Effect of sulfur on corrosion behavior of Q235 and 16Mn steel in sodium aluminate solutions

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Abstract

This study investigates the effect of sulfur on Q235 steel and 16Mn steel corrosion in sodium aluminate solution. The corrosion rate of Q235 steel and 16Mn steel reaches the maximum respectively when \(S^{2-}\) and \(S_2O_3^{2-}\) form synergistic corrosion and \(S^{2-}\) is contained alone. But, the size of corroded particles is smaller in the solution containing only \(S_2O_3^{2-}\) for two kinds of steel. The corrosion rate of 16Mn steel is greater than Q235 steel. Surface corrosion of two kinds of steel is both composed of sulfides (FeS and FeS\(_2\)) and oxides (Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), Al\(_2\)O\(_3\) and NaFeO\(_2\)). The crystal particles of steel surface are mainly iron oxides according to EDS analysis. Nyquist plots of Q235 steel with different forms of sulfur have two capacitance-resistance arcs and no diffusion impedance. Nyquist plots of 16Mn steel with \(S_2O_3^{2-}\) alone is consistent with Q235 steel. But, Nyquist plots of 16Mn steel presents a typical Warburg diffusion phenomenon with containing \(S^{2-}\) alone and forming synergistic corrosion.

1. Introduction

In the production process of high-sulfur bauxite alumina, new resistant materials such as duplex stainless steel are being selected for equipment in many processes [1], yet carbon steel continues to be utilized for a significant amount of new and existing equipment and can be subjected to conditions beyond the initial design parameters [2]. Q235 steel and 16Mn steel are commonly used as alumina production equipment materials, which are used to dissolution equipment, dilution tank and Bayer mother liquor evaporation equipment etc.

Because of the shortage of high-quality bauxite alumina in recent years, the use of high-sulfur bauxite makes solutions contains high level of \(S^{2-}\) and a certain amount of \(SO_4^{2-}\), \(S_2O_3^{2-}\), \(SO_3^{2-}\), etc [3]. Among them, \(S_2O_3^{2-}\) and \(S^{2-}\) is considered the most aggressive species of Bayer Liquor [4, 5]. The concentration of \(SO_4^{2-}\), \(S_2O_3^{2-}\), \(SO_3^{2-}\) and \(S^{2-}\) is 0.8, 1.2, 0.4, 1.6 g L\(^{-1}\) respectively in Bayer liquor. With the recycling of mother liquor, when the total sulfur concentration in the solution accumulates to 1.7 g/L [6], the sulfur of mother liquor will cause relatively serious corrosion to the equipment, which results in a great economic loss, corrosion cracking and pitting of steel equipment has been experienced in different alumina industry [7, 8]. So, the study on sulfur corrosion and control of Q235 steel and 16Mn steel is a very urgent problem in the alumina industry.

Due to the complex composition of Bayer liquid, which contains less base higher concentrations of caustic and sulfur-contained species, besides, it also contains a lot of aluminate, the corrosion behavior of steel is relatively less studied, and the corrosion characteristics are lack of sufficient systematic understanding. The electrochemical and formation mechanism of the passive film of sulfur on steel corrosion has been always studied in sodium aluminate solution by some scholars. Corrosion behavior of 16Mn steel in sulfide-containing Bayer solutions was researched by Chen Wen-mi [7]. The results indicate that \(S^{2-}\) was found to increase significantly the corrosion rate of steel and \(S_2O_3^{2-}\) had no effect on the corrosion of steel. However, interaction between \(S^{2-}\) and \(S_2O_3^{2-}\) is often referred to the corrosion of steel in the literature [9, 10]. RAJAGOPAL SRIRAM discussed emphatically the influence of aluminate anion on the corrosion of steel, which indicates the presence of \(AlO_2^{2-}\) species changes the deactivation kinetics [11]. A J McLeod [5] found that the corrosion morphology of...
the steel surface is related to the steel substrate. Synergy corrosion of Q235 steel was examined in sodium aluminate solutions by the author [12]. However, as our knowledge, the comparison of corrosion properties on Q235 steel and 16Mn steel in sodium aluminate solution has not been reported. Appropriate material selection in alumina production process has a great impact on equipment corrosion. Therefore, this paper will discuss the corrosion behavior of Q235 steel and 16Mn steel in sodium aluminate solution in order to provide the basis for equipment material selection. The corrosion rate of Q235 steel and 16Mn steel in high temperature corrosion media with different forms of sulfur was obtained using a weight-loss method via SEM (scanning electron microscope), EDS (Energy Dispersive Spectrometer), XRD (x-ray powder diffraction) and electrochemical measurements. The synergistic effect between S^{2−} and S_{2}O_{3}^{2−} will be discussed in detail. Their synergism was also explained with a proposed mechanism.

