



Initial Corrosion Behavior of 12Cr1MoV Steel in Thiosulfate-Containing Sodium Aluminate Solution

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Abstract: When alumina is produced by the Bayer process with high-sulfur bauxite, the sulfur would strongly corrode the 12Cr1MoV steel made heat exchanger. This study investigated the initial corrosion behavior of the 12Cr1MoV steel exposed to a thiosulfate-containing sodium aluminate (TCSA) solution under the evaporation conditions of alumina production. The obtained corrosion rate equation is $V = 6.306 \cdot t \cdot \exp(-0.71)$. As corrosion progressed, with the corrosion product film growing, the corrosion current density declines slowly, and the corrosion resistance of the steel is increased. At 1–3 days, the corrosion product film consisted of FeO, Fe₂O₃, and FeOOH. S₂O₃^{2–} lead to corrosion in local areas of the steel and pits appeared. AlO₂⁻ is transformed into Al(OH)₃ and filled in the corrosion pits. At 4 and 5 days, Fe₃O₄ is generated in the outermost layer, and Al(OH)₃ is shed from the corrosion pits. The corrosion mechanism of 12Cr1MoV steel in a TCSA solution is proposed based on the experimental results.

Keywords: 12Cr1MoV steel; corrosion; sodium aluminate solution; corrosion time; S₂O₃²⁻

1. Introduction

High-sulfur bauxite is used for the industrial production of alumina, where sulfur, in the form of pyrite (FeS₂), is converted into S^{2-} , $S_2O_3^{2-}$ and other ions in a sodium aluminate solution [1–3]. The accumulation of sulfur in the solution causes a series of hazards, such as the loss of alkalinity and the reduction of the alumina dissolution rate [4]. During the evaporation of the sodium aluminate solution, the sulfur strongly corrodes the heat exchanger made from 12Cr1MoV steel [5]. Although some desulfurization methods, such as roasting desulfurization [6] and wet desulfurization [7], can remove most of the sulfur, the sulfur concentration would continue to increase as the number of sodium aluminate solution cycles increasing. Thus, the corrosion behavior of 12Cr1MoV steel in the sodium aluminate solution has become an important problem to study.

Currently, the mechanism of 12Cr1MoV steel corrosion, especially in solutions containing thiosulfate $(S_2O_3^{2^-})$, remains unclear. In the mid-1940s, corrosion failures caused by $S_2O_3^{2^-}$ were observed in the paper and pulp industry [8–10]. In areas where the passivation film on the steel surface is broken, $S_2O_3^{2^-}$ tends to be reduced to S by the following reaction:

$$S_2 O_3^{2-} + 6H^+ + 4e^- = 2S + 3H_2 O$$
⁽¹⁾

Sulfur hinders the repair of the passivation film because the S deposited during this reaction stimulating the anode process on the active surface, and it prevents the adsorption of OH⁻. Due to the



inhibitory effect of the oxide film, S can only form on the active surface of the steel. In addition, acidic solutions promote the formation of the S. Some studies [11–13] proposed that the corrosion caused by $S_2O_3^{2-}$ occurs only in the presence of a substance that could attack the passivation film or when the passivation film was damaged due to mechanical stress. In addition, there are a few studies on the corrosion behavior of sulfur in the sodium aluminate solution on steel [14–16]. Xie et al. [14] found that the mechanism of corrosion in S^{2-} -containing sodium aluminate solutions became similar to active dissolution. Through electrochemical corrosion and spray corrosion tests, Fu et al. [15] found that the corrosion degree of Q345 steel increased with the increase of sulfide ion concentration. In a solution containing S^{2-} and $S_2O_3^{2-}$, an increased $S_2O_3^{2-}$ concentration led to more significant corrosion of the steel, and a good product film protective matrix was formed on its surface, which has been reported by Quan et al. [16]. However, few studies have been carried out on sodium aluminate solutions containing solely $S_2O_3^{2-}$. Therefore, the corrosion behavior of steel in a thiosulfate-containing sodium aluminate (TCSA) solution was studied, which was of great significance to the formulation of anti-corrosion scheme and the production and application of high-sulfur bauxite.

