

# High-temperature corrosion of aluminized-AISI 1020 steel with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits

*By* Muhammad Badaruddin



4

## High-temperature corrosion of aluminized-AISI 1020 steel with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits

M BADARUDDIN<sup>1,\*</sup>, SUGIYANTO<sup>1</sup> and D ASMI<sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering