Effects of W and Mo Additions on Wet-dry Acid Corrosion Behavior of Low-Alloy Steels Under Different O₂ Concentrations

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Abstract Effects of W and Mo additions on wet-dry acid corrosion behavior of low-alloy steels under different O₂ concentrations were investigated. The results showed that W and Mo-containing steels presented excellent wet-dry corrosion resistance under O₂ concentrations of both 1 and 5%. The roles of W and Mo played in increasing corrosion resistance of the steels were different. W could improve the thermodynamic stability of the steel substrate, while Mo could promote the formation of protective rust. Interaction between W, Mo and O₂ concentration greatly influenced wet-dry acid corrosion of low-alloy steels. W addition was more effective for depressing charge transfer process at the rust/substrate interface and presented higher enhanced effect on increasing corrosion resistance than Mo under O₂ concentration of 1%. Mo was more effective on increasing rust compactness and showed higher enhanced effect on increasing corrosion resistance than W under O₂ concentration of 5%.

KEY WORDS: Wet-dry acid corrosion; Steel; Corrosion resistance; Electrochemical impedance spectroscopy (EIS); Rust

1 Introduction

W and Mo were two important alloying elements to increase corrosion resistance of the low-alloy steels. The effects of W and Mo have been reported in some corrosion environments, such as marine/industrial atmospheric corrosion, and sulfuric acid dew point corrosion environment [1–3]. Generally, under the above corrosion environments of wet-dry cyclic process, the dense protective rust could form on the steel surface to prevent corrosive species, such as O₂, SO₄^{2−}, Cl[−], [1, 2]. W and Mo existed in the form of

WO₄^{2−} or MoO₄^{2−} ions in the rust, which changed the selective permeability from anion selectivity to cation selectivity, and therefore prevented the transportation of SO₄^{2−} and Cl[−] ions, and decreased corrosion rate of the steels [3]. Meanwhile, W and Mo could also form non-soluble W (VI) and Mo (VI)-containing compounds in inner corrosion product, especially at the bottom of corrosion nest at the steel/rust interface, which inhibited corrosion of the steel [3, 4].

W and Mo were usually added to the steels in combination with certain content of Cu and Cr to improve corrosion resistance in O₂-containing acid corrosion environment [5, 6]. Mo could form inclusions in the steels, such as MoS₂, by which corrosion resistance of the steels was deteriorated, while W rarely formed inclusions [7, 8]. Park et al. [1] reported that the corrosion rate of W (0.05 wt%) steel was lower than Mo (0.05 wt%) steel in 10 wt% sulfuric acid solution, due to the relatively fewer type and quantity of inclusions in W steel (MnS) than in

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Mo steel (MnS, MoS₂). Moreover, W and Mo existing as solid solution state in the ferrite of steel could effectively improve acid corrosion resistance [9, 10]. When W was added by more than 0.5% or Mo by more than 0.2%, localized corrosion resistance of the steel was deteriorated rather than improved, as well as the weldability and toughness of the steel [11, 12].

Steels of the upper deck of cargo oil tanks of crude oil tankers suffered a special kind of wet-dry acid corrosion, which contained considerable amount of O₂, H₂S, and water vapor originated from crude oil, and condensed water with lower pH formed and appeared on the back side of upper deck due to the cyclic temperature change in day and night [13, 14]. Such corrosion environment was different from the industrial/marine atmospheric corrosion and sulfuric acid dew point corrosion, due to the existence of H₂S and O₂, and the concentration of O₂ was usually controlled below 5% [14–16]. The effects of W and Mo on corrosion resistance of the steels in some corrosion circumstances have been reported, but the effects of W and Mo were still unclear in wet-dry acid corrosion atmosphere containing O₂ and H₂S. The aim of the present research is to compare the effects of W and Mo on wet-dry acid corrosion of the steel under different O₂ concentrations by corrosion loss, corrosion morphologies, rust compositions and structures as well as electrochemical measurements.

