along with polarization resistance values gathering.

The Nyquist plots of TWIP steel obtained in 3.5 wt.% NaCl solution with and without MTI were shown in figure 3. A depressed semicircle with the center below the horizontal axis in high frequency was observed. The phenomenon is dielectric relaxation. The surface roughness, non-uniformity and adsorption effects are the main reasons for the deviation from the ideal capacitive behavior [12, 25]. Only one capacitive arc, which corresponds to the charge transfer process of corrosion reaction at the interface between metal surface and the solution, can be observed in the Nyquist plot of the sample in blank solution. After adding the inhibitor, a big capacitive arc followed by a small depressed capacitive arc at low frequency can be observed, indicating two time constants. The first time constant at high frequency corresponds to the electrochemical response of the inhibitor films adsorbed at the sample surface, and the one at low frequency can be assigned to the electrochemical process of corrosion reaction under the inhibitor film. It is observed from figure 3 that the impedance spectra measured in the 3.5% sodium chloride solution containing 15 mg l$^{-1}$ and 30 mg l$^{-1}$ of MTI exhibit the Warburg

| Conc. (g·L$^{-1}$) | $I_{corr}$ (µA·cm$^{-2}$) | $E_{corr}$ (mV) | $\beta_a$ (mV) | $\beta_c$ (mV) | $\eta$ (%) |
|------------------|------------------------|----------------|---------------|---------------|-----------|
| 3.5 wt.% NaCl | 4.331 | -703.600 | 45.521 | 100.515 | — |
| 3.5 wt.% NaCl + 15 mg l$^{-1}$ MTI | 3.101 | -716.406 | 38.118 | 110.481 | 28.35 |
| 3.5 wt.% NaCl + 30 mg l$^{-1}$ MTI | 1.739 | -730.345 | 42.264 | 107.718 | 58.84 |
| 3.5 wt.% NaCl + 45 mg l$^{-1}$ MTI | 3.076 | -738.409 | 37.737 | 68.904 | 30.00 |
| 3.5 wt.% NaCl + 60 mg l$^{-1}$ MTI | 3.788 | -755.473 | 45.552 | 94.426 | 12.54 |
| 3.5 wt.% NaCl + 75 mg l$^{-1}$ MTI | 3.960 | -764.683 | 45.254 | 65.211 | 8.6 |

$$\eta = \frac{I_{corr} - I_{corr}(inh)}{I_{corr}} \times 100\%$$ (1)
impedance and the diameter of the capacitive loop increases obviously. The diffusion of dissolved oxygen from the bulk solution to the surface of the TWIP causes the appearance of the Warburg impedance at the tail of the capacitive loop [26]. When MTI concentration increased to 45 mg l\(^{-1}\), the Warburg impedance disappeared, as shown in figure 3. The disappearance of Warburg impedance indicates that the corrosion reaction is not controlled by the diffusion process of reactants when the concentration of the inhibitor is not less than 45 mg l\(^{-1}\). It also can be seen that the size of the capacitance loop decreased, indicating that the corrosion inhibition ability was decreased when concentration of MTI increased to 45 mg l\(^{-1}\). This phenomenon may be due to the adsorption of more MTI layers on the surface of TWIP steel in the solution containing MTI inhibitors. In this condition, excess MTI may cause partial desorption or dissolution of the TWIP steel surface [12, 27, 28].

For fitting experimental data, extracting corrosion parameters and characterizing the corrosion process, establishing a suitable circuit for EIS is necessary. Based on the analysis above, the EIS spectra were analyzed using the equivalent circuits depicted in figure 4. The impedance data is interpreted according to three suitable equivalent circuits shown in figure 4. The equivalent circuit in figure 4(a) is used for the EIS data of 0 mg l\(^{-1}\) MTI, the one in figure 4(b) is used to fit the EIS data of 15–30 mg l\(^{-1}\) MTI; while the one in figure 4(c) is used for the EIS data of 45–70 mg l\(^{-1}\) MTI. The fitting results are shown by solid lines with different colors in figure 3, and the electrochemical parameters obtained from fitting results were presented in table 2.