2. Experiment

2.1. Specimens and test solutions
The chemical compositions of Q235 steel and 16Mn steel selected in this study are listed in table 1. The steel coupons were machined from steel. The dimension of Q235 steel and 16Mn steel is respectively 15 mm × 15 mm × 1.0 mm and 20 mm × 10 mm × 1.0 mm. Surface preparation of the specimens was achieved by grinding up to 1800 grit SiC abrasive paper and acetone accompanying with intermediate water rinses respectively. The surface morphology of the polished steel is shown in figure 1. Corrosive medium is the sulfur-containing sodium aluminate solutions in the experiments. 110 g·l⁻¹ sodium aluminate solutions were prepared by dissolving NaOH and Al(OH)₃ in 1000 ml of deionized water in a three-necked, round-bottomed flask at 80 ~ 90 °C by magnetic stirring. The sodium aluminate solution was prepared and used at the time. The sulfur of solutions can be got by dissolving Na₂S·9H₂O and Na₂S₂O₃·5H₂O, which contained different concentrations of S^{2−} and S_{2}O_{3}^{2−}. Herein, the amount of sulfur refers to the amount of single sulfur. All reagents are analytical pure.

2.2. Corrosion experiment
All of the corrosion experiments were carried out for 120 h at 383 K in the autoclave. Five Q235 coupons and five 16Mn coupons were used in each experiment. Three coupons of each steel were used to measure the weight change, while the other two coupons were used for morphology observation and phase composition respectively. The experiment started when the required test conditions were met. The corrosion test lasted 120 h. The corrosion products were removed using the chemical products-cleanup method (GB/T 6074-1992). The corrosion rate R (mm·a⁻¹) was evaluated using weight-loss test method [11, 12].
2.3. Surface analysis

The morphology and element composition of surface corrosive was observed with scanning electron microscopy (SEM) (SUPRA 40) and energy dispersive spectroscopy (EDS) (AZ tec.). The chemical composition of the passive film was analyzed by means of x-ray diffraction (XRD, X-pert Pro MPD PANalytical).

2.4. Electrochemical measurement

Electrochemical testing was carried out in a conventional three-electrode Polytetrafluoroethylene (PTFE) cell with the counter electrode made of platinum and a saturated calomel electrode as reference electrode was used during the electrochemical experiments at 338 K. The cell was placed in a water-bath to achieve the test temperature. Potentiodynamic polarization curves measurements were performed at a potential scan rate of 1 mV·s$^{-1}$. The potential range was from $-1.50$ to $0.50$ V. The EIS measurements were carried out at OCP over the frequency from $100$ kHz to $10$ mHz by 5 points per decade. All potentials reported in this paper were measured with respect to the SCE, which was connected to the cell through a Luggin capillary tip arrangement and a salt bridge to avoid amplification of the electrolyte from constituents of the reference electrode. All the tests were repeated to obtain reproducibility of results.

3. Result and discussion

3.1. Corrosion rate

Figure 2 shows the corrosion rate of Q235 steel and 16Mn steel based on weightlessness corrosion experiment with different forms of sulfur. The corrosion rate of steels varies greatly. It shows that sulfide and thiosulfate have some certain effect on steel corrosion. The corrosion rate of Q235 steel reaches the maximum when $S^{2-}$ and $S_2O_3^{2-}$ form synergistic corrosion, and the corrosion rate of 16Mn steel reached maximum when $S^{2-}$ exist alone in the solution, are respectively 0.131 mm·a$^{-1}$ and 1.661 mm·a$^{-1}$. The main reason is perhaps that the kinetics of Q235 steel and 16Mn steel is different when the concentration of sulfide is relatively low ($\leq 3$ g/L). Therefore, the corrosion rate trend of two kinds of steel is different with different forms of sulfur. The corrosion rate of 16Mn steel is greater than Q235 steel. Because of $E_{Fe}^{0} < E_{Mn}^{0}$, when iron and manganese exist at the same time, it can be calculated from equation (3), $\Delta G^0 < 0$, under the standard state, manganese is more likely to lose electrons in the anode, and its thermodynamic stability is less than that of iron. Corrosion of 16Mn steel was accelerated by the reaction of $S^{2-}$ in solution.