2 Experimental

2.1 Tested Steels

Table 1 shows the chemical composition of the tested steels. Steels were prepared by melting the constituent elements in a vacuum induction furnace and then were casted into slabs. The slabs were reheated at 1200 °C for 2 h and then hot-rolled into the plates with a thickness of 18 mm. The size of the specimens was 60 mm × 25 mm × 5 mm for the measurement of corrosion loss, and 10 mm × 10 mm × 5 mm for rust analysis, respectively. Specimens were grounded gradually down to 800# grade with SiC paper, cleaned with acetone and ethanol, and then stored in a desiccator for 24 h. The tested specimens were weighed on an electronic balance with accuracy of 0.1 mg, and the width

and length of exposure surface of the specimens were measured by vernier caliper with accuracy of 0.02 mm. Before corrosion tests, the tested specimens were sealed by silica gel with exposure area of 15 cm² for weight loss measurements and 1 cm² for electrochemical measurements, respectively.

2.2 Corrosion Test

Figure 1 shows the schematic of wet-dry acid corrosion test device. The specimens were fixed on back of top cover of the experimental device, and the temperature of specimens was controlled by controlling temperature of top cover. The temperature of the specimens was controlled at 25 °C for 3 h, 50 °C for 7 h, the transition time between 25 and 50 °C was 1 h, and one wet-dry corrosion cycle time (CCT) was 12 h. The temperature of distilled water was between 30 and 32 °C. When the specimens were controlled at 25 °C, condensate water could form on the specimen surface, and when the specimens were controlled at 50 °C, the condensate water could evaporate. Thus, the wet-dry process of the specimen surface could be simulated. The gas composition in simulated wet-dry acid corrosion consisted of: a) O₂ 1%–H₂S 500 ppm–SO₂ 100 ppm–CO₂ 13%–N₂ balance; and b) O₂ 5%–H₂S 500 ppm–SO₂ 100 ppm–CO₂ 13%–N₂ balance, to illustrate acid corrosion behavior of the steels under different O₂ concentrations. Before experiment, N₂ was inlet into the device with gas flow rate larger than 500 mL/min, to clear O₂ inside the device. Then, the mixed gas was inlet into the device. The minimum gas flow rate was 100 mL/min for first 24 h, and then 20 mL/min after 24 h. Distance between the specimen surface and distilled water was 180 mm, avoiding the splash of distilled water. Thus, the wet-dry acid corrosion of the steels could be simulated.

Rusts formed after different corrosion times were removed using blade and pickling solution (HCl 500 mL + H₂O 500 mL + C₆H₁₂N₄ 3.5 g) in accordance with standard ASTM G1-03 [17], and then the specimens were cleaned and dried in ethanol, weighed on an electric balance with accuracy of 0.1 mg. Corrosion loss of the specimens was calculated by formula 1:

$$C_L = \frac{W_0 - W_1}{S \times \rho} \quad (1)$$

Table 1 Chemical composition of tested steels (wt%)

Steels	C	Si	Mn	S	P	Cu	Ni	Cr	Mo	W	Fe
Blank steel	0.08	0.24	1.09	0.002	0.01	0.28	0.20	0.17	–	–	Bal.
W steel	0.08	0.24	1.05	0.002	0.01	0.27	0.19	0.18	–	0.22	Bal.
Mo steel	0.07	0.24	1.04	0.002	0.01	0.28	0.20	0.17	0.25	–	Bal.

Fig. 1 Schematic of wet-dry acid corrosion test device

where C_L was corrosion loss (μm); W_0 was specimen weight before corrosion (g); W_1 was specimen weight after corrosion (g); S was corrosion area (cm^2); and ρ was the density of tested steels (7.85 g/cm^3).

2.3 Rust Analyses

The microstructures of bare steels and cross-sectional morphologies of rusted steels were observed by SEM. Rust was stripped mechanically using blade and carefully collected. Rust powder was prepared for quantitative phase analysis using XRD method. ZnO was used as internal standard for quantitative analyses of rust composition, and ZnO/rust ratio was 1:9 [18, 19]. Crystalline rust phases contained $\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$, Fe_3O_4 , Fe_xS_y and S. The diffraction intensities of (011) reflection of $\alpha\text{-FeOOH}$, (020) reflection of $\gamma\text{-FeOOH}$, (220) reflection of Fe_3O_4 , (331) reflection of Fe_xS_y and (220) reflection of S were measured and compared with (100) reflection of ZnO. Thus, the content of crystalline rust phases could be obtained, and the amorphous phase was balance. Specific surface area (SSA) of the rust was measured using N_2 adsorption and calculated by BET equation.

