Effect of Small Content of Chromium on Wet–Dry Acid Corrosion Behavior of Low Alloy Steel

Qing-He Zhao¹ · Wei Liu¹ · Yi-Chun Zhu¹ · Bin-Li Zhang¹ · Shuan-Zhu Li¹ · Min-Xu Lu¹

Received: 8 July 2016/Revised: 3 September 2016/Published online: 4 November 2016
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Abstract Effect of small content of chromium (Cr) on wet–dry acid corrosion behavior of low alloy steels has been investigated. The results show that the corrosion resistance of the steels increased with increasing Cr content from 0.10 to 0.50 wt%. Higher content of Cr promotes initial corrosion and accelerates the formation of dense and protective rust in long-term corrosion. The enhanced protectiveness of the rust is closely related to its composition. High content of Cr increases the content of amorphous phases and decreases the content of γ -FeOOH in the rust, resulting in the high compactness of the rust and low electrochemical activity in acid condition. Cr dopes in rust and depresses the transformation from amorphous phases to α -FeOOH, as well as the growth process of FeOOH particles, which is responsible for the enhanced compactness of rust in long-term corrosion.

KEY WORDS: Low alloy steel; Chromium; Corrosion; EIS; TEM

1 Introduction

Alloying chromium (Cr) has been proved to be effective in increasing the corrosion resistance of low alloy steel under various corrosion environments, such as atmospheric corrosion and oil and gas industrial CO₂ corrosion [1–5]. In atmospheric corrosion, Cr is enriched in the inner rust of the steel after long-term corrosion [6–9]. Cr-rich dense and protective inner rust mainly consists of nano-sized goethite [10, 11], which is electrochemically stable, and depresses both metal dissolution and oxygen reduction process of the rusted steel due to the strongly aggregated structure [12, 13].

Ion selectivity of rust changes from anion selectivity to cation selectivity with certain amount of Cr³⁺ ions (about 5–10 wt%) substituting Fe³⁺ ions in goethite, and the penetration of corrosive anions such as Cl[−] and SO₄^{2−} can be hindered [14, 15]. Cr can also inhibit cathodic corrosion process during drying-out stage of atmospheric corrosion [16, 17]. In CO₂ corrosion conditions, Cr (≥ 2 wt%) promotes its enrichment in corrosion scale, preventing both anodic dissolution and cathodic reduction process of steel [5, 18].

The enhancing effect of Cr on corrosion resistance of the steel in atmospheric corrosion and CO₂ corrosion conditions has been widely reported, but the effect of Cr on wet–dry acid corrosion behavior of the steels in vapor space of crude oil tanker was rarely investigated, where the steel is exposed to the acid corrosive atmosphere containing certain amount of O₂, H₂S, CO₂ and SO₂ with cyclic wet–dry process [19–21]. The corrosion of the steel in such a wet–dry acid corrosion condition was severe, and corrosion resistant low alloy steel can be an effective way to prolong the service life of crude oil tanker [22, 23]. Besides, Cr content of steel in above investigations was all higher than

Available online at <http://link.springer.com/journal/40195>

✉ Wei Liu
weiliu@ustb.edu.cn

¹ Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

1 wt%, and rare investigations focused on corrosion behavior of steel with Cr content smaller than 0.5 wt%, which was vital for developing economic corrosion resistant steel [24]. Thus, it is of great importance to illustrate the effect of small content of Cr on wet–dry acid corrosion behavior of low alloy steel.

The effect of small content of Cr on wet–dry acid corrosion behavior of steels was investigated in this paper. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are used to analyze the electrochemical corrosion behavior of the steels. Other analytical methods such as XRD, SEM, TEM and N₂ adsorption are used to analyze the phase composition, morphologies and compactness of the rust.