\[
\text{Mn} \rightarrow \text{Mn}^{2+} + 2e^- \quad E_{\text{Mn}}^{0} = -1.185 \text{ V} \quad (1)
\]
\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad E_{\text{Fe}}^{0} = -0.345 \text{ V} \quad (2)
\]
\[
\Delta G^0 = -nF(E_{\text{Fe}}^{0} - E_{\text{Mn}}^{0}) \quad (3)
\]

3.2. Characteristics of surface corrosion

The surface SEM images and composition of Q235 steel and 16Mn steel surface corrosive with different forms of sulfur are shown in figure 3. It can be seen that the surface SEM images of Q235 steel and 16Mn steel was almost similar from the low magnification diagram for different forms of sulfur and the corrosion of steel surface does...
not totally cover the metal and cannot be considered as a homogeneous layer but rather as a defective layer, the corrosion of two kinds of steel preferentially takes place at defect, which view consistent with the analysis before [10] and the literature [13]. The sample appeared terribly corroded after 120 h, but the surface profile can be observed to be greatly different from that of the original sample (figure 1) indicating the corrosion is accelerated. When the solution contained only S_2O_3^{2−}, the size of corroded particles of Q235 steel and 16Mn steels surface is smaller than that of S^{2−}, because the impetus of grain formation is larger when S^{2−} is present, which indicates that thiosulfate is less corrosive to steel than sulfide. When S^{2−} and S_2O_3^{2−} are present at the same time and form synergistic corrosion, images of surface corrosion are relatively complex, they mainly contain two kinds of corrosive with different shapes, one is octahedral crystal particles with better crystallization, the other is flocculent deposits. The corrosive is not uniformly distributed on the surface, which has less diffusion resistance to corrosive ions, and the corrosion rate is fast. The results are consistent with those of the weightlessness method. Among, the corrosion product is generally featured with a crystal particle, octahedral structure, depositing loosely on the steel surface [14]. EDS analysis shows that octahedral grain area was composed of three elements (O, Fe and Al). Figure 4 is XRD analysis of Q235 steel and 16Mn steel surface corrosive with different forms of sulfur. The XRD patterns of corrosive are very similar, indicating that sulfur only affects the strength of the XRD diffraction peak, while the composition of surface corrosive is same, which are composed of sulfides (FeS and FeS_2) and oxides (Fe_2O_3, Fe_3O_4, Al_2O_3 and NaFeO_2) [2, 11]. The crystal particles are mainly iron oxides according to EDS analysis. Figure 5 is E-pH diagram of Fe-Al-S-H_2O at 110 °C, derived from a chemical equilibrium and reaction software database [15]. The diagram shows the thermodynamically favored phases that exist for Fe-Al-S-H_2O systems at different pHs and potentials. The pH range tested, solid oxide formations of Fe_2O_3 and Fe_3O_4, and soluble anion compounds FeO_2(−a) and HFeO_2(−a) are expected. Figure 5 indicates that in the pH range of 14-15, the stable phase at the steel surface can be a Fe_2O_3 or Fe_3O_4 film or it can be soluble FeO_2(−a) and HFeO_2(−a) ion. If an insoluble film is stable, the corrosion process is suppressed, the corrosion rate is slower and depend on the stability and electronic conductivity properties of the passive film. Figure 5 shows the formation of FeO.777 S is not thermodynamically favorable above the pH of 15. However, the work by
Tromans [16] has shown that sulfur is incorporated into Fe3O4 film in the region of critical current density, below the active-passive transition region of the polarization curve. Similar results were found in this study.