2.4 Electrochemical Measurements

Potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) of the bare and rusted steels were measured using a three-electrode system and an electrochemical work station. All specimens for electrochemical test were enclosed with epoxy resin with an exposed area of 1 cm^2 . The working electrode was the bare and rusted steels, the reference electrode was a saturated calomel electrode, and the auxiliary electrode was a platinum electrode. The test electrolyte was $0.01 \text{ M Na}_2\text{SO}_4$ solution, with pH 3.0 and at temperature of $25 \text{ }^\circ\text{C}$. The

corresponding mixed gas composing of O_2 , H_2S , SO_2 , CO_2 and N_2 was inlet into test electrolyte with minimum gas flow rate of 100 mL/min for 1 h before electrochemical tests. For measurements of potentiodynamic polarization curves of the steels, the polarization potential was swept from -0.4 V to 1.6 V vs. open circuit potential (OCP) with scan rate of 0.5 mV/s . For EIS measurements, the frequency ranged from 100 kHz to 10 mHz , and the signal amplitude was 5 mV . The measured EIS plots were calculated using ZSimpWin software.

3 Results

3.1 Microstructure of Steels

Figure 2 gives the microstructure of the tested steels. The results indicate that the microstructures of the steels were all mainly composed of the ferrite and small amount of pearlite, which distributed on the grain boundaries of ferrite. W and Mo-containing steel had lower content of the pearlite in fraction comparing with blank steel, indicating that W and Mo additions could reduce the formation of the pearlite in the steel. The grain size of the ferrite in W and Mo-containing steels was smaller than that of blank steel, indicating that W and Mo additions could depress the growth of the ferrite during rolling process. Meanwhile, W steel had smaller content of pearlite than Mo steel, and Mo steel presented finer grain size of ferrite than W steel. The inclusions were rarely observed in W and Mo-containing steels due to low contents of carbon and sulfur in the steels, and W and Mo mainly existed in a form of solid solution in the ferrite of tested steels.

3.2 Corrosion Kinetics

Figure 3a shows that corrosion loss of the steels with increasing corrosion time under O_2 concentration of 1%, and corrosion loss at 42 CCT decreased in the following order: blank steel > Mo steel > W steel. The results indicated that W and Mo additions could obviously decrease corrosion loss of the steels under concentration of 1%, and the decreasing effect of W was higher than that of Mo. Figure 3b shows that corrosion loss of the steels under O_2 concentration of 5% was much higher than that of 1%, which indicated that the increased O_2 concentration made wet-dry acid corrosion more severe. Meanwhile, corrosion loss at 42 CCT is given as: blank steel > W steel > Mo steel. The results indicated that W and Mo additions could decrease the corrosion loss of the steels under O_2 concentration of 5%, and the decreasing effect of Mo was better than that of W. Therefore, both W and Mo could decrease the corrosion loss of low-alloy steels, and the enhanced effects of W and Mo were different.

Fig. 2 SEM micrographs of the bare steels: **a** blank steel; **b** W steel; **c** Mo steel

Fig. 3 Corrosion loss of the steels in wet-dry acid corrosion environments with different O₂ concentrations of **a** 1%; **b** 5%

3.3 Electrochemical Measurements

Figure 4 shows potentiodynamic polarization curves of the bare steels in 0.01 M Na₂SO₄ solution with pH 3.0 and at temperature of 25 °C. The results indicated that the cathodic polarization behaviors of the tested steels were nearly the same, while the anodic polarization behaviors were different. Cathodic polarization behavior of the bare

Fig. 4 Potentiodynamic polarization curves of the bare steels in 0.01 M Na₂SO₄ solution with pH 3.0 and at temperature of 25 °C

steels was mainly influenced by acid electrolyte, while anodic polarization behavior of the bare steels was mainly affected by alloying elements in the steels [20, 21]. W and Mo additions could obviously reduce anodic current density of the bare steels when polarization potential was more positive than $-0.35 V_{SCE}$, and reducing effect of W was better than that of Mo, indicating that W had higher enhanced effect on depressing dissolution process of the steels under strongly polarizing condition.