The purpose of this study is to investigate the corrosion behavior of the 12Cr1MoV steel in a TCSA solution by simulating the evaporation conditions of sodium aluminate during alumina production. The initial corrosion behavior mechanism was revealed in terms of the corrosion rate, characterization and composition of the corrosion products, and electrochemical analysis.

2. Materials and Methods

2.1. Materials and Solution

12Cr1MoV steel was used in this study, and its chemical compositions are shown in Table 1. The samples were machined into $15 \times 10 \times 2$ mm blocks for the corrosion experiments and electrochemical measurements. The working electrode (WE) was connected to a copper wire and mounted in epoxy resin with a 1.5 cm² area exposed. The specimens were sequentially ground using SiC paper from 180 to 1500 grit, polished with a 2.5 µm diamond powder, rinsed with deionized water and alcohol, and dried in cold air. The TCSA solution contained 255 g·L⁻¹ Na₂O, 110 g·L⁻¹ dissolved alumina (as Al₂O₃), and an amount of Na₂S₂O₃·5H₂O that was equivalent to 5 g·L⁻¹ S₂O₃²⁻ (pH = 14.6). The solution was prepared by using analytical-grade reagents and deionized water.

Table 1. Chemical compositions of 12Cr1MoV steel (wt%).

С	Cr	Mo	V	Si	Mn	Fe
0.14	0.98	0.22	0.18	0.23	0.61	Balance

2.2. Corrosion Experiments

The specimens were placed in 120 mL of TCSA solution. Corrosion experiments were conducted at 110 °C for different times (1, 2, 3, 4, or 5 days (d)) in an autoclave. Three specimens were used for each experiment. The corrosion products were washed by immersion in a solution (500 mL HCl + 5 g $C_6H_{12}N_4$ + 500 mL H_2O) and the change in weight due to material lost over time was used to calculate the average corrosion rate by Equation (2) [5]:

$$V_{corr} = (m_0 - m_1)/At$$
 (2)

where V_{corr} is the average corrosion rate (g·m⁻²·d⁻¹); m_0 and m_1 are the initial and final masses of the sample (g), respectively; A is the surface area of sample (m²); and t is the corrosion time (d).

2.3. Analysis of Corrosion Products

After the corrosion experiments, the morphology and composition of the corrosion products on 12Cr1MoV steel were analyzed by scanning electron microscopy (SEM, SUPRA 40, Zeiss, Jena, Germany)

and energy dispersive spectroscopy (EDS, AZtec, Oxford Instruments, Oxon, UK). The components of the corrosion products were analyzed X-ray diffraction (XRD, X'pert Pro MPD, Panalytical, Almelo, The Netherlands) with CuK α radiation (0.15406 nm) at 40 kV and 40 mA. The scanning range of 2 θ was set from 10° to 90°. The software of HighScore Plus (Panalytical, Almelo, The Netherlands) was selected to analyze the data. X-ray photoelectron spectroscopy (XPS) (K-Alpha+ (hv = 1486.6 eV), Thermo Fisher Scientific, Waltham, MA, USA) was carried out to further understand the phase composition and structure of the corrosion products. The C1s peak at 284.8 eV was used as a reference to adjust the shifted charge and the data was conducted via the commercial software XPSpeak version 4.1.

2.4. Electrochemical Tests

Electrochemical tests were performed using a potentiostat (VPS, Bio-Logic Science Instruments, Claix, France) equipped with a three-electrode cell. A platinum wire was used as the counter electrode (CE), and a saturated calomel electrode (SCE) was used as the reference electrode (RE). The SCE needs to work at temperatures less than 60 °C. So, the cell was placed in a water bath to maintain the temperature at 55 °C. The TCSA solution was used as the corrosion medium. Before the electrochemical measurements were performed, the WE was immersed in the TCSA solution to be corroded for different times (1, 2, 3, 4, or 5 d) at 95 °C. Due to experimental conditions, the immersion corrosion temperature was set at 95 °C. The tests were repeated three times to guarantee the repeatability. Electrochemical impedance spectroscopy (EIS) measurements were taken at the open-circuit potential in the 100 kHz–10 mHz frequency range with a perturbing signal of 10 mV. The polarization curve was measured by sweeping the potential in the positive direction at 0.5 mV·s⁻¹. The potential ranged from $-1.5 V_{SCE}$ to 1.0 V_{SCE} . Before each test, the electrode potential was held for at least 30 min to ensure that the system was stabilized.

