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High Temperature Corrosion of Aluminized AISI 4130 Steel with the Different Composition of NaCl/Na$_2$SO$_4$ Deposits

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Abstract

The high temperature corrosion of AISI 4130 steel can be increased by hot-dip aluminizing coating. The aluminized steel specimens with the deposit composition of 100/0, 30/70, 50/50, 70/30, and 0/100 (wt.%) NaCl/Na$_2$SO$_4$ were oxidized at 750 °C for 1−49 h periods. According to a parabolic rate constant ($k_p$) value, the aluminized steel with deposit composition of 70/30 NaCl/Na$_2$SO$_4$ shows the highest $k_p$ value ($3.71 \times 10^{-11}$ g$^2$ cm$^{-4}$ s$^{-1}$), later followed by the $k_p$ value of 3.35 $\times$ 10$^{-11}$ g$^2$ cm$^{-4}$ s$^{-1}$ for 100/0 and the lowest $k_p$ value is 7.731 $\times$ 10$^{-12}$ g$^2$ cm$^{-4}$ s$^{-1}$ for 0/100. Whereas, the $k_p$ value for the aluminized steel without NaCl/Na$_2$SO$_4$ deposit is around 2.23 $\times$ 10$^{-13}$ g$^2$ cm$^{-4}$ s$^{-1}$. The presence of both salts and their mixtures destroyed protective Al$_2$O$_3$ layer on the aluminized steel, leading to the Fe$_2$O$_3$ growth locally. Whereas, the penetration of sulfur into the Al$_2$O$_3$ scale lead to the formation of Al$_2$S$_3$ and FeS in the aluminide coating. Therefore, the kinetics rate was increased. Furthermore, mixtures of 70 wt. % NaCl in Na$_2$SO$_4$ depositing on the aluminized steel produced the highest parabolic rate constant because the aluminate layer on the steel substrate experienced severe corrosion attack, leading to fail in formation of protective Al$_2$O$_3$ layer.

1. Introduction

AISI 4130 steel can be used as a candidate material for pipe component in the Geothermal Power Plants (GPP), operating under a high-pressure condition. The pipe is recommended to operate at temperatures about 370 °C [1]. The presence of corrosive elements such as chlorine and sulfur with water vapor can be considered as a very important problem in the pipeline [2,3]. Although, AISI 4130 steel contains Cr approximately 1.10 wt.%, the steel in the pipe components can be subjected to steam oxidation and corrosion attacks. Several studies have
shown that the formation of protective Cr₂O₃ layer on iron-chromium alloys (Fe-Cr alloys) is inhibited by forming chromium hydroxide (CrO₂(OH)₂) due to water vapor oxidation [4], oxychloridation [5], and sulphidation [6]. Therefore, the process of the pipe component design for the use of a steam pipe in the geothermal production wells should be considered comprehensively with respect to the oxidation and corrosion resistance and its strength of materials.

One appropriate solution in increasing the oxidation and corrosion resistance of AISI 4130 steel at high temperatures is the hot-dip aluminizing coating. The aluminide layer formed on the steel can form a protective Al₂O₃ layer during a high temperatures service. The alumina (Al₂O₃) scale is more protective and stable at high temperature than the chromia scale (Cr₂O₃) [7]. In the present study, the influence of deposits NaCl, Na₂SO₄, and mixtures of both salts deposited on the aluminized AISI 4130 steel was studied by isothermal oxidation testing at 750 °C for a duration of time 1-49 h.

2. Experiment

AISI 4130 steel plate with a chemical composition (wt. %): 0.3C−1.10Cr−0.25Mo−0.60Mn−0.035P−0.045S−0.30Si and Fe−balance, were cut into a coupon with 20 mm × 10 mm × 2 mm size. Details of specimen preparation and aluminizing process with Al−99 wt.% at 700 °C for 16 s was similar to the previous study [8]. Solution of NaCl/Na₂SO₄ with a composition ratio (wt.%): 100/0, 30/70, 50/50, 70/30 and 0/100 were prepared into 200 mL sprayer gun, respectively. All aluminized specimens were placed on the hot-plate at 200 °C, and then sprayed by solution of NaCl/Na₂SO₄ until both of the largest specimen surface respectively formed salt deposits with the total weight of 2 mg/cm². Each specimen was put into a mini crucible of 15 mL and then exposed to a box furnace at 750 °C for 1, 4, 9, 25, and 49 h in static air.