2 Experimental

2.1 Tested Steels and Corrosion Test

Table 1 shows the chemical composition of the tested steels with increasing Cr content from 0.10 to 0.50 wt%. The steels were obtained by melting the constituent elements in a vacuum induction furnace and then followed by casting the melt into slabs. The cast slabs were reheated at 1200 °C for 2 h and then hot rolled into the plates with thickness of 18 mm. The microstructures of three steels consist of fine acicular ferrite as dominant phases with small amount of carbon-rich phases (Fig. 1). The microstructures of 0.50Cr and 0.20Cr steels are finer than that of 0.10Cr steel. Cr exists mainly in ferrite of the steels as solid solution state.

The specimens were machined into the size of 60 mm × 25 mm × 5 mm and then abraded gradually to 600 grade with silicon carbide emery paper. Then the specimens were cleaned in acetone and alcohol, weighted by an electronic analytical balance with an accuracy of 0.1 mg. The width and length of the specimens were measured by a vernier caliper with an accuracy of 0.02 mm and then stored in a moisture-free desiccator. Before corrosion test, the specimens were enclosed with silica gel with an exposure area of 60 mm × 25 mm (1500 mm²).

Figure 2 shows the schematic of test device for simulating the wet–dry acid corrosion environment. The test device is composed of temperature control and record system, acid gas

atmosphere control system, and a closed container. The acid gas inside the test device consists of 4 vol.% O₂, 13 vol.% CO₂, 500 ppm H₂S, 100 ppm SO₂ and N₂ balance, and is continuously put into and flew out of the container. The gas flow rate is 100 mL/min in first 24 h, then 10 mL/min after 24 h. Specimens are fixed on the top of the container, and the temperature of the specimens is controlled by controlling the temperature on top cover of the container. Specimens are kept at 50 °C for 19 h, 25 °C for 3 h, and the transition time between 50 and 25 °C is 2 h. Each cycle equals to 24 h. The distilled water is beneath the specimens, and the temperature of distilled water is kept between 30 and 32 °C. The distance between the specimens and distilled water is 180 mm to avoid the splash of water [23, 24]. Thus, the acid electrolyte film forms and disappears cyclically on the specimen surface, and electrochemical corrosion occurs. The total corrosion time is 98 days, and the specimens are corroded with 7, 21, 35, 49 and 98 days, respectively.

2.2 Rust Analysis

The surface and cross-sectional morphologies of the rust are characterized by SEM. Quantitative analysis of phase composition of the rusts is analyzed using XRD with a Cu target. Rust powders are prepared for quantitative phase analysis, and ZnO is the internal standard [25]. The scan speed of XRD is 2.0°/min, and the range of 2 θ is from 10° to 60°. Rust in wet–dry acid corrosion condition mainly contains amorphous phases, goethite (α -FeOOH), lepidocrocite (γ -FeOOH), magnetite (Fe₃O₄) and elemental S. The diffraction intensities of (011) reflection of α -FeOOH, (020) reflection of γ -FeOOH, (220) reflection of Fe₃O₄ and (222) reflection of elemental S are measured and compared with (100) reflection of ZnO powder. The ZnO/rust ratio is 1:9. Thus, the content of α -FeOOH, γ -FeOOH, Fe₃O₄ and elemental S can be obtained, and amorphous phases are the balance.

The adsorption isotherm of N₂ on the rust is measured using a surface area and pore size analyzer, and the specific surface area (SSA) of the rust is determined by fitting the BET equation to the adsorption isotherms using cross-sectional area (0.162 nm²) of N₂ molecule [3, 16]. The morphology and electronic diffraction patterns of the rust are characterized using TEM (FEI Tecnai F20).

2.3 Electrochemical Tests

The electrochemical tests are conducted by an electrochemical workstation with a three-electrode system. The working electrode is corroded steels, the auxiliary electrode is the platinum plate with size of 15 mm × 15 mm × 0.5 mm, and the reference electrode is saturated calomel electrode. The condensate water in the wet–dry acid environments contains certain amount of SO₄²⁻ due to the existence of SO₂

Table 1 Chemical compositions of tested steels (wt%)

Steel	C	Si	Mn	S	P	Cu	Ni	Cr	Fe
0.10Cr	0.08	0.24	1.05	0.002	0.007	0.30	0.20	0.10	Bal.
0.20Cr	0.08	0.24	1.06	0.002	0.006	0.30	0.20	0.20	Bal.
0.50Cr	0.08	0.24	1.04	0.002	0.006	0.30	0.20	0.50	Bal.

