

High Temperature Corrosion of Aluminized AISI 4130 Steel with the Different Composition of NaCl/Na₂SO₄ 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/Na₂SO₄ 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/Na₂SO₄ shows the highest k_p value ($3.71 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$), later followed by the k_p value of $3.35 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ for 100/0 and the lowest k_p value is $7.731 \times 10^{-12} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ for 0/100. Whereas, the k_p value for the aluminized steel without NaCl/Na₂SO₄ deposit is around $2.23 \times 10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$. The presence of both salts and their mixtures destroyed protective Al₂O₃ layer on the aluminized steel, leading to the Fe₂O₃ growth locally. Whereas, the penetration of sulfur into the Al₂O₃ scale lead to the formation of Al₂S₃ and FeS in the aluminide coating. Therefore, the kinetics rate was increased. Furthermore, mixtures of 70 wt. % NaCl in Na₂SO₄ depositing on the aluminized steel produced the highest parabolic rate constant because the aluminide layer on the steel substrate experienced severe corrosion attack, leading to fail in formation of protective Al₂O₃ layer.

Abstrak

Korosi Temperatur Tinggi Baja AISI 4130 Lapis Aluminium dengan Komposisi Endapan NaCl/Na₂SO₄ Berbeda. Ketahanan korosi temperatur tinggi baja AISI 4130 dapat ditingkatkan melalui pelapisan aluminium celup panas. Larutan NaCl/Na₂SO₄ dengan komposisi 100/0, 30/70, 50/50, 70/30, dan 0/100 (wt.%) diendapkan pada permukaan spesimen baja lapis aluminium dan kemudian dioksidasi pada 750 °C selama 1 sampai 49 h. Berdasarkan nilai konstanta laju parabolik (k_p) baja lapis aluminium dengan komposisi endapan 70/30 NaCl/Na₂SO₄ menghasilkan nilai k_p yang tertinggi, yaitu $k_p = 3.71 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$, kemudian diikuti nilai $k_p = 3.35 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ untuk 100/0 dan nilai k_p yang terendah adalah $7.731 \times 10^{-12} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ untuk 0/100. Sedangkan nilai k_p untuk baja lapis aluminium tanpa endapan NaCl/Na₂SO₄ adalah $2.23 \times 10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$. Keberadaan NaCl, Na₂SO₄ dan campuran keduanya merusak pembentukan lapisan protektif Al₂O₃ pada baja lapis aluminium, yang memicu pertumbuhan Fe₂O₃ secara lokal. Sedangkan, masuknya sulfur ke dalam lapisan Al₂O₃ memicu pembentukan Al₂S₃ dan FeS. Oleh karena itu, laju kinetika korosi ditingkatkan. Selanjutnya, endapan campuran 70% NaCl dalam Na₂SO₄ pada baja lapis aluminium menghasilkan nilai k_p tertinggi karena lapisan intermetalik Fe-Al pada substrat baja mengalami serangan korosi yang parah, menghasilkan kegagalan dalam pembentukan lapisan protektif Al₂O₃.

Keywords: aluminized steel, corrosion resistance, Al₂O₃ layer, NaCl/Na₂SO₄ deposit, parabolic rate constant

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 Cr_2O_3 layer on iron-chromium alloys (Fe-Cr alloys) is inhibited by forming chromium hydroxide ($\text{CrO}_2(\text{OH})_2$) 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 Al_2O_3 layer during a high temperatures service. The alumina (Al_2O_3) scale is more protective and stable at high temperature than the chromia scale (Cr_2O_3) [7]. In the present study, the influence of deposits NaCl, Na_2SO_4 , 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–0.04S–0.30Si and Fe–balance, were cut into a coupon with 20 mm \times 10 mm \times 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/ Na_2SO_4 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 to the hot-plate at 200°C , and then sprayed by solution of NaCl/ Na_2SO_4 until both of the largest specimen surface respectively formed salt deposits with the total weight of 2 mg/cm^2 . 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/cm^2) 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/ Na_2SO_4 deposit with respect to oxidation kinetics. The weight gain and oxidation time for the aluminized specimen coated with and without NaCl/ Na_2SO_4 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/ Na_2SO_4) 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 under went 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 Na_2SO_4 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).