Table 2 gives the fitted parameters of potentiodynamic polarization curves in Fig. 4. The results showed that the corrosion current density i_{corr} of W steel was lower than that of blank steel, while i_{corr} of Mo steel was higher than that of the blank steel, indicating that W could reduce and Mo could accelerate the dissolution process of the bare steels in acid electrolyte. Corrosion potential E_{corr} of W steel was more positive, while E_{corr} of Mo steel was more negative than that of blank steel, which indicated that W could increase thermodynamic stability of steel in acid electrolyte, and Mo presented an opposite effect. The above difference of corrosion current i_{corr} and corrosion potential E_{corr} of three bare steels which was related to the enhanced effect of elements W and Mo might contribute to the different corrosion performances in wet-dry acid corrosion.

Table 2 Fitted parameters for potentiodynamic polarization curves of the bare steels

Steels	E_{corr} (mV _{SCE})	i_{corr} ($\mu\text{A cm}^{-2}$)	β_a (mV/dec)	β_c (mV/dec)
Blank steel	−612	84.3	25.4	265.4
W steel	−587	73.1	22.6	249.1
Mo steel	−630	103.1	27.3	292.3

Figure 5 shows the EIS plots of the bare steels. Bode plots showed one time constant in middle frequency region, which was related to charge transfer resistance (R_{ct}). Inductance was also observed in low-frequency region due to the uneven adsorption of FeOH^+ on steel surface [22, 23]. Figure 6 shows the equivalent circuit for fitting EIS plots of bare steels. R_s is the resistance of test electrolyte. Q_{dl} is the capacitance of electric double layer, and R_{ct} is the charge transfer resistance. R_L is the inductance resistance, and L is the inductance element. Table 3 shows the fitted parameters of measured EIS plots using the equivalent circuit. The results showed that R_{ct} of bare W steel was higher than that of the blank steel, and R_{ct} of Mo steel was lower than that of blank steel, which indicated that W could increase, while Mo could decrease corrosion resistance of the steel in acid electrolyte, which were correspondent to i_{corr} in Table 2.

Figure 7 shows the EIS plots of the rusted steels under O_2 concentration of 1%. Figure 7a, c and e indicates that all Nyquist plots of the rusted steels consist of two depressed semicircles in high- and low-frequency regions. Figure 7b, d and f indicates that all Bode plots of rusted steels show two time constants in high- and low-frequency region. The semicircles in high-frequency regions of Nyquist plots were related to rust resistance (R_{rust}), and the semicircles in low-frequency regions of Nyquist plots reflected charge transfer resistance (R_{ct}). Figure 8 shows the equivalent circuit for fitting EIS plots of the rusted steels [24]. Q_{rust} is the rust capacitance, and R_{rust} is the rust

Fig. 6 Equivalent circuit for fitting EIS plots of the bare steels tested

resistance. Q_{dl} is the capacitance of electric double layer, and R_{ct} is the charge transfer resistance. W is the Warburg impedance, which is related to diffusion of corrosive species in rust.

Table 4 gives the fitted electrochemical parameters from EIS plots of the rusted steels under O_2 concentration of 1%. The results indicated that R_{rust} and R_{ct} of the rusted steels increased with increasing corrosion time. R_{rust} of the blank steel increased from 111.3 to 163.8 $\Omega \text{ cm}^2$, R_{rust} of W steel increased from 108.8 to 156.9 $\Omega \text{ cm}^2$, and R_{rust} of Mo steel increased from 126.1 to 178.5 $\Omega \text{ cm}^2$. Meanwhile, R_{ct} of the blank steel increased from 292.9 to 306.7 $\Omega \text{ cm}^2$, R_{ct} of W steel increased from 348.8 to 469.6 $\Omega \text{ cm}^2$, and R_{ct} of Mo steel increased from 283.4 to 399.3 $\Omega \text{ cm}^2$. The results showed that R_{ct} presented obvious difference, while R_{rust} presented little difference among the rusted steels, which indicated that W and Mo additions could depress the charge transfer process of the rusted steels to obtain higher