Fig. 1 Microstructures of the tested steels with different Cr contents: **a** 0.10Cr; **b** 0.20Cr; **c** 0.50Cr

Fig. 2 Schematic diagram of the wet-dry acid corrosion test device

and O_2 , pH value of which is about 2–4 [20]. 0.1 mol/L Na_2SO_4 solution with pH value of 3.0 and temperature of 25 °C is used for the electrochemical tests. Electrochemical tests are conducted in acid electrolyte after the immersion of 30 min when open-circuit potential (OCP) of corroded steels is stabilized. Linear polarization test is conducted at a sweep rate of 0.167 mV/s in the range of ± 10 mV versus OCP for obtaining linear polarization resistance R_p . Potentiodynamic polarization curves of the steels are conducted at a sweep rate of 0.5 mV/s in the range of ± 250 mV versus OCP. EIS is measured at the frequency range from 100 kHz to 10 mHz at OCP with perturbing sinusoidal excitation signal of 5 mV, and there are twelve points per frequency decade. The measured EIS plots are fitted and calculated by ZSimpWin software, and the relative error is lesser than 5%.

3 Results

3.1 Corrosion Kinetics

Figure 3 shows the corrosion loss and corrosion rate of the tested steels in wet-dry acid corrosion environment. The

corrosion loss increases gradually with increasing corrosion time. The corrosion rate of the steels firstly increased from 7 to 21 days and then decreased from 21 to 98 days. Corrosion rate of the steels at corrosion time of 21 days is in the following order: 0.50Cr > 0.20Cr > 0.10Cr, which indicates that increasing content of Cr accelerates the initial wet-dry acid corrosion rate of steel. Meanwhile, corrosion rate at corrosion time of 98 days from high to low is as follows: 0.10Cr > 0.20Cr > 0.50Cr, which indicates that high content of Cr decreases the long-term corrosion rate of the steels.

Table 2 gives the fitted corrosion kinetics of tested steels in wet-dry acid corrosion. The corrosion kinetics of the steels can be fitted by the formula of $C_L = A \times C_T^b$ [26], where C_L is the corrosion loss (mm), C_T is the corrosion time (day), A and b are the constants relating to the corrosion kinetics. b value in the formula reflects the characteristics of corrosion kinetics of steels. $b < 1$ means a corrosion deceleration process, $b = 1$ means a constant corrosion process, and $b > 1$ means a corrosion acceleration process [26]. b value is 0.859, 0.827 and 0.877 for 0.10Cr, 0.20Cr and 0.50Cr steel, respectively, indicating that high Cr steel presents enhanced corrosion resistance in wet-dry acid corrosion.

3.2 Potentiodynamic Polarization Curves

Figure 4 shows the potentiodynamic polarization curves of the tested steels. Figure 4a shows that the cathodic polarization reaction of bare steels is mainly controlled by the reduction of dissolved oxygen, while the anodic polarization reaction of bare steels is dominated by the steel dissolution process [27]. Meanwhile, the self-corrosion potential of 0.50Cr steel is more negative than that of 0.10Cr and 0.20Cr steel.

Figure 4b–f indicates that the cathodic polarization reaction of the rusted steel is different from that of bare steel, and is mainly dominated by the reduction of electrochemical active rust, and the anodic polarization reaction is depressed by the coverage of the rust [28]. The

Fig. 3 Corrosion kinetics of the tested steels under wet–dry acid corrosion environment: **a** corrosion loss–corrosion time; **b** corrosion rate–corrosion time

Table 2 Fitted corrosion kinetics of tested steels in wet–dry acid corrosion environment