Both weight gain (mg/cm²) and oxidation time (h) data were respectively plotted in the linear and parabolic curves. The morphology, microstructure, and chemical composition of samples were observed and analyzed using Optical Microscope (OM), Scanning Electron Microscopy (SEM), and Electron Dispersive Spectroscopy (EDS), and the oxide scales and intermetallic phases formed in the aluminide layer were identified using X-ray diffraction (XRD).

3. Results and Discussion

The effect of NaCl/Na₂SO₄ deposit with respect to oxidation kinetics. The weight gain and oxidation time for the aluminized specimen coated with and without NaCl/Na₂SO₄ are shown in Fig. 1a. It can be seen that weight gain increased as oxidation time was prolonged to 49 h.

Figure 1a shows that the oxidation kinetics for the aluminized steel followed a parabolic trend. The specimens with the salt deposit of 70/30 (NaCl/Na₂SO₄) had the highest weight gains and then followed by 100/0 NaCl (Fig. 1a). During the oxidation time of 1−4 h, the specimens with salt deposits of 100/0 underwent the highest increase in weight gain compared with the other specimens as shown in Fig. 1a. Obviously, the aluminized AISI 4130 steel with the NaCl and Na₂SO₄ deposits oxidized at 750 °C for 49 h markedly affected the oxidation kinetics. Specimens without a salts deposit exposed to dry air oxidation experienced the lowest weight gain (Fig. 1a).
Plot of weight gain versus square root of oxidation time was performed to determine the value of the parabolic rate constants ($k_p$) (Fig. 1b). According to the results of linear regression, the $k_p$ value of aluminized AISI 4130 steel with 70/30 (NaCl/Na$_2$SO$_4$) deposits was around $3.71 \times 10^{-11}$ g$^2$ cm$^{-4}$ s$^{-1}$, later followed by the $k_p$ value of $3.35 \times 10^{-11}$ g$^2$ cm$^{-4}$ s$^{-1}$ for 100/0, the $k_p$ value of $2.59 \times 10^{-11}$ g$^2$ cm$^{-4}$ s$^{-1}$ for 50/50, the $k_p$ value of $1.88 \times 10^{-11}$ g$^2$ cm$^{-4}$ s$^{-1}$ for 30/70 and the $k_p$ value of $7.731 \times 10^{-12}$ g$^2$ cm$^{-4}$ s$^{-1}$ for 0/100, respectively. Whereas the $k_p$ value of aluminized AISI 4130 steel without NaCl/Na$_2$SO$_4$ deposit oxidized in dry air was around $2.23 \times 10^{-13}$ g$^2$ cm$^{-4}$ s$^{-1}$. Figure 1b also shows an increase in the weight gain for the aluminized specimens without salt deposits after 4 h oxidation time, the kinetics rate was running in a steady state condition. The parabolic rate constants of the aluminized AISI 4130 steel with a different compositions of NaCl/Na$_2$SO$_4$ deposits showed two orders of magnitude higher than that of the aluminized AISI 4130 steel without salts deposits oxidized in dry air. In addition, the $k_p$ value for the aluminized AISI 4130 steel with Na$_2$SO$_4$ deposit was an order of magnitude higher than that of the same steel without salt deposit. It shows that the presence of NaCl, Na$_2$SO$_4$ deposits and mixtures of both salts on the surface of the aluminized AISI 4130 steel, oxidized at 750 °C, could accelerate the process of oxidation and corrosion by means of destroying the Fe–Al intermetallic layers formed. Therefore, the formation of a protective Al$_2$O$_3$ scale was inhibited.

Characterization of oxidation products. The phase diagram of NaCl/Na$_2$SO$_4$ system is shown in Fig. 2 [9]. Mixtures of 30/70, 50/50, and 70/30 wt.% NaCl/Na$_2$SO$_4$ compositions showed that all salts deposits on the aluminized AISI 4130 steel were completely molten at 750 °C. The deposit of mixtures of both salts fluxes triggered the formation of acids and basids, which would take a place in the hot corrosion process [10]. The typical cross-sectional micrographs of the aluminate layer after the aluminized AISI 4130 steel oxidized for 49 h are shown in Fig. 3. Intermetallic phases and the metal oxide scale formed on the aluminate layer were examined by the X-ray diffraction analysis (Fig. 4). The intermetallic layer formed in the outermost is Fe$_2$Al$_5$ phase and the FeAl$_2$ layer was formed beneath of between Fe$_2$Al$_5$ layer and FeAl layer on the steel substrate as shown in Fig. 3(a–e).