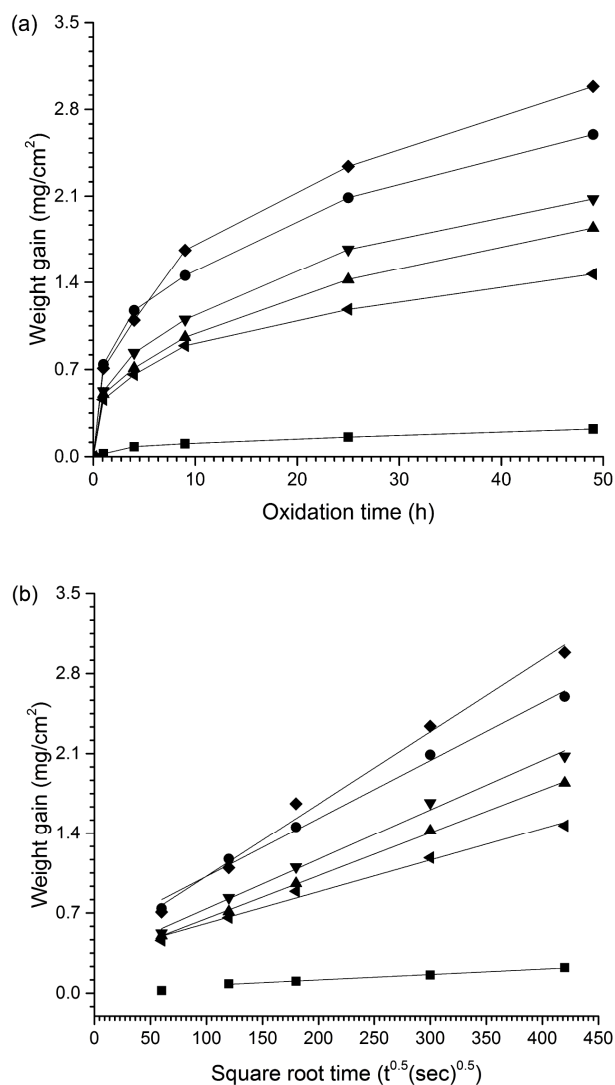


Figure 1. (a) Plot of Weight Gain vs. Oxidation Time and (b) Plot of Parabolic Weight Gain vs. $t^{0.5}$ for the aluminized AISI 4130 Steel with and without NaCl/ Na_2SO_4 Deposits oxidized at 750°C , ■0/0, ●100/0, ▲30/70, ▼50/50, ◆70/30, ◀0/100

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/Na₂SO₄) deposits was around $3.71 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$, later followed by the k_p value of $3.35 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ for 100/0, the k_p value of $2.59 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ for 50/50, the k_p value of $1.88 \times 10^{-11} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ for 30/70 and the k_p value of $7.731 \times 10^{-12} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ for 0/100, respectively. Whereas the k_p value of aluminized AISI 4130 steel without NaCl/Na₂SO₄ deposit oxidized in dry air was around $2.23 \times 10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$. 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/Na₂SO₄ 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 Na₂SO₄ deposit was an order of magnitude higher than that of the same steel without salt deposit. It shows that the presence of NaCl, Na₂SO₄ 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 Al₂O₃ scale was inhibited.

Characterization of oxidation products. The phase diagram of NaCl/Na₂SO₄ system is shown in Fig. 2 [9]. Mixtures of 30/70, 50/50, and 70/30 wt.% NaCl/Na₂SO₄ 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 bacids, which would take a place in the hot corrosion process [10]. The typical cross-sectional micrographs of the aluminide 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 aluminide layer were examined by the X-ray diffraction analysis (Fig. 4). The intermetallic layer formed in the outermost is Fe₂Al₅ phase and the FeAl₂ layer was formed beneath of between Fe₂Al₅ 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 Fe₂Al₅ phase and 56.63% for FeAl₂ phase [8]. Both of the intermetallic phases were the largest aluminum atoms supplier to form a protective Al₂O₃ scale. It can be observed clearly in Fig. 3(a–d), that the intermetallic layer of Fe₂Al₅ and FeAl₂ on all steel substrate specimens experienced severe damage in the aluminide coating. The protective alumina scale (Al₂O₃) 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 Fe₂Al₅ and FeAl₂ layers.