3.3. Potentiodynamic polarization

Figure 6 is the potentiodynamic polarization curves of Q235 steel and 16Mn steel with different forms of sulfur. Two kinds of steel can be observed in the polarization curves with the same cathodic reaction which has little relationship with S2− and S2O32−. Oxygen absorption occurs when the current density is high, hydrogen evolution occurs when the current density is small, the reactions are equations (4) and (5) respectively. The anode part of the polarization curve shows significant passivation, including the activation zone, transition zone, passivation zone and over-passivation zone, which indicate that the steel surface formed a compact corrosion products film at a later stage. When the solution contains S2− or S2O32− alone, the potential range of the activation zone was Ecorr ∼ −1.18 V, the potential range of the transition zone was −1.18 V ∼ −0.7 V, and the potential range of the passivation zone was −0.7 V ∼ 0.3 V. Compared with the corrosion of single sulfide, the potential of each region on the anode polarization curve shifted positively when S2− and S2O32− form synergistic corrosion, indicating that corrosion was more difficult to carry out the thermodynamics. There are three humps in the anodic transition zone of the two kinds of steel, and different humps correspond to different potential values, that is, different anodic reactions occur, mainly the transformation reaction of initial surface corrosive, and finally the formation of oxide (Fe3O4) with stable structure isolates the steel matrix from the solution and prevents the corrosion from proceeding. This could be due to the fact that the corrosion process involved transformation of corrosion products, always maintaining the surface activation [17].
The determination of corrosion parameters (E_{corr} and I_{corr}) could provide more information about the overall corrosion process\cite{18, 19}. Table 2 shows the corrosion potentials (E_{corr}), polarization resistances (R_p), Tafel slopes ($\beta_a$ and $\beta_c$ represent anodic and cathodic, respectively), corrosion currents (I_{corr}) and corrosion rate obtained from Tafel fitting of the polarization curves data. The higher current density, the faster the corrosion rate. The relation of corrosion current of Q235 steel and 16Mn steel in the three solutions containing different forms of sulfur is respectively equations (6) and (7).

$$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq})$$  \hspace{1cm} (4) \\
$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- (\text{aq})$$  \hspace{1cm} (5) \\
$$I_{corr}(S^{2-} + S_2\text{O}_3^{2-}) = 866.94 \mu\text{A} \cdot \text{cm}^{-2} > I_{corr}(S^{2-}) = 163.68 \mu\text{A} \cdot \text{cm}^{-2}$$  \hspace{1cm} (6) \\
$$I_{corr}(S^{2-}) = 1114.8 \mu\text{A} \cdot \text{cm}^{-2} > I_{corr}(S^{2-} + S_2\text{O}_3^{2-}) = 791.28 \mu\text{A} \cdot \text{cm}^{-2}$$  \hspace{1cm} (7)

For Q235 steel, I_{corr} of synergistic corrosion is larger than that of S_2\text{O}_3^{2-} or S^{2-} alone. But, I_{corr} of 16Mn steel electrode is largest when S^{2-} was contained alone. The reason is perhaps that the addition of S^{2-} or S_2\text{O}_3^{2-} alone reacts with the steel substrate to loss of electron reactions (equations (8)–(10)) which generate iron compound to inhibit the corrosion. When S^{2-} and S_2\text{O}_3^{2-} exist at the same time, the corrosion rate of steel is reduced due to loss of electron reaction (equation (11)), which prevents the anodic dissolution of iron. The results are consistent with those of the weightlessness method.

$$\text{Fe} + S^{2-} \rightarrow \text{FeS} + 2\text{e}^-$$  \hspace{1cm} (8) \\
$$\text{Fe} + 2S^{2-} \rightarrow \text{FeS}_2 + 4\text{e}^-$$  \hspace{1cm} (9) \\
$$\text{Fe} + S_2\text{O}_3^{2-} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 + S^{2-} + \text{SO}_4^{2-}$$  \hspace{1cm} (10) \\
$$2S^{2-} + S_2\text{O}_3^{2-} + 6\text{OH}^- \rightarrow S_2^{2-} + 2\text{SO}_4^{2-} + 3\text{H}_2\text{O} + 6\text{e}^-$$  \hspace{1cm} (11)