Fig. 5 EIS plots of the bare steels tested in 0.01 M Na_2SO_4 solution with pH 3.0 and at temperature of 25 °C

Table 3 Fitted parameters of EIS plots of bare steels in acid electrolyte

Steels	Q_{dl} (F cm ⁻²)	n_{dl}	R_{ct} (Ω cm ²)	R_L (Ω cm ²)	L (H cm ⁻²)
Blank steel	1.23E-08	0.938	142.3	32.4	247.8
W steel	3.87E-08	0.836	149.1	23.5	161.7
Mo steel	1.51E-08	0.927	132.6	42.7	378.5

Fig. 7 EIS plots of rusted steels in 1% O₂ wet-dry acid corrosion: **a, b** 14 CCT; **c, d** 28 CCT; **e, f** 42 CCT

corrosion resistance. W steel presented the largest R_{ct} among the steels during corrosion process. R_{ct} of Mo steel showed little difference in first 28 CCT, and obvious increase at 42 CCT comparing with that of the blank steel. The results indicated that both W and Mo addition could

increase R_{ct} of the steels, and W had higher enhanced effect than Mo under O₂ concentration of 1%.

Figure 9 gives the EIS plots of the rusted steels under O₂ concentration of 5%. Nyquist plots of the rusted steels were all composed of two depressed semicircles, as shown in

Fig. 8 Equivalent circuit for fitting EIS plots of rusted steels

Fig. 9a, c and e. Meanwhile, Bode plots of the rusted steels showed two time constants in high- and low-frequency region, as shown in Fig. 9b, d and f. Time constant in high-frequency region was related to the rust resistance R_{rust} , and time constant in low-frequency region reflected the charge transfer resistance R_{ct} . Phase angle of time constant in low-frequency region decreased with increasing corrosion time, which was different from that under O_2 concentration of 1%. The difference of Bode plots under O_2 concentrations of 1% and 5% might be caused by the different characteristics of the rusts. EIS plots in Fig. 9 could also be fitted by the equivalent circuit shown in Fig. 8.

Table 5 shows the fitted electrochemical parameters under O_2 concentration of 5%. The results showed that R_{rust} of the blank steel increased from 76.7 to 232.3 $\Omega \text{ cm}^2$, R_{rust} of W steel increased from 128.6 to 303.7 $\Omega \text{ cm}^2$, and R_{rust} of Mo steel increased from 214.4 to 475.1 $\Omega \text{ cm}^2$. Meanwhile, R_{ct} of the blank steel increased from 296.2 to 501.3 $\Omega \text{ cm}^2$, R_{ct} of W steel increased from 329.1 to 556.6 $\Omega \text{ cm}^2$, and R_{ct} of Mo steel increased from 249.8 to 678.5 $\Omega \text{ cm}^2$. It could be seen that both R_{rust} and R_{ct} of the rusted steels increased obviously with increasing corrosion time under O_2 concentration of 5%, which was different from that under O_2 concentration of 1%. W and Mo additions could increase R_{rust} and R_{ct} of the rusted steels, and the enhanced effect of Mo was better than that of W.

3.4 Rust Analysis

Tables 6 and 7 give the phase composition of the rusts at 42 CCT under O_2 concentrations of 1 and 5%, respectively. The results indicated that the rust formed in wet-dry acid corrosion was mainly composed of amorphous phase, γ -FeOOH, α -FeOOH, Fe_xS_y , S and Fe_3O_4 . The content of the crystalline phases in the rust including γ -FeOOH, α -FeOOH, Fe_xS_y , S and Fe_3O_4 decreased, while the content of amorphous phase increased with increasing O_2 concentration. Higher O_2 concentration in wet-dry acid corrosion promoted the formation of amorphous phase, which was the main component of dense and protective rust [25]. Thus, the rust formed under O_2 concentration of 5% presented higher R_{rust} than that under O_2 concentration of 1%. The different rust compositions under O_2 concentrations of 1 and 5% changed the characteristic of the rust, as well as the roles W and Mo played in corrosion resistance of the rusted steels.