Many studies have reported that the reaction of metal (Fe, Cr and Al alloys) with a molten salt of NaCl/Na₂SO₄ 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/Na₂SO₄ deposits on the aluminized steel surface caused severe degradation of the Fe₂Al₅ and FeAl₂ 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], Fe₂Al₅ and FeAl₂ are unstable phases at high temperatures because they have large vacancy defects, leading to the formation of voids and cracks in the aluminide layer. Whereas FeAl has higher oxidation resistance and toughness than those of Fe₂Al₅ and FeAl₂ [14]. The intermetallic layer formed in the outermost was in Fe₂Al₅ phase, and the FeAl₂ layer was formed beneath of between Fe₂Al₅ 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 Fe₂Al₅ and a molten salt flux from mixtures of NaCl/Na₂SO₄ would be separated. Thus, the oxychloridation reaction at an early stage could be inhibited for a certain amount of time.

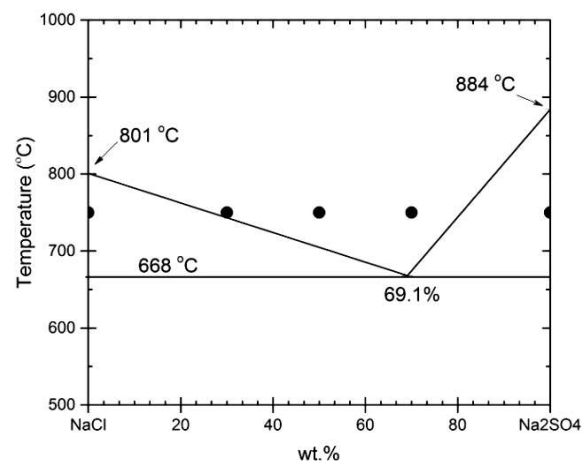


Figure 2. The Hypothetical Phase Diagram of the NaCl/Na₂SO₄ System [9]. Bullets Stand corresponding to the Experimental Temperature at 750 °C with a Different Composition of NaCl/Na₂SO₄

As already mentioned above, voids and cracks that were generated in the Fe_2Al_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_2O_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_2O_3 and Fe_2O_3 . Iron oxide (Fe_2O_3) together Al_2O_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 stel with NaCl , Na_2SO_4 and mixtures of both salts deposit are shown in Fig. 5(a–c). Whisker of Al_2O_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_2O_3 layer and Fe_2O_3 scale grew apart, causing non-uniform Al_2O_3 growth (Fig. 5b). It can also be observed that Fe_2O_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_2SO_4 deposits increased by one order of magnitude higher than those of aluminized AISI 4130 steel oxidized in dry air, even though Fe_2Al_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_2O_3 , Al_2O_3 , Na_2SO_4 , FeS and Al_2S_3 (Fig. 4), while the intermetallic phase formed on aluminized steel with 100 wt.% Na_2SO_4 deposit was similar to aluminized steel with 100, 30, 50, 70 wt.% NaCl in Na_2SO_4 , oxidized at 750°C : Fe_2Al_5 , FeAl_2 and FeAl . The results of XRD analysis also showed that NaCl and Na_2SO_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_2SO_4 (884°C) [15], was a reason for both salts remaining on the sample surface after oxidation process occurring.