Steel	Fitted kinetics	R^2
0.10Cr	$C_L = 0.0026 \times C_T^{0.859}$	0.964
0.20Cr	$C_L = 0.0030 \times C_T^{0.827}$	0.956
0.50Cr	$C_L = 0.0035 \times C_T^{0.777}$	0.960

cathodic and anodic currents of the rusted steels increased with increasing content of Cr at corrosion time of 7 and 21 days, while it shows the opposite results at corrosion time from 35 to 98 days, indicating that high content of Cr promotes the initial corrosion, and depresses the long-term

corrosion of rusted steels. Particularly, at corrosion time of 98 days, high Cr steel (0.50Cr) presents more positive corrosion potential, and lower corrosion current in acid corrosion condition.

Table 3 gives the fitted parameters of linear polarization and potentiodynamic polarization curves. Linear polarization resistance R_p of the steels is calculated from the linear polarization plots using equation of $R_p = dE/di$, where E is polarization potential of the steels versus SCE, and i is polarization current density of the steels corresponding potential [29]. Self-corrosion current densities (i_{corr}) of bare and rusted steels are calculated with equations of $i_{\text{corr}} = B/R_p$, and $B = \beta_a \beta_c / (\beta_a + \beta_c)$ [30], where i_{corr} is self-corrosion current density of the steels, R_p is linear

Fig. 4 Potentiodynamic polarization curves of the tested steels with increasing corrosion time: **a** bare steels; **b** 7 days; **c** 21 days; **d** 35 days; **e** 49 days; **f** 98 days

Table 3 Fitted parameters of the linear polarization and potentiodynamic polarization curves of bare and rusted steels

Steel	β_a (mV/dec)	β_c (mV/dec)	R_p ($\Omega \text{ cm}^2$)	E_{corr} (V _{SCE})	i_{corr} ($\mu\text{A}/\text{cm}^2$)
Bare					
0.10Cr	29.2	221.3	400.2	−0.625	64.4
0.20Cr	29.9	224.6	371.5	−0.628	71.0
0.50Cr	31.0	205.7	338.4	−0.654	79.6
7 days					
0.10Cr	121.0	48.0	276.0	−0.605	124.6
0.20Cr	107.4	39.9	194.3	−0.604	149.6
0.50Cr	108.7	39.1	162.3	−0.599	177.3
21 days					
0.10Cr	122.7	57.4	191.8	−0.550	203.9
0.20Cr	129.1	74.2	197.6	−0.540	238.4
0.50Cr	119.7	78.9	169.3	−0.535	281.0
35 days					
0.10Cr	117.9	100.3	784.7	−0.381	69.1
0.20Cr	119.8	96.6	925.0	−0.371	57.8
0.50Cr	117.1	91.5	1057.3	−0.365	48.6
49 days					
0.10Cr	103.2	103.2	2069.0	−0.421	25.5
0.20Cr	102.2	89.3	2330.5	−0.401	20.3
0.50Cr	104.6	90.0	2929.1	−0.395	16.5
98 days					
0.10Cr	115.1	126.6	3293.2	−0.374	18.3
0.20Cr	116.0	129.4	4649.6	−0.354	13.2
0.50Cr	118.8	126.7	7086.5	−0.340	8.7

polarization resistance, B is a constant relating to cathodic and anodic polarization behavior of the steels, and β_a and β_c are anodic and cathodic polarization rates.

With increasing Cr content from 0.10 to 0.50 wt%, i_{corr} increases for bare steel and at corrosion time of 7 and 21 days, respectively, indicating that high content of Cr can promote the initial corrosion of the steel, which is consistent with corrosion rate results in Fig. 3. i_{corr} of the steels decreases rapidly from corrosion time of 21–35 days, which may be related to dense protective rust forming on steel surface. i_{corr} of the steels continues to decrease from corrosion time of 35–98 days, indicating that the protectiveness of rust increases as corrosion proceed. i_{corr} of the rusted steels decreases with increasing Cr content from corrosion time of 35–98 days, which indicates that high content of Cr can depress the long-term corrosion of rusted steels.