Figure 10 gives specific surface area (SSA) of the rust at 42 CCT under O_2 concentrations of 1 and 5%. SSA of the rust was an important parameter for evaluation of barrier effect to corrosive species [25, 26]. The rust with higher SSA presented higher barrier effect to corrosive species. The results indicated that the rust formed under O_2 concentration of 5% presented higher SSA than that under O_2 concentration of 1%. Higher O_2 concentration greatly increased SSA of the rust due to the increasing content of amorphous phase, which was the main component of dense and protective rust [26, 27]. The roles W and Mo played in SSA of the rust were different and were greatly influenced by O_2 concentration. Under O_2 concentration of 1%, W addition slightly decreased SSA of the rust, and Mo slightly increased SSA of the rust. However, under O_2 concentration of 5%, both W and Mo obviously increased SSA of the rust, and the enhanced effect of Mo was higher than that of W.

Figure 11 shows cross-sectional morphologies of the rust formed on the three tested steels at 42 CCT under O_2 concentrations of both 1% and 5%. The rust formed under

Table 4 Fitted parameters of EIS plots for the rusted steels in 1% O_2 wet-dry acid corrosion

Steels	CCT	Q_{rust} (F cm^{-2})	n_{rust}	R_{rust} ($\Omega \text{ cm}^2$)	Q_{dl} (F cm^{-2})	n_{dl}	R_{ct} ($\Omega \text{ cm}^2$)	W ($\Omega \text{ cm}^2$)
Blank steel	14	1.71E-07	0.987	111.3	0.0011	0.151	292.9	0.0255
	28	2.56E-08	0.938	130.9	0.00502	0.118	289.8	0.0508
	42	3.17E-08	0.884	163.8	0.00802	0.348	306.7	0.0957
W steel	14	9.04E-08	0.974	108.8	0.00254	0.173	348.8	0.0268
	28	3.88E-08	0.893	130.6	0.0119	0.336	376.2	0.0475
	42	1.97E-08	0.962	156.9	0.00548	0.125	469.6	0.0744
Mo steel	14	1.59E-07	0.953	126.1	0.00122	0.135	283.4	0.0297
	28	1.94E-08	0.941	128.5	0.0155	0.265	298.6	0.0442
	42	6.31E-08	0.851	178.5	0.0111	0.404	399.3	0.0895

Fig. 9 EIS plots of the rusted steels in 5% O_2 wet-dry acid corrosion: **a, b** 14 CCT; **c, d** 28 CCT; **e, f** 42 CCT

1% O_2 presented higher rust thickness and obvious double-layer structure comparing with that under O_2 concentration of 5%, which indicated that higher O_2 concentration contributed to the formation of thinner and compacter rust, and was corresponding to the results shown in Fig. 10.

Figure 11a, b and c shows the cross-sectional morphologies of the rust under O_2 concentration of 1%. Figure 11a presents large cracks inside rust of the blank steel, and the inner layer of the rust was loose and less protective. Figure 11b and c shows much compacter rust of W steel and Mo steel, and the rust/substrate interface was more even, comparing with that of the blank steel. Meanwhile, the rust of W

steel presented single-layer structure, and the highest rust compactness among three steels.

Figure 11d, e and f shows the cross-sectional morphologies of the rusts under O_2 concentration of 5%. Figure 11d presents obvious and continuous cracks inside the rust of the blank steel. Figure 11e and f shows that the rust of W steel and Mo steel was compacter and thicker, and the rust/substrate interface was more even than that of the blank steel, which indicated that W and Mo could reduce the selective corrosion of the steel. Moreover, some tiny cracks could also be seen in the rusts of W steel and Mo steel, and the rust of Mo steel was compacter than that of W steel.