### 3.4. Electrochemical impedance spectrum

Figure 7 is the EIS of Q235 steel and 16Mn steel with different forms of sulfur. Nyquist plots of Q235 steel with different forms of sulfur were all the same from figure 7, which have only two capacitance-resistance arcs and no
diffusion impedance, indicating that the corrosion layer is relatively loose and the corrosion process is mainly controlled by charge transfer. The Nyquist plots of 16Mn steel with $S_2O_3^{2−}$ consisted of flattened semicircle, indicating that the impedance caused by concentration polarization in the corrosion process could be ignored, and the entire corrosion was mainly controlled by charge transfer, the corrosion kinetics is consistent with that of Q235 steel. The difference is that the Nyquist diagram of 16Mn steel presents a typical Warburg diffusion phenomenon with containing $S_2^{−}$ alone and forming synergistic corrosion, which means that the corrosion layer is relatively dense and prevents the diffusion of ions to the steel substrate. At this time, the corrosion is mainly controlled by the mass transfer process. The Bode diagram shows that Q235 steel is two time constant ($τ_{ct}$ and $τ_f$) respectively is the charge transfer of intermediate frequency response and surface film layer of high frequency response. 16Mn steel is the same as Q235 steel with containing $S_2O_3^{2−}$ alone, and there are two time constants. With containing $S_2^{−}$ alone and forming synergistic corrosion, besides two time constants and there are Warburg impedance caused by ion diffusion.

Based on the above analysis, the EIS fitting of figure 7 was carried out by using the equivalent circuit of figure 8 by means of Zview software. Electrochemical parameters are shown in table 3. In the equivalent circuit, $R_s$ is solution resistance, $R_f$ and $Q_f$ (CPE1) are the corrosion layer resistance and capacitance respectively, $R_{ct}$ and $Q_{dl}$ (CPE2) are charge transfer resistance and dual-layer capacitance respectively, and $Z_W$ represents Warburg diffusion of ions. The reason of $Q$ for capacitors in analysis of impedance spectra is that the corrosion layer does not consider as a homogeneous layer but rather as a defective layer. The impedance of $Q$ is defined as:

$$Z_Q = Y_0^{-1}(jω)^{-n}$$

where $ω$ is the angular frequency (rad s$^{−1}$), $j^2 = (-1)$, $Y_0$ is the admittance magnitude of CPE which can be approximately transformed into a capacitance, and $n$ is the exponential term, most of between 0.5 and 1.0. The value of $n$ is greater, the better corrosion resistance. When $n = 0.5$, $Z_W$ is the Warburg impedance.
Table 3. Fitting of EIS results for Q235 steel and 16Mn steel with different forms of sulfur.

| Electrochemical parameters | Q235 steel | 16Mn steel |
|----------------------------|------------|------------|
|                             | 3 g/LS\(^{2-}\) | 3 g/LS\(^{2-}\) | 3 g/LS\(^{2-}\) + 3 g/LS\(^{2-}\) | 3 g/LS\(^{2-}\) | 3 g/LS\(^{2-}\) | 3 g/LS\(^{2-}\) + 3 g/LS\(^{2-}\) |
| \(R_s/\Omega \cdot \text{cm}^{-2}\) | 1.456 | 1.452 | 1.457 | 1.191 | 1.277 | 3.307 |
| \(R_f/\Omega \cdot \text{cm}^{-2}\) | 1.328 | 11.31 | 1.956 | 0.019 | 2.879 | 0.493 |
| CPE\(_f(Y_0)\)/\(\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-n}\) | 0.010 | 0.007 | 0.015 | 0.124 | 0.002 | 0.004 |
| \(n_1\) | 0.93 | 0.79 | 0.89 | 0.73 | 0.94 | 0.84 |
| \(R_{0}/\Omega \cdot \text{cm}^{-2}\) | 396.3 | 537.2 | 612.0 | 88.93 | 344.2 | 0.039 |
| CPE\(_{dl}(Y_0)\)/\(\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-n}\) | 0.005 | 0.005 | 0.014 | 0.018 | 0.002 | 0.009 |
| \(n_2\) | 0.96 | 0.81 | 0.90 | 0.87 | 0.94 | 0.99 |
| \(R_{0}/\Omega \cdot \text{cm}^{-2}\) | — | — | — | 1.177 | — | 4.236 |
| \(W_T\) | — | — | — | 0.03 | — | 0.06 |
| \(W_P\) | — | — | — | 0.45 | — | 0.48 |
| \(R^2\) | 8e-4 | 2e-4 | 9e-4 | 2e-4 | 7e-4 | 3e-4 |
The electrochemical impedance for the circuit of figures 6(a) and (b) can be expressed by equations (11) and (12) [20].