The impedance spectra of the samples obtained in solutions with and without inhibitor were appropriately analyzed by fitting to the equivalent circuit model \(R_s(Q_{dl}R_{ct})\), \(R_s(Q_{dl}(R_{ct}(Q_{dl}R_{ct})))\) and \(R_s(Q_{dl}(R_{ct}(Q_{dl}R_{ct}W))))\), respectively, where \(R_s\) is solution resistance, the pair of \(Q_{dl}/R_{ct}\) are the capacitance and resistance of inhibitor film, and \(Q_{dl}/R_{ct}\) are the charge transfer resistance and a double layer capacitance, and \(W\) is Warburg impedance. \(Q_{dl}\) and \(n\) represents for a constant phase element (CPE) which normally be used to substitute for a capacitor to compensate for the heterogeneity of electrode surface induced deviations [29]. Inhibition efficiencies (\(\eta\)) can be calculated using the following equation (2).

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**Figure 3.** Nyquist plot for TWIP steel in 3.5 wt.% NaCl solutions containing various concentrations of MTI.

**Figure 4.** Equivalent circuits (ECs) applied for fitting of the impedance spectra. (a) EC for blank solution; (b) EC for solution with 15 and 30 mg l\(^{-1}\) MTI; (c) EC for solution with 45, 60 and 75 mg l\(^{-1}\) MTI.
Table 2. Equivalent electric circuit parameters and inhibition efficiency obtained for TWIP steel immersed in 3.5 wt.% NaCl with and without MTI. $C_{dl}/(\text{mF} \cdot \text{cm}^{-2})$.

| Conc. (g·L$^{-1}$) | $R_i/(\Omega \cdot \text{cm}^2)$ | $C_{dl}/(\text{mF} \cdot \text{cm}^{-2})$ | $n_1$ | $R_{ct}/(K\Omega \cdot \text{cm}^2)$ | $C_p/(\text{mF} \cdot \text{cm}^{-2})$ | $n_2$ | $R_t/(\Omega \cdot \text{cm}^2)$ | $R_p/(K\Omega \cdot \text{cm}^2)$ | $W/(\Omega \cdot s^{1/2})$ | $\eta(\%)$ |
|---------------------|---------------------------------|---------------------------------|-------|---------------------------------|---------------------------------|-------|---------------------------------|---------------------------------|--------------------------|-----------------|
| 3.5wt.% NaCl        | 6.145                           | 1.13                            | 0.8577| 1.106                           | —                               | —     | —                               | 1.106                           | —                        | —               |
| 3.5wt.% NaCl + 15 mg L$^{-1}$ MTI | 6.605                           | 0.2813                          | 0.8332| 1.561                           | 0.4142                          | 0.8292| 25.5                           | 1.587                           | 0.015                   | 20.31           |
| 3.5wt.% NaCl + 30 mg L$^{-1}$ MTI | 7.091                           | 0.30                            | 0.8339| 1.727                           | 0.42                            | 0.8446| 19.55                          | 1.747                           | 0.008                   | 36.69           |
| 3.5wt.% NaCl + 45 mg L$^{-1}$ MTI | 5.466                           | 0.61                            | 0.8954| 1.278                           | 0.61                            | 0.88  | 17.73                          | 1.305                           | —                       | 15.25          |
| 3.5wt.% NaCl + 60 mg L$^{-1}$ MTI | 5.420                           | 0.61                            | 0.904 | 1.172                           | 0.47                            | 0.88  | 95.55                          | 1.268                           | —                       | 12.78          |
| 3.5wt.% NaCl + 75 mg L$^{-1}$ MTI | 6.057                           | 0.18                            | 0.8498| 0.642                           | 0.72                            | 1     | 602.8                          | 1.245                           | —                       | 12.39          |
Where $R_p$ and $R_p(\text{inh})$ were charge transfer resistance ($R_{ct}$) of blank solution and polarization resistance ($R_i + R_{ct}$) of inhibited solutions, respectively.