Table 5 Fitted parameters of EIS plots for the rusted steels in 5% O₂ wet-dry acid corrosion

Steels	CCT	Q_{rust} (F cm ⁻²)	n_{rust}	R_{rust} (Ω cm ²)	Q_{dl} (F cm ⁻²)	n_{dl}	R_{ct} (Ω cm ²)	W (Ω cm ²)
Blank steel	14	3.33E-08	0.764	76.7	0.00762	0.342	296.2	0.0142
	28	3.83E-08	0.884	189.3	0.00304	0.334	340.4	–
	42	3.65E-08	0.88	232.3	0.00302	0.269	501.3	–
W steel	14	8.61E-08	0.835	128.6	0.00701	0.359	329.1	0.0168
	28	6.74E-08	0.857	139.4	0.00298	0.353	468.2	–
	42	2.48E-08	0.894	303.7	0.00262	0.249	556.6	–
Mo steel	14	3.05E-08	0.883	214.4	0.00957	0.267	249.8	0.0259
	28	1.81E-08	0.912	262.5	0.00312	0.304	423.3	–
	42	2.38E-08	0.867	475.1	0.00223	0.141	678.5	–

Table 6 Mass ratio of the rust phases at 42 CCT in 1% O₂ wet-dry acid corrosion (wt%)

Steels	γ-FeOOH	α-FeOOH	Fe _x S _y	S	Fe ₃ O ₄	Amorphous phase
Blank steel	1.52	6.23	2.77	1.29	1.19	87.00
W steel	1.59	5.72	3.58	1.84	1.26	86.01
Mo steel	1.42	6.16	3.26	1.94	0.89	86.33

Table 7 Mass ratio of the rust phases at 42 CCT in 5% O₂ wet-dry acid corrosion (wt%)

Steels	γ-FeOOH	α-FeOOH	Fe _x S _y	S	Fe ₃ O ₄	Amorphous phase
Blank steel	0.72	3.30	1.58	0.43	0.77	93.96
W steel	0.58	3.22	2.15	0.64	0.75	91.40
Mo steel	0.72	3.70	2.06	0.72	0.66	92.76

Fig. 10 SSA of the rust at 42 CCT in wet-dry acid corrosion with O₂ concentrations of **a** 1%; **b** 5%

Figure 12 shows the distribution of the elements W and Mo in the rusts after 42 CCT under O₂ concentrations of both 1 and 5%. Figure 12a and b shows that the elements W and Mo uniformly distribute in the rust under O₂ concentration of 1%, while Fig. 12c and d presents that W and Mo are enriched in inner layer of the rust under O₂

concentration of 5%. The results indicated that the existence of W and Mo in the rust was greatly influenced by O₂ concentration, and higher O₂ concentration promoted the enrichment of elements W and Mo in inner layer of the rust.

4 Discussion

The phenomenon most deserving of attention in this study was that the elements W and Mo had different enhanced effects on corrosion resistance of the steels under O₂ concentrations of both 1 and 5%. The obtained results reflected the interaction between the alloying elements W and Mo and O₂ on the wet-dry acid corrosion behavior of the low-alloy steels. W and Mo additions changed the electrochemical property of the bare steel, and then changed the characteristics of the rust formed on the steel surface.

W and Mo influenced electrochemical property of the bare steel through solid solution in ferrite [9, 10]. W increased R_{ct} and decreased i_{corr} of the bare steel, while Mo decreased R_{ct} and increased i_{corr} of the bare steel in acid

Fig. 11 Cross-sectional morphologies of the rusts at 42 CCT in wet-dry acid corrosion: **a–c** for the blank steel, W steel, and Mo steel under O_2 concentration of 1%; **d–f** for the blank steel, W steel, and Mo steel under O_2 concentration of 5%

electrolyte, which indicated that W could depress the dissolution process of the bare steel, while Mo presented an opposite effect. When polarization potential of the steel was more positive than $-0.35 V_{SCE}$, both W and Mo could depress dissolution process of the bare steel, and the depression effect of W was higher than that of Mo. Meanwhile, W and Mo could reduce the content of pearlite, and decrease the grain size of ferrite of the steel, as shown in Fig. 2. Homogeneous microstructure of W and Mo-containing steels could reduce the selective corrosion around pearlite with large grain size [28, 29], which resulted in the more even rust/substrate interface, as shown in Fig. 11.