3.3 EIS Plots

Figure 5 shows the EIS plots of bare steels in acid electrolyte. Figure 5a shows that the Nyquist plots of bare

steels consist of one semicircle representing the charge transfer process, and one inductance impedance [21, 31]. Figure 5b indicates that the time constant relating to the charge transfer process is located in the middle-frequency region, and the inductance impedance is observed in the low-frequency region.

A proposed general equivalent electrical circuit is depicted in Fig. 6. Elements are as follows: R_s is electrolyte resistance, R_{ct} is charge transfer resistance in steel/rust interface, Q_{dl} is double-layer capacitance as a constant phase-angle element (CPE), R_L is electrical inductance, and L is inductance element [21]. Table 4 shows the fitted parameters for bare steels. The results shows that R_{ct} of bare steels decreased with increasing Cr content, indicating that high content of Cr promotes the dissolution of bare steel in acid electrolyte.

Figure 7 shows the EIS plots of rusted steels. Figure 7a, c, e, g, i shows that the Nyquist plots of the rusted steel consist of one incomplete impedance semicircle in the high-frequency region, and another incomplete impedance semicircle with a diffusion tail in middle- and low-frequency region [21, 32]. Figure 7b shows two time constants at high- and

Fig. 5 EIS plots of bare steels in 0.1 mol/L Na₂SO₄ solution with pH 3.0 and at the temperature of 25 °C: **a** Nyquist plots; **b** Bode plots

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

low-frequency regions, relating to the rust resistance R_{rust} and charge transfer resistance R_{ct} in steel/rust interface, respectively [33]. As corrosion proceeds, the phase angle of the rusted steels decreases in low-frequency region, and increases in the high-frequency region.

A proposed general equivalent electrical circuit is depicted in Fig. 8. Elements are as follows: R_s is electrolyte resistance, Q_{rust} is capacitance resistance, and R_{rust} is rust resistance, R_{ct} is charge transfer resistance, and Q_{dl} is double-layer capacitance in steel/rust interface, W is Warburg resistance relating to diffusion of corrosive species [21, 32].

Table 5 gives the fitted parameters of EIS plots for the rusted steels. For the rusted steels at corrosion time of 7 days, R_{rust} shows little difference, while R_{ct} decreases obviously with increasing Cr content. And for the rusted steels at corrosion time of 21 days, R_{rust} increases slightly, while R_{ct} decreases obviously with increasing Cr content. The above results indicate that high Cr content increases

R_{rust} slightly, and decreases R_{ct} of the rusted steels obviously in initial corrosion stage.

At corrosion time of 35 days, both R_{rust} and R_{ct} increase rapidly comparing with that at 21 days, indicating the formation of protective rust. Meanwhile, R_{rust} and R_{ct} increase with increasing Cr content, indicating that high Cr content increases both R_{rust} and R_{ct} of the rusted steels at the corrosion time of 35 days. As corrosion proceeds, both R_{rust} and R_{ct} increase rapidly from corrosion time of 35–98 days. The above results indicate that high Cr content can effectively increase R_{rust} of the rusted steels in long-term corrosion, and then R_{ct} in steel/rust interface increases with the coverage of dense protective rust.

3.4 Rust Characteristics

Figure 9 shows the quantitative rust analysis of the steels at the corrosion time of 21 and 98 days, respectively. The rusts are mainly composed of amorphous phases, α -FeOOH, γ -FeOOH, Fe_3O_4 and element S. The content of amorphous phases in the rust increases, while the contents of γ -FeOOH, Fe_3O_4 and element S decrease from corrosion time of 21–98 days. The rust composition of the tested steels presents little difference at corrosion time of 21 days, whereas, for the rusts at corrosion time of 98 days, the content of amorphous phases increases obviously, and the contents of α -FeOOH and γ -FeOOH decrease slightly with increasing Cr content. The results indicate that high content of Cr promotes the formation of amorphous phase, and