Table 2 shows that once MTI added in, no matter any concentration, the decline of interfacial capacitance was observed, which indicates that MTI adsorbed on TWIP steel surface at all concentrations. The decrease of $C_{dl}$ values usually considered as a outcome from an increase in the double-layer thickness and/or a decrease in the dielectric constant, in this case could owing to that MTI molecules adsorb at the sample plane and block the active sites on the metal surface \[30-32\]. It can be seen that the $\eta$ values obtained from the EIS were basically identical those obtained from Tafel polarization measurements.

Combined with the above analysis, the corrosion inhibition mechanism is the adsorption of MTI molecules on the active sites of TWIP steel surface and/or deposition of the corrosion products on the TWIP steel surface \[33, 34\].

### 3.2. SEM analysis

The scanning electron microscopy (SEM) images for TWIP steel surface after 5 h immersion in 3.5% NaCl without and with different concentration of MTI were shown in figure 5. A comparison between SEM images obtained in the absence and presence of the inhibitors can be used to prove the inhibition effect of MTI.

Figure 5 shows the SEM images of the TWIP steel samples after removing the corrosion products layer from the surface. It can be observed that the number and depth of the pits and cavities in figure 5(a) are the most among all the samples, indicating that the steel surface was strongly damaged in the absence of MTI comparing with other samples. However, in the presence of MTI (figures 5(b)–(f)), the less pits and cavities were observed in comparison with the steel surface in the absence of inhibitor. This improvement in surface morphology was probably due to the formation of protective molecular film of MTI which was responsible for the corrosion inhibition. For TWIP steel treated by the inhibitor MTI with a concentration of 30 mg l\(^{-1}\) (figure 5(c)), the corrosion marks observed on the sample were obviously the least, indicating that the corrosion inhibition efficiency was the highest when the MTI concentration was 30 mg l\(^{-1}\), which was consistent with the electrochemical results. With the increase of concentration of inhibitor, the pits and cavities with roughness showed a small increase trend, but compared with figure 5(a), it still had an obvious corrosion inhibition effect.

### 3.3. White light interferometer (WLI) analysis

In order to further study the relationship between corrosion inhibition effect and concentration of corrosion inhibitor, TWIP steel samples were measured and analyzed by WLI. The same immersion conditions as used in SEM samples were applied on TWIP steel. After immersion all TWIP steel samples were to clean up corrosive products on the surface because rough and floppy corrosive products will scatter lights and reduce light intensity to receiver.

WLI results (table 3) show that the deepest corrosion pit was 5548.302 nm on the blank TWIP steel samples, while much less deeper pits can be observed on those with MTI inhibitor. After adding corrosion inhibitor, the corrosion of metal surface was weakened and the roughness ($R_a$) was reduced. With the increase of MTI

\[
\eta = \frac{R_p(\text{inh}) - R_p}{R_p(\text{inh})} \times 100\%
\]
addition, it can be seen that $R_a$ and the depth of corrosion pits on the surface of TWIP steel first decreased and then increased. When the corrosion inhibitor concentration was 30 mg l$^{-1}$, $R_a$ and the depth of pits were the smallest. When the concentration of MTI exceeded 30 mg l$^{-1}$, $R_a$ and the depth of pits began to increase. This results and images in figure 3 were consistent with the results of electrochemical analysis.

### 3.4. Raman spectroscopy

Raman spectra of TWIP steels after immersion for 150 min in 3.5% NaCl with different concentration of MTI are shown in figure 7.

The corresponding characteristic peak-to-peak values were shown in the table 4.