The atomic composition of aluminum was approximately 61.34% for Fe$_2$Al$_5$ phase and 56.63% for FeAl$_2$ phase [8]. Both of the intermetallic phases were the largest aluminum atoms supplier to form a protective Al$_2$O$_3$ scale. It can be observed clearly in Fig. 3(a–d), that the intermetallic layer of Fe$_2$Al$_5$ and FeAl$_2$ on all steel substrate specimens experienced severe damage in the aluminate coating. The protective alumina scale (Al$_2$O$_3$) played an important role as a protective coating for the steel in dry air environment at high temperatures. However, the presence of corrosive chlorine and sulfur elements could destroy the intermetallic Fe$_2$Al$_5$ and FeAl$_2$ layers.

Many studies have reported that the reaction of metal (Fe, Cr and Al alloys) with a molten salt of NaCl/Na$_2$SO$_4$ mixtures can occur in an oxychloridation process, where the metal reacts with oxygen and then reacts again with either chlorine or sulfur [11–13]. Optical microscope observations as shown in Fig. 3(a–d) showed that the presence of NaCl/Na$_2$SO$_4$ deposits on the aluminized steel surface caused severe degradation of the Fe$_2$Al$_5$ and FeAl$_2$ layers due to a corrosion attack by the chlorine. While FeAl layer still remains towards the steel substrate to support in the formation of protective alumina layer (Fig. 3d). As reported by Kobayashi and Yakou [14], Fe$_2$Al$_5$ and FeAl$_2$ are unstable phases at high temperatures because they have large vacancy defects, leading to the formation of voids and cracks in the aluminate layer. Whereas FeAl has higher oxidation resistance and toughness than those of Fe$_2$Al$_5$ and FeAl$_2$ [14]. The intermetallic layer formed in the outermost was in Fe$_2$Al$_5$ phase, and the FeAl$_2$ layer was formed beneath of between Fe$_2$Al$_5$ layer and FeAl layer on the steel substrate, as shown in Fig. 3(a–e).

X-ray diffraction patterns and SEM surface topography of the aluminized steel are respectively shown in Fig. 4 and in Fig. 5. As shown in Fig. 5a, NaCl salt was still found on each specimen surface after the oxidation time was prolonged to 25 h. When the protective alumina scale was formed at the early oxidation stage, the contact between Fe$_2$Al$_5$ and a molten salt flux from mixtures of NaCl/Na$_2$SO$_4$ would be separated. Thus, the oxychloridation reaction at an early stage could be inhibited for a certain amount of time.
As already mentioned above, voids and cracks that were generated in the Fe$_2$Al$_5$ layer were sources for chlorine and sulfur gasses to penetrate into the aluminide layer when the partial pressure of oxygen at the interface of aluminide layer/oxidant gas undergoes to a low partial pressure because of the formation of Al$_2$O$_3$. Chlorine would react with aluminum and iron to form metal-chloride: AlCl$_3$ and FeCl$_3$. In fact, AlCl$_3$ and FeCl$_3$ has the melting point of 182 °C and 304 °C [15], respectively. Therefore, AlCl$_3$ and FeCl$_3$ would vapourize at 750 °C. Then, AlCl$_3$ and FeCl$_3$ was released and reacted again with oxygen to form metal-oxides: Al$_2$O$_3$ and Fe$_2$O$_3$. Iron oxide (Fe$_2$O$_3$) together Al$_2$O$_3$ scale was found on the aluminized specimens after 49 h oxidation, as shown in Fig. 4. The SEM topographies of the aluminized AISI 4130 steel with NaCl, Na$_2$SO$_4$ and mixtures of both salts deposit are shown in Fig. 5(a−c). Whisker of Al$_2$O$_3$ can be observed in Fig. 5b as the result of reaction oxygen with AlCl$_3$ in the crucible with the closed system (crucible volume of 15 mL with a cup). A thin Al$_2$O$_3$ layer and Fe$_2$O$_3$ scale grew apart, causing non-uniform Al$_2$O$_3$ growth (Fig. 5b). It can also be observed that Fe$_2$O$_3$ scale only grew in voids or cracks zone in the aluminide layer. Increasing in thickness of oxide layer on the aluminide layer, as shown in Fig. 3(a−d), was as result of an oxychloridation process after all aluminized specimens were oxidized for 49 h at 750 °C.