Elements W and Mo affected the characteristic of the rust under O_2 concentrations of both 1 and 5%. The rust formed under O_2 concentration of 1% was loose and less protective with double-layer structure, while the rust formed under O_2 concentration of 5% was dense and compact with single-layer structure, as shown in Fig. 11. The different characteristics of the rust under O_2 concentrations of 1 and 5% were mainly caused by the different

rust compositions, as shown in Tables 6 and 7. The rust under O_2 concentration of 5% contained higher content of amorphous phase, and lower content of γ -FeOOH, α -FeOOH, Fe_xS_y , S and Fe_3O_4 than that under O_2 concentration of 1%. Amorphous phase was the main component of dense and protective rust in atmospheric corrosion [30]. Higher content of amorphous phase in the rust under O_2 concentration of 5% contributed to the enhanced rust compactness, as well as higher corrosion resistance of the rusted steel, comparing with that under O_2 concentration of 1%.

The enhanced effect of W on corrosion resistance of the steels was better than that of Mo under O_2 concentration of 1%, as shown in Fig. 3a. W was more effective on increasing R_{ct} of the steel than Mo. Mo had better enhanced effect on corrosion resistance of the steel than W under O_2 concentration of 5%, as shown in Fig. 3b. Mo had higher promotion effect on increasing both R_{rust} and R_{ct} , as shown in Tables 4 and 5. The above results indicated that the roles W and Mo played were greatly influenced by O_2 concentration.

Fig. 12 Distribution of the elements W and Mo in the rust at 42 CCT in wet-dry acid corrosion: **a** W 1% O₂; **b** Mo 1% O₂; **c** W 5% O₂; **d** Mo 5% O₂

Under O₂ concentration of 1%, the rust was loose and porous with obvious double-layer structure. The protectiveness of the rust was weak, and W-containing steel presented higher R_{ct} and identical R_{rust} comparing with Mo-containing steel, as shown in Table 4. W addition could depress the charge transfer process in the rust/substrate interface, and increase resistance of inner layer of the rust, which improved corrosion resistance of the rusted steel, whereas, under O₂ concentration of 5%, the rust was thinner and compacter comparing with that under O₂ concentration of 1%. Mo-containing steel presented higher R_{ct} and R_{rust} than W-containing steel, as shown in Table 5. Mo addition could increase the rust compactness through forming dense and protective rust, and the enhanced effect of Mo on rust compactness was better than that of W.

5 Conclusions

The effects of W and Mo additions on corrosion behavior of the low-alloy steels in wet-dry acid corrosion with different O₂ concentrations were studied, and the conclusions could be summarized as follows:

1. W and Mo-containing steels presented higher corrosion resistance than blank steel under O₂ concentrations of both 1 and 5%. The corrosion behavior of the steels was greatly affected by O₂ concentration. W-containing steel presented higher corrosion resistance than Mo-containing steel under O₂ concentration of 1%, while Mo-containing steel presented higher corrosion resistance than W-containing steel under O₂ concentration of 5%.
2. W addition could depress the metal dissolution of bare steel in acid electrolyte, while Mo presented the opposite effect. Both W and Mo could depress the dissolution of bare steel in acid electrolyte when polarization potential was more positive than $-0.35 V_{SCE}$, and the depression effect of W was better than that of Mo.
3. The rust composition was greatly influenced by O₂ concentration. Higher O₂ concentration could increase the amount of amorphous phase and decrease the amount of γ -FeOOH, α -FeOOH, Fe_xS_y , S and Fe_3O_4 in the rust. Higher content of amorphous phase was responsible for the higher rust compactness under O₂ concentration of 5%, comparing with that under O₂ concentration of 1%.

4. Rust formed under O₂ concentration of 1% was less protective with double-layer structure, and rust formed under O₂ concentration of 5% was dense and compact with single-layer structure, due to different rust compositions. The enhanced effect of W on corrosion resistance of the rusted steel under O₂ concentration of 1% was better than that of Mo, because W was more effective to increase R_{ct} of the rusted steel than Mo. Mo addition had better enhanced effect on corrosion resistance of the rusted steel than that of W under O₂ concentration of 5%, because Mo had higher promotion effect on increasing both R_{rust} and R_{ct} of the rusted steel.

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