\[
Z_a = R_S + \frac{1}{j\omega Q_f + \frac{1}{R_f + \frac{1}{j\omega Q_{ab} + \frac{1}{R_{ab}}}}}
\]

\[
Z_b = R_S + \frac{1}{j\omega Q_f + \frac{1}{R_f + \frac{1}{j\omega Q_{ab} + \frac{1}{R_{ab}}}}}
\]

When Zview software processes electrochemical impedance spectrum data, Rct and Rf are sometimes difficult to distinguish, so the polarization resistance Rp represents Rct and Rf to analyze the corrosion process of steel and the corrosion product layer. The relation of polarization resistance of Q235 steel and 16Mn steel in the three solutions containing different forms of sulfur is respectively equations (13) and (14). It shows that Rp of the corrosion layer on Q235 steel surface is the smallest when S\(_2^--\) is alone in the solution, which indicates that the structure of the corrosion layer is relatively loose, with little resistance to the diffusion of ions. When S\(_2O_3^{2-}\) is alone, Rp of the corrosion layer of Q235 steel and 16Mn steel surface is relatively large, which indicates that the corrosion layer has small particles and dense structure, and the resistance to ion diffusion is relatively large. It is consistent with SEM morphology.

\[
R_p(S_2^-) = 397.63 \, \text{\Omega} \cdot \text{cm}^2 < R_p(S_2O_3^{2-})
\]

\[
= 568.51 \, \text{\Omega} \cdot \text{cm}^2 < R_p(S_2^- + S_2O_3^{2-}) = 613.96 \, \text{\Omega} \cdot \text{cm}^2
\]

\[
R_p(S_2^- + S_2O_3^{2-}) = 0.53 \, \text{\Omega} \cdot \text{cm}^2 < R_p(S_2^2^-)
\]

\[
= 88.95 \, \text{\Omega} \cdot \text{cm}^2 < R_p(S_2O_3^{2-}) = 347.08 \, \text{\Omega} \cdot \text{cm}^2
\]

\[
R_{ab}(S_2^-) = 1.177 \, \text{\Omega} \cdot \text{cm}^2 < R_{ab}(S_2^- + S_2O_3^{2-}) = 4.236 \, \text{\Omega} \cdot \text{cm}^2
\]

Figure 9 shows a schematic diagram of Q235 steel and 16Mn steel corrosion scale with different forms of sulfur. The model is proposed based on the reaction mechanism through the analysis of SEM, EDS, XRD and EIS, at the same time, based on the literature [21, 22]. Element Fe in the steel reacts preferentially with the anions to form iron sulfide and oxide, as showed in figure 9(b). As corrosion progresses, the surface iron sulfide is further converted into iron oxide (figure 9(c)). Therefore, the corrosion on the steel surface is composed of two layers. The inner layer is mainly iron sulfide, and the outer layer is mainly octahedral crystal oxide.

4. Conclusions

(i) Corrosion rate of Q235 steel reaches the maximum under synergistic corrosion, and that of 16Mn steel reached maximum when S\(_2^-\) was contained alone. Corrosion rate of 16Mn steel is greater than Q235 steel. The size of corroded particles is smaller containing only S\(_2O_3^{2-}\) for two kinds of steel. Surface corrosion
contains two kinds of corrosion with different shapes under synergistic corrosion, one is octahedral crystal particles with better crystallization, the other is flocculent deposits.

(ii) Surface corrosion of two kinds of steel is composed of sulfides (FeS and FeS2) and oxides (Fe2O3, Fe3O4, Al2O3 and NaFeO2). The crystal particles are mainly iron oxides according to EDS analysis.

(iii) $I_{\text{corr}}$ of Q235 steel and 16Mn steel is largest under synergistic corrosion and containing $S^{2-}$ alone respectively. Nyquist plots of Q235 steel were all the same with different forms of sulfur, which contain two capacitance–resistance arcs and no diffusion impedance. The impedance of 16Mn steel containing $S_2O_3^{2-}$ alone is consistent with Q235 steel. The difference is that the Nyquist diagram of 16Mn steel presents a typical Warburg diffusion phenomenon with containing $S^{2-}$ alone and synergistic corrosion.

Acknowledgments

This work was supported by National Nature Science Foundation of China (grant no. 51474079, 51574095), Guizhou platform for talents ([2016]5626), SRT of Guizhou University([2018]315) and Introduction talent fund project of Guizhou university ([2019]43).

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