3. Results and Discussion

3.1. Corrosion Rate Analysis

The corrosion rates of 12Cr1MoV steel with different corrosion times at 110 °C are shown in Figure 1. With the corrosion time increased, the corrosion rate decline slowly. There is a marked decrease in the corrosion rate between 1 d and 3 d. At 4 d and 5 d, the corrosion rate is low. As corrosion products formed on the entire surface, the active corrosion reaction is inhibited, and the corrosion rate decreased [17]. The corrosion rate equation is fitted as follows [5]:

$$V = 6.306 \cdot t \cdot \exp(-0.71) \tag{3}$$

where *V* is the corrosion rate $(g \cdot m^{-2} \cdot d^{-1})$; *t* is the corrosion time (d); 6.306 is the corrosion coefficient; and -0.71 is the corrosion trend. The R^2 value is 0.9971.



Figure 1. Corrosion rates of 12Cr1MoV steel for different corrosion times.

3.2. SEM-EDS Analysis

Figure 2 presents the microstructure and EDS point results of the 12Cr1MoV steel after being corroded for different times in the TCSA solution. After 1 d, many small isolated pits appear on the steel; after 2 d, the pits expand to form corrosion pits, and a white substance accumulates in the corrosion pits. After 3 d, the white substance covers the surface of the corrosion pits. However, after 4 d, particulate corrosion products cover the steel surface, and the white substance in the corrosion pit gradually fall off. This is corresponded to the corrosion rate rapidly decreasing. The EDS analysis of the white substance is carried out in the points marked as A1, A2, and A3 (Figure 2b–d). Those points primarily contain O and Al, and the atomic ratio of Al to O is close to 3 (Figure 2f). Fu et al. [14] found that sodium aluminate was decomposed and the Al(OH)₃ formed adhered to the surface of the corrosion products on the steel surface are partially shed. The corrosion rate declines slowly and tends to be stable. This type of particulate corrosion product is very important for decreasing in the corrosion rate.



Figure 2. SEM morphologies (**a**–**e**) and EDS (**f**) point measurements of 12Cr1MoV steel after corroded for (**a**) 1, (**b**) 2, (**c**) 3, (**d**) 4, and (**e**) 5 d in the thiosulfate-containing sodium aluminate (TCSA) solution at 110 °C.

Table 2 shows the EDS mapping results of the 12Cr1MoV steel corroded for different times in the TCSA solution. At 1–3 d, the O content is relatively low, and the S content is almost non-existent.

A small amount of Al element is present. At this stage, the corrosion products are composed mainly of an oxygen-iron compound. This also reveals that no sulfides are produced on the surface of the steel. In addition, some compounds containing Al formed and decline slowly in size. Between 4 and 5 d, the O content rapidly increase, and the Al content declines slowly. This reveals that the corrosion products are mainly composed of iron oxides. In addition, the small amounts of the aluminum compounds which formed earlier in the corrosion process begin to decrease gradually.

Time/d	0	S	Cr	Mn	Al	Na	Fe
1	6.59	-	0.62	0.28	0.15	0.32	Balance
2	4.26	-	0.75	0.46	0.35	0.26	Balance
3	6.37	-	0.74	0.42	1.15	0.01	Balance
4	27.22	0.15	1.06	0.77	1.06	0.43	Balance
5	26.80	0.18	0.83	0.62	0.37	0.25	Balance

Table 2. EDS mapping results of 12Cr1MoV steel corroded for different times in the TCSA solution (wt%).

3.3. Analysis of the Phase and Chemical Composition of the Corrosion Products

The XRD patterns of the 12Cr1MoV steel after being corroded for different times at 110 °C in the TCSA solution are shown in Figure 3. At 1, 2, and 3 d, only the matrix iron (Fe) peaks are found in XRD patterns, which indicate that the corrosion is not significant, and the product film is thin at this stage. After being corroded for 4 and 5 d, the corrosion product is composed of Fe₃O₄, and the peak intensities increase gradually, which indicate that the crystallinity of Fe₃O₄ is stronger.