Generally it is believed that the failure mechanism of protective metal-oxides due to the penetration of sulfur into the oxide cause cracking and delamination of oxide scale [16]. Nucleation and growth of metal-sulphides occur at the interface oxide/gas initiated by penetrating sulfur into the oxide scale through grain boundaries (short-circuit diffusion) [17] or transport of gas molecules through physical defects (pores or cracks) [18]. In addition, the presence of sulfur on the metal oxide interface can increase the flux of cations that form metal-sulphides in the oxide scale [19].

The results of research showed that the parabolic rate constants ($k_p$) for the aluminized AISI 4130 steel with Na$_2$SO$_4$ deposits increased by one order of magnitude higher than those of aluminized AISI 4130 steel oxidized in dry air, even though Fe$_2$Al$_5$ and FeAl$_2$ layers did not degrade due to sulfur corrosion attack, as shown in Fig. 3e. The results of XRD analysis indicated that the other constituent phases consisted of Fe$_2$O$_3$, Al$_2$O$_3$, Na$_2$SO$_4$, FeS and Al$_2$S$_3$ (Fig. 4), while the intermetallic phase formed on aluminized steel with 100 wt.% Na$_2$SO$_4$ deposit was similar to aluminized steel with 100, 30, 50, 70 wt.% NaCl in Na$_2$SO$_4$, oxidized at 750 °C: Fe$_2$Al$_5$, FeAl$_2$ and FeAl. The results of XRD analysis also showed that NaCl and Na$_2$SO$_4$ were still found on the specimen surface after being oxidizing for 49 h (Fig. 4). The high temperature of the molten both salts: NaCl (801 °C) and Na$_2$SO$_4$ (884 °C) [15], was a reason for both salts remaining on the sample surface after oxidation process occurring.

![Figure 3. Cross-sectional Micrographs of aluminized Steel with a Different Composition of NaCl/Na$_2$SO$_4$ Mixtures Deposits after being oxidized at 750 °C for 49 h](image-url)
Buscaglia et al. [20] studied the hot corrosion behavior of pure iron with Na₂SO₄ deposit at a temperature lower than the melting point of Na₂SO₄. The results showed that sulfate particles dissolved in the oxide matrix for a longer oxidation time. Salt decomposition occurred at a lower oxygen partial pressure, due to the formation of metal-oxide on a metal surface. Therefore, the sulfur produced would be a source for the formation of metal-sulphides (Fig. 4). During the oxidation process progressing, the iron atoms could diffuse through Al₃ vacancy defects via the alumina layer due to the relatively high activity of iron atom at the interface oxide/Na₂SO₄ and a lower partial pressure of oxygen at the interface. Due to a great affinity iron for oxygen, Fe₂O₃ finally grew at the Al₂O₃ scale (Fig. 5c).

4. Conclusions

Mixtures of 70 wt. % NaCl in Na₂SO₄ depositing on the aluminized steel produced the highest parabolic rate constant due to severe aluminide layer damage on the steel. Consequently, the parabolic rate constants (k_p) were increased by two orders of magnitude. Only Al₂O₃ and Fe₂O₃ scale was found on the aluminide layer. All the intermetallic phases formed in the aluminide layer, consisted of Fe₂Al₅, FeAl₂, FeAl, and Fe₂O₃, Al₂S₃, FeS, NaCl, Na₂SO₄. During the oxidation process, the iron atoms could diffuse through Al₃ vacancy defects via the alumina layer due to the relatively high activity of iron atom at the interface oxide/Na₂SO₄ and a lower partial pressure of oxygen at the interface. Due to a great affinity iron for oxygen, Fe₂O₃ finally grew at the Al₂O₃ scale (Fig. 5c).

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References