Table 4 Fitted parameters of EIS plot for bare steels in acid electrolyte

Steel	R_s ($\Omega \text{ cm}^2$)	Q_{dl} (F cm^{-2})	n_{dl}	R_{ct} ($\Omega \text{ cm}^2$)	R_L ($\Omega \text{ cm}^2$)	L (H cm^{-2})
0.10Cr	1.2	2.88E-04	0.851	397.3	130.4	91.7
0.20Cr	1.4	2.21E-04	0.869	369.1	83.7	56.9
0.50Cr	1.3	3.29E-08	0.796	336.6	93.2	43.5

Fig. 7 EIS plots of the rusted steels in 0.1 mol/L Na_2SO_4 solution with pH 3.0 and at temperature of 25 °C: **a, b** 7 days; **c, d** 21 days; **e, f** 35 days; **g, h** 49 days; **i, j** 98 days

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

depresses the formation of $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$ in the rust in the long-term corrosion.

Figure 10 gives the specific surface areas (SSAs) of the rust obtained from N_2 adsorption method at the corrosion time of 21 and 98 days, respectively. SSA is an important index to evaluate the protectiveness of the rust during corrosion [33]. Higher SSA indicates higher compactness and barrier effect of the rust [34]. With increasing Cr content, SSA of the rust increases slightly at corrosion time

Table 5 Fitted parameters of EIS plots for rusted specimens at different corrosion time

Corrosion time	Steel	R_s (Ω cm ²)	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)
7 days	0.10Cr	1.2	2.91E−7	0.897	30.8	2.45E−3	0.617	245.2	0.0059
	0.20Cr	1.4	9.72E−7	0.797	24.8	5.78E−3	0.479	169.5	0.0048
	0.50Cr	1.3	4.11E−7	0.846	26.8	6.28E−3	0.474	135.5	0.0049
21 days	0.10Cr	1.3	2.13E−7	0.890	27.5	1.35E−2	0.284	164.3	0.0015
	0.20Cr	1.1	1.23E−7	0.920	42.7	9.62E−3	0.261	154.9	0.0023
	0.50Cr	1.3	7.88E−8	0.953	54.9	7.65E−3	0.218	114.4	0.0014
35 days	0.10Cr	1.4	1.31E−8	0.974	248.1	2.59E−3	0.219	536.6	0.0045
	0.20Cr	1.1	9.52E−9	0.985	377.0	2.10E−3	0.121	548.0	0.0079
	0.50Cr	1.2	9.15E−9	0.989	440.6	1.71E−3	0.118	616.7	0.0069
49 days	0.10Cr	1.1	7.56E−9	0.974	854.5	2.34E−3	0.101	1214.5	0.0101
	0.20Cr	1.3	9.02E−9	0.961	1038.6	1.52E−3	0.104	1291.9	0.0132
	0.50Cr	0.9	1.12E−8	0.962	1295.4	1.01E−3	0.149	1633.7	0.0224
98 days	0.10Cr	0.9	9.80E−9	0.992	1188.0	5.87E−3	0.134	2105.2	0.0249
	0.20Cr	1.2	1.69E−8	0.963	1588.3	3.01E−3	0.192	3061.3	0.0356
	0.50Cr	1.3	2.56E−8	0.975	2171.4	1.36E−3	0.109	4915.1	0.0591

Fig. 9 Quantitative rust analysis of the tested steels at different corrosion time: **a** 21 days; **b** 98 days **Fig. 10** SSA of the rust of the tested steels in wet-dry acid corrosion: **a** 21 days; **b** 98 days

of 21 days and increases obviously at corrosion time of 98 days. The results indicate that high content of Cr increases the compactness and barrier effect of rust in the long-term corrosion.

Figure 11 shows the surface morphologies of the rusts at corrosion time of 98 days. Figure 11a shows large cracks and pores on the rust of 0.10Cr steel. Figure 11c presents no cracks and lesser pores on the rust of 0.20Cr steel, and the size of the rust particles of 0.20Cr steel is also smaller than that of 0.10Cr steel. Figure 10e shows no obvious pores on the rust of 0.50Cr steel, which is the most compact among tested steels. The above results indicate that high content of Cr decreases the amount of the cracks and pores in the rust, as well as the size of the rust particles in the long-term corrosion.