As shown in figure 7, the peaks of corrosion products were collected on the surface of TWIP steel before adding MTI. The bands at 308 cm$^{-1}$ and 668 cm$^{-1}$ were assigned as characteristic peaks of Fe$_3$O$_4$, and peaks at 612 cm$^{-1}$ and 1320 cm$^{-1}$ were assigned as characteristic peaks of $\alpha$-Fe$_2$O$_3$. The intensity of corrosion products' peaks decreased remarkably after the addition of corrosion inhibitor. On the one hand, the adsorption of amino acids on the surface prevents the contact between the corrosive medium and the matrix so that the degree of corrosion was reduced. On the other hand, the inhibitor molecules may also adsorb on the surface of corrosion products. Therefore the intensity of corrosion products' peaks decreased significantly. Since Raman signals of amino acids were relatively weak, no signal of amino acids was detected in this experiment [36].

| Conc. (g L$^{-1}$)          | $R_a$ (nm) | $R_t$ (nm) | $R_v$ (nm) |
|-----------------------------|------------|------------|------------|
| 3.5wt.% NaCl                | 209.331    | 8544.37    | −5548.302  |
| 3.5wt.% NaCl + 15 mg l$^{-1}$ MTI | 153.976    | 5458.921   | −2842.698  |
| 3.5wt.% NaCl + 30 mg l$^{-1}$ MTI | 150.581    | 4831.54    | −2447.489  |
| 3.5wt.% NaCl + 45 mg l$^{-1}$ MTI | 165.396    | 5108.005   | −3867.133  |
| 3.5wt.% NaCl + 60 mg l$^{-1}$ MTI | 187.595    | 5088.535   | −3606.828  |
| 3.5wt.% NaCl + 75 mg l$^{-1}$ MTI | 197.52     | 6903.308   | −4523.107  |
4. Conclusions

Electrochemical research methods, SEM, WLI and Raman spectra were used to study corrosion process of TWIP steel in 3.5 wt.% NaCl solution at different MTI concentrations. The main conclusions of this study were given below:

Table 4. The corresponding characteristic peak-to-peak values.

| Conc. (g·L⁻¹) | Components of surface | Locations of standard Raman peaks (cm⁻¹) [35] | Locations of Raman peaks of surface components (cm⁻¹) |
|---------------|-----------------------|-----------------------------------------------|---------------------------------------------------|
| 3.5wt.% NaCl  | α−Fe₂O₃               | 1320                                          | 1356                                              |
|               | Fe₃O₄                 | 308, 670                                      | 312, 674                                          |
| 3.5wt.% NaCl + 15 mg·L⁻¹ MTI | α−Fe₂O₃ | 612, 1320                                     | 619, 1349                                         |
|               | Fe₃O₄                 | 308                                           | 311                                               |
| 3.5wt.% NaCl + 30 mg·L⁻¹ MTI | α−Fe₂O₃ | 1320                                          | 1345                                              |
|               | Fe₃O₄                 | 308, 670                                      | 312, 671                                          |
| 3.5wt.% NaCl + 45 mg·L⁻¹ MTI | α−Fe₂O₃ | 1320                                          | 1345                                              |
|               | Fe₃O₄                 | 670                                           | 667                                               |
| 3.5wt.% NaCl + 60 mg·L⁻¹ MTI | α−Fe₂O₃ | 1320                                          | 1344                                              |
|               | Fe₃O₄                 | 670                                           | 668                                               |
| 3.5wt.% NaCl + 75 mg·L⁻¹ MTI | α−Fe₂O₃ | 612, 1320                                     | 604, 1337                                         |
|               | Fe₃O₄                 | 308                                           | 282                                               |

Figure 7. Raman spectra of TWIP steel after immersion for 150 min in 3.5% NaCl with different concentrations of MTI. All spectra were vertically shifted for clarity.
(1) MTI was considered to be a mixed type corrosion inhibitor.

(2) With the increasing inhibitor concentration, corrosion inhibition rate first increased and then decreased. The highest inhibition effect was 30 mg l$^{-1}$.

(3) Corrosion products of TWIP steel in NaCl solution mainly consist of α-Fe$_2$O$_3$ and Fe$_3$O$_4$.

(4) The intensity of Raman peaks of corrosion products decreased with the increasing MTI concentration due to the adsorption of the inhibitor on the surface.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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