Figure 3. XRD patterns of 12Cr1MoV steel corroded for different times at 110 °C in the TCSA solution.

To further understand the corrosion products, XPS characterizations were used to survey the elemental states of the Fe, O, and Al species. Figure 4 shows the XPS results of the 12Cr1MoV steel corroded in the TCSA solution for 1, 3, and 5 d for the Fe2p, O1s, and Al2p spectra. As shown in Figure 4a, the Fe2p spectra can be separated into several constituent peaks representing the FeO (708.6 \pm 0.3 eV), Fe₂O₃ (710.1 \pm 0.3 eV), and FeOOH (711.9 \pm 0.3 eV) [18–20]. After 5 d, the Fe₂O₃/FeO intensity ratio of 1.5 is markedly above that corresponding to Fe₃O₄ and Fe₂O₃ (ratio of 1). Figure 4b shows that three peaks for O1s are observed in the spectra at 529.6 \pm 0.3, 531.4 \pm 0.3, and 532.4 \pm 0.3 eV, which corresponded to O^{2–}, FeOOH, and Al(OH)₃ [21–23], respectively. It was noted that the OH⁻ peaks are very weak after only 1 d of corrosion. This indicates that the dominant O species in the corrosion products changes from O^{2–} to OH⁻ as the corrosion time increases. The Al2p band consists of one peak at 74.2 \pm 0.2 eV, which corresponds to Al(OH)₃ [22], as shown in Figure 4c. Combining

the XRD and EDS results, the corrosion products of 12Cr1MoV steel corroded for 1 d were mainly composed of Fe₂O₃, FeOOH, and FeO, with a smaller amount of Al(OH)₃. After 3 d, a measurable amount of FeOOH form on the steel surface. Xia [24] also found that OH⁻ formed later than O²⁻ and was enriched in the outermost passive film layer. After 5 d, the corrosion products are mainly composed of Fe₃O₄.



Figure 4. XPS spectra of 12Cr1MoV steel corroded in the TCSA solution for 1, 3, and 5 d: (**a**) Fe2p, (**b**) O1s, and (**c**) Al2p.

3.4. Analysis of the Polarization Curves

Figure 5 illustrates the polarization curves of 12Cr1MoV steel corroded for different time in the TCSA solution at 55 °C. The anodic polarization curves could be divided into four regions: active, active-passive transition, passive, and transpassive regions. The corrosion potential was around -1.2 V vs. SCE.



Figure 5. Polarization curves of 12Cr1MoV steel corroded in the TCSA solution for different times (1 d, 2 d, 3 d, 4 d, or 5 d) at 55 °C.

According to previous studies [5,14,16], the following reactions occur. The peak A at $-1.1 V_{SCE}$ is attributed to the Fe matrix actively dissolving to form Fe(OH)₃⁻ through Equation (4).

$$Fe + 3H_2O \rightarrow Fe(OH)_3^- + 3H^+ + 2e^-$$
 (4)

The peak B at -0.8 V versus SCE may be associated with the formation of Fe₃O₄ through Equation (5). However, as the corrosion time increases, peak B gradually disappears, implying that the corrosion product film has a significant effect on the passivation behavior. In addition, S₂O₃^{2–} may participate in the reaction through Equations (6) and (7).

$$3Fe(OH)_3^- + H^+ \rightarrow Fe_3O_4 + 5H_2O + 2e^-$$
 (5)

$$S_2O_3^{2-} + 8H^+ + 8e^- \rightarrow 2HS^- + 3H_2O$$
 (6)

$$Fe_3O_4 + 3HS^- + 5H^+ + 2e^- \rightarrow 3FeS + 4H_2O$$
 (7)

The peak C at -0.6 V versus SCE may be associated with the formation FeOOH or Fe₃O₄, as shown in Equations (8) and (9).

$$Fe_3O_4 + 2H_2O \rightarrow 3FeOOH + H^+ + e^-$$
(8)

$$2Fe_{3}O_{4} + 2OH^{-} \rightarrow 3Fe_{2}O_{3} + H_{2}O + 2e^{-}$$
(9)

Table 3 shows E_{corr} and the corrosion current density (J_{corr}), and the Tafel slope values, which are obtained from Figure 5 using EC-Lab V11.20 software (Bio-Logic Science Instruments, Claix, France). The value of E_{corr} shifts toward negative potentials as the corrosion time increased. In contrast, the J_{corr} value decreases from 265.6 to 41.192 μ A·cm⁻² when the corrosion time increases from 1 to 5 d. The J_{corr} value decreases rapidly from 132.344 to 49.328 μ A·cm⁻² at 4 d, implying that the formation of the corrosion product film affects the corrosion rate of the steel.