Fig. 11 Surface morphologies of the rusted steels at 98 days in wet–dry acid corrosion environment: **a** 0.10Cr; **b** 0.20Cr; **c** 0.50Cr

The surface morphologies of the rusts are observed in higher magnification to obtain more detailed information. Figure 11b shows the bulky and acicular micron-sized rust particles of 0.10Cr steel, and the rust presents large pores facilitating the diffusion of corrosive species. Figure 11d indicates that the micron-sized rust particles disappear and the flocculent rust particles with lesser pores form on the surface of 0.20Cr steel, comparing with that of 0.10Cr steel in Fig. 11b. Figure 11f shows the nano-sized flocculent rust particles of 0.50Cr steel, which has the highest rust compactness among tested steels. The results indicate that the microstructure of the rust changes from micron-sized acicular rust to nano-sized flocculent rust with increasing content of Cr, which decreases the grain size of the rust, and reduces the amount of the pores and cracks in the rust.

Figure 12 shows the cross-sectional morphologies of the rusts at corrosion time of 98 days. Rusts become thicker and compacter with increasing Cr content. The continuous pits are observed in the steel/rust interface of 0.10Cr and

0.20Cr steel, which may be attributed to the co-existence of O_2 and SO_2 in wet–dry acid corrosion environment [30]. The corrosion morphology of the pits in steel/rust interface disappears when Cr content increases to 0.50 wt%. The above results indicate that high Cr content increases the protectiveness of the rust, and also inhibits the inward diffusion of corrosive species, such as SO_2 , H_2S and O_2 .

Figure 13 gives TEM images and corresponding SAED patterns (insets) of α -FeOOH and amorphous phases for the rusts at corrosion time of 98 days for 0.10Cr and 0.50Cr steel, respectively. Figure 13a, b shows the morphologies of crystalline α -FeOOH and corresponding SAED from the points A and B. α -FeOOH of 0.50Cr steel is flaky and has much smaller particle size comparing with that of 0.10Cr steel, indicating that high content of Cr decreases the particle size of crystalline α -FeOOH. SAED patterns of α -FeOOH for 0.10Cr and 0.50Cr steel are quite different, due to the partial substitution of Cr^{3+} on position of Fe^{3+} in α -FeOOH network [6, 7]. Figure 12c, d shows the compact

Fig. 12 Cross-sectional morphologies of the rusted steels at 98 days in wet–dry acid corrosion environment: **a** 0.10Cr; **b** 0.20Cr; **c** 0.50Cr

Fig. 13 TEM morphologies and corresponding SAED patterns (*insets*) of the rust for 0.10Cr and 0.50Cr steel at the corrosion time of 98 days: **a** 0.10Cr α -FeOOH; **b** 0.50Cr α -FeOOH; **c** 0.10Cr amorphous phase; **d** 0.50Cr amorphous phase

and homogeneous amorphous phase and corresponding SAED from the points C and D, and presents a halo-like ED pattern for both 0.10Cr and 0.50Cr steel.

4 Discussion

The effect of small content of Cr on wet–dry acid corrosion behavior of low alloy steel has been investigated in this paper. Due to the higher activity of Cr than Fe, high content of Cr accelerates the anodic dissolution process (Fig. 4), and then, the initial corrosion of the steel is promoted (Fig. 3). High initial corrosion rate of the steel results in the quick accumulation of the rust and promotes the formation of dense protective rust (Figs. 9, 10), leading to high rust resistance R_{rust} , charge transfer resistance R_{ct} and low corrosion current i_{corr} of high Cr steel (Tables 3, 5). Thus, high content of Cr depresses the long-term corrosion rate of

the steel in wet–dry acid corrosion (Fig. 3). Rust with high density and compactness is the leading cause for good long-term corrosion resistance of high Cr steel in wet–dry acid corrosion condition.