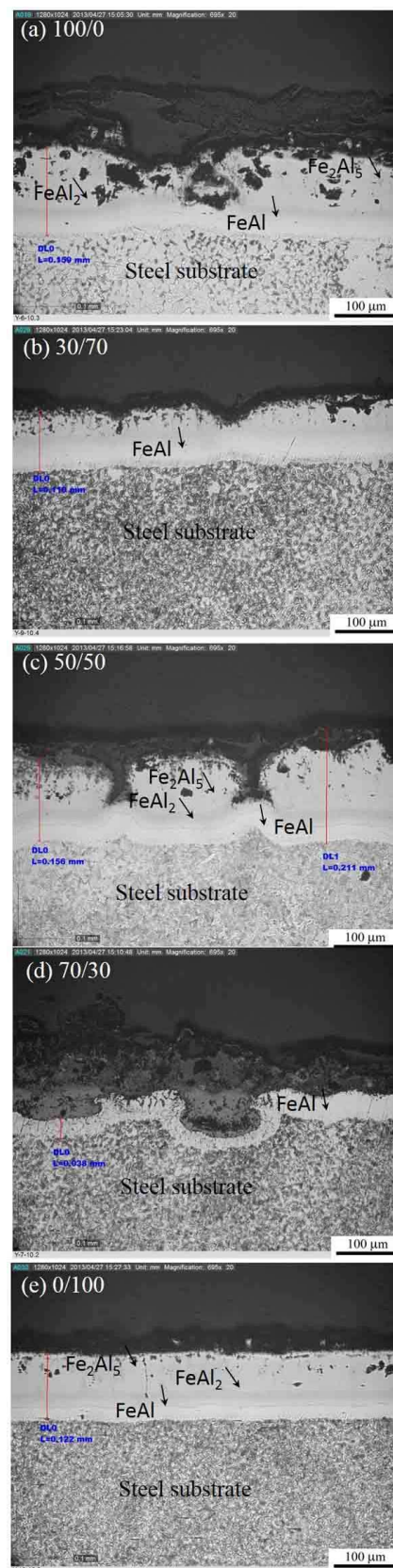


Figure 3. Cross-sectional Micrographs of aluminized Steel with a Different Composition of $\text{NaCl}/\text{Na}_2\text{SO}_4$ Mixtures Deposits after being oxidized at 750°C for 49 h

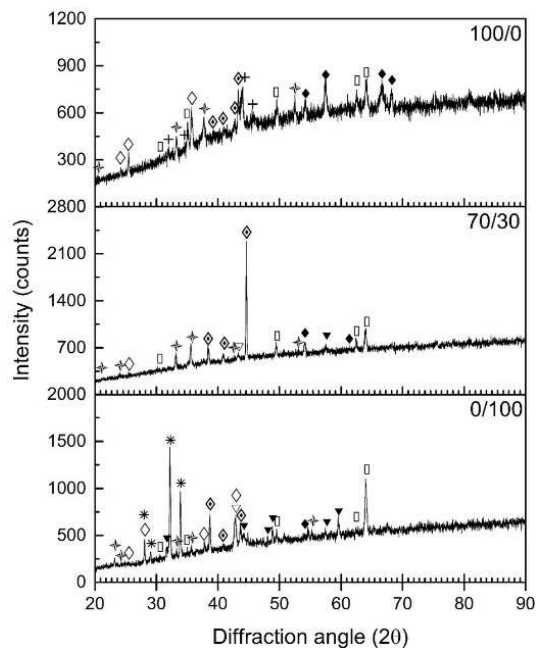


Figure 4. X-ray Diffraction Patterns of the aluminized AISI 4130 Steel with NaCl/Na₂SO₄ Deposits oxidized at 750 °C for 49 h, \diamond Fe₂Al₅, \blacklozenge FeAl₂, \blacklozenge FeAl, \blacklozenge Al₂O₃, \square Fe₂O₃, \blacktriangledown Al₂S₃, ∇ FeS, $+$ NaCl, $*$ Na₂SO₄

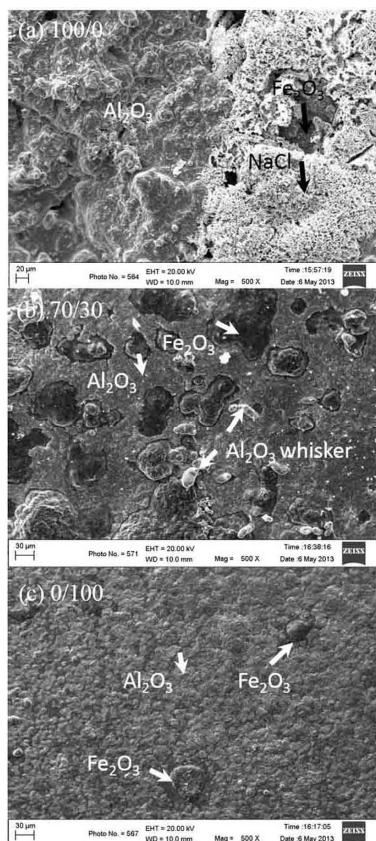


Figure 5. SEM of Surface Topographies of the Aluminized AISI 4130 Steel with (a) 100/0, (b) 70/30 and (c) 0/100 NaCl/Na₂SO₄ Deposits Oxidized at 750 °C for 25 h

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 Al^{III} 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 and FeAl for all aluminized steel with and without NaCl, Na₂SO₄, and mixtures of both salts deposits after the aluminized steel was oxidized at 750 °C. The protective Al₂O₃ layer failed to protect the steel due to local formation of Fe₂O₃ scale. The cyclic oxychloridation process producing the AlCl₃ and FeCl₃ was responsible to destroy the aluminide layer. However, for the long-term oxidation time of 49 h, the FeAl layer on the steel substrate was much more resistant with respect to corrosion attack. Penetration of sulfur into the Al₂O₃ layer generated a metal-sulphides formation; Al₂S₃ and FeS. In addition, a high affinity of iron caused Fe₂O₃ growth locally, resulting an increase in the parabolic rate constant of one higher magnitude order.

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