Table 3. Polarization results of 12Cr1MoV steel.

Time (d)	E_{corr} (mV)	J _{corr} (µA·cm ^{−2})	eta_a (mV·dec ⁻¹)	eta_c (mV·dec ⁻¹)
1	-1208.46	265.6	55.8	83.8
2	-1205.59	226.392	63.2	86.3
3	-1222.86	132.344	77.7	77.4
4	-1267.89	49.328	252.7	19.4
5	-1271.53	41.192	308.8	141.8

3.5. EIS Analysis

The EIS spectra of 12Cr1MoV steel after being corroded for different times in the TCSA solution at 55 °C are shown in Figure 6. The capacitive reactance arc in the high frequency region corresponds to the passive film, whereas the low frequency region corresponds to the charge transfer process at the film/solution interface [25]. While the absolute value of the maximum phase angle is smaller, the corrosion product film on the steel surface is rougher. At 1 d, the steel has the smoothest surface. According to Nyquist plots, Bode plots, and the relevant literature analysis, two time constants (state variables) should be considered, one of which reflects the nature of the surface layer and the other reflects charge transfer on the surface of the electrode [14].



Figure 6. Electrochemical impedance spectroscopy (EIS) spectra results of 12Cr1MoV steel corroded for different times in the TCSA solution at 55 °C: (**a**) Nyquisy piot, (**b**) Bode plot (log|Z| vs. frequency), (**c**) Bode plot (phase angle vs. frequency).

The EIS spectra were fitted with the electrochemical equivalent circuit using EC-Lab V11.20 software. The equivalent circuit is shown in Figure 7 and impedance parameters obtained on the 12Cr1MoV steel electrode after corroded different time in TCSA solution is shown Table 4. The equivalent circuit diagram $R_s + Q_f/(R_f + Q_{dl}/R_{ct})$ has an electric double-layer capacitance with two time constants [14,16]. R_s stands for the solution resistance, R_{ct} and R_f represent the charge-transfer resistances and corrosion product film, respectively, and Q_f and Q_{dl} represent the product layer capacitance and constant-potential capacitance, respectively. The value of R_f is relatively high from 4 to 5 d, which may be associated with the growth of the corrosion product film. In particular, the R_{ct} values of the samples corroded for 4 and 5 d are higher than those of the samples corroded 1–3 d, suggesting that the charge-transfer phenomena is more difficult. Based on the above electrochemical results, it can be clarified that as the corrosion time increased, the corrosion product film gradually formed, and the corrosion resistance of the steel gradually improved [25,26]. The enhanced corrosion resistance should be related to the changes in the composition of the product film [27].



Figure 7. The equivalent electric circuit used to fit the impedance data.

Table 4. Impedance parameters obtained on the 12Cr1MoV steel electrode after corroded different timein TCSA solution.

Time (d)	R_s ($\Omega \cdot cm^2$)	R_{ct} ($\Omega \cdot cm^2$)	$\begin{array}{c} Q_{dl} \\ \text{(S cm}^{-2} \text{ s}^n\text{)} \end{array}$	n _{dl}	R_f ($\Omega \cdot \mathrm{cm}^2$)	$\begin{array}{c} Q_f \\ (\text{S cm}^{-2} \text{ s}^n) \end{array}$	n _f	X ² (10 ⁻⁴)
1	0.8	154	0.001	0.74	122	0.024	0.74	7.54
2	1.0	179	0.031	0.86	229	0.048	0.84	6.81
3	1.2	491	0.026	0.74	550	0.082	0.93	7.96
4	0.7	593	0.003	0.97	690	0.002	0.59	6.35
5	0.8	643	0.0001	0.69	1281	0.010	0.66	5.26

3.6. Analysis of the Cross-Section of the Corrosion Product Film

Figure 8 shows the morphologies, elemental mapping, and line scan of the cross-section of the corrosion product film on the 12Cr1MoV steel after corroding for 5 d in the TCSA solution. A uniform and continuous product film is observed. The O and Fe contents are enriched in the film. Small amounts of Al are also presented in the corrosion product layer. A line scan and element mapping of the cross section reveal that the growth of the film is driven by diffusion. From Figure 8 b, the strength of the Fe peaks gradually decreases from surface to steel matrix as well as the strength of the Al peaks. The amount of O gradually increased and then slightly decreased. According to the distribution of O, there are two layers in the film: the inner and outer layer. The XRD analysis confirms the presence of Fe_3O_4 on the steel surface (Figure 3). From the results of the SEM-EDS and XPS analysis (Figure 2,

Table 2, and Figure 4), the inner layer is mainly composed of FeO, Fe_2O_3 , FeOOH, and a smaller amount of Al(OH)₃. The outer layer is mainly consisted of Fe_3O_4 .



Figure 8. Morphologies, elemental mapping, and line scan of the cross-section of the corrosion product film on the 12Cr1MoV steel after 5 d of corrosion in the TCSA solution.

3.7. Corrosion Mechanism

Based on the above results and relevant previous studies [28–31], a schematic of the corrosion product film on the 12Cr1MoV steel after corrosion in the TCSA solution is proposed, as is shown in Figure 9.



Figure 9. Schematic (**a**–**e**) of the corrosion product film formed on the 12Cr1MoV steel surface when immersed in the TCSA solution.

In the early stage (1–3 d), there is a competitive adsorption of OH^- , AlO_2^{-} , and $S_2O_3^{2-}$ in the solution. OH^- is adsorbed onto the surface of the steel to form FeO, Fe₂O₃, and FeOOH easier than other ions in the early stage (Figure 9a,b). Some studies [15,16] have reported that these corrosion products exist after the steel being corroded in sodium aluminate solution. $S_2O_3^{2-}$ is adsorbed in the steel and forms SO_4^{2-} , FeS, and pits on the surface of the steel (Figure 9a,b). However, SO_4^{2-} and FeS were dissolved in the solution. There is a wide consensus that $S_2O_3^{2-}$ and its decomposition products did not occur in the film [8,32]. As corrosion progresses, pits continue to form corrosion pits. Interestingly, AlO_2^- can be converted into $Al(OH)_3$ in the corrosion pits (Figure 9c) [33]. The crystallization precipitation of $Al(OH)_3$ was related to pH value. It may be concluded that a large amount of $Al(OH)_3$

are formed with lower pH value in the corrosion pits [34]. Meanwhile, the corrosion current density and the corrosion rate decrease gradually.

In the later stages (4 and 5 d), Fe_3O_4 is generated in the outermost film, and Al(OH)₃ sheds from the corrosion pits (Figure 9d). There are defects in the area near the corrosion product film on the steel surface (Figure 9e). The formation of the product film has an important influence on the corrosion process: the corrosion current density decreases, and the corrosion resistance of the steel gradually improved. The film has a strong protection capability.

4. Conclusions

The initial corrosion behavior of the 12Cr1MoV steel in a TCSA solution was explored in this paper. As the corrosion time increased, the corrosion rates declined slowly. The corrosion rate equation is $V = 6.306 \cdot t \cdot \exp(-0.71)$. According to the electrochemical results, the corrosion current density gradually decreases, and the corrosion resistance of steel is increased. The corrosion mechanism of the 12Cr1MoV steel in a TCSA solution is proposed. In the early stages (1–3 d), the corrosion product film consisted of FeO, Fe₂O₃, and FeOOH. S₂O₃^{2–} caused by corrosion in local areas of steel and pits appeared. AlO₂⁻ is transformed into Al(OH)₃ and fills in the corrosion pits. In the later stages (4 and 5 d), Fe₃O₄ is generated in the outmost layer, and Al(OH)₃ is shed from the corrosion pits.

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