The protectiveness of the rust is closely related to its composition. Rusts forming on steel surface mainly consist of amorphous phases, α -FeOOH, γ -FeOOH, Fe_3O_4 and element S. High content of Cr obviously increases the content of amorphous phases and slightly decreases the contents of α -FeOOH and γ -FeOOH in the rusts (Fig. 8). Amorphous phases in the rust consist mainly of nano-sized ferric oxide or hydroxide, and are the main component of dense and protective rust [35]. Rust containing higher content of amorphous phases presents higher compactness, or higher barrier effect to corrosive species [33]. It is reported that α -FeOOH can be transformed from amorphous phases through solid-state transformation during wet–dry corrosion [36, 37]. High content of Cr inhibits the

phase transformation from amorphous phases to α -FeOOH, which is responsible for higher content of amorphous phases in the rust, as well as higher SSA of rust for 0.50Cr steel at corrosion time of 98 days (Fig. 9). γ -FeOOH is an effective cathodic depolarizer during electrochemical corrosion, which accelerates the corrosion of the steel [38]. In conclusion, high Cr content increases the rust compactness and electrochemical stability of the rusted steel in long-term corrosion by changing its composition.

The effect of alloying Cr on the formation of superfine rust is also illustrated. TEM results (Fig. 13) identified the doping of Cr^{3+} in amorphous phases and α -FeOOH, indicating that alloying Cr can participate in the formation process of ferric oxyhydroxides ($(\text{Fe}_x\text{Cr}_{1-x})\text{OOH}$). Rust is mainly composed of several kinds of ferric oxyhydroxides (FeOOH), i.e. amorphous phases, α -FeOOH and γ -FeOOH. All kinds of FeOOH are composed of $\text{Fe}(\text{O},\text{OH})_6$ octahedra, but with different stacking sequences [39]. Alloying Cr can participate in the formation process of $(\text{Fe}_x\text{Cr}_{1-x})(\text{O},\text{OH})_6$ octahedra, and the $(\text{Fe}_x\text{Cr}_{1-x})(\text{O},\text{OH})_6$ octahedra with higher content of doping Cr presents irregular sequence due to the difference of ion radius of Cr^{3+} and Fe^{3+} , which makes FeOOH crystals difficult to grow up [40]. Thus, micron-sized rust particles can be observed in the rust of low Cr steel, and nano-sized rust particles are observed in the rust of high Cr steel (Fig. 11). The Cr-doping ferric oxyhydroxides with small particle size lead to lower amount of the voids and pores in the rust, which is responsible for the enhanced rust compactness of high Cr steel (Fig. 10). The protective rust with lesser cracks and pores inhibits the transportation of corrosive particles in the rust, such as O_2 , SO_4^{2-} , and then the long-term corrosion resistance of the steel is increased with increasing content Cr.

5 Conclusions

Effect of small content of Cr on the wet–dry acid corrosion behavior of low alloy steel is investigated, and the conclusions are as follows:

1. Steels present excellent corrosion performance with increasing Cr content from 0.10 to 0.50 wt% in wet–dry acid corrosion.
2. High content of Cr promotes anodic dissolution of bare steel and accelerates the initial corrosion. When dense and protective rust forms, high Cr content increases rust resistance R_{rust} and charge transfer resistance R_{ct} , lowers corrosion current i_{corr} of the rusted steel in long-term corrosion.
3. The corrosion resistance of the rusted steels is closely related to rust composition. Rusts are all composed of

amorphous phases, α -FeOOH, γ -FeOOH, Fe_3O_4 and element S. High content of Cr obviously increases the content of amorphous phases and slightly decreases the content of γ -FeOOH, leading to high rust compactness and electrochemical stability of the rusted steel in long-term corrosion.

4. High content doping Cr in the ferric oxyhydroxides in the rusts inhibits the transformation from amorphous phases to α -FeOOH and increases content of amorphous phases in the rust, which is responsible for the high rust compactness of high Cr steel.

Acknowledgements The authors thank for the funding support from the National Natural Science Foundation of China (Project No. 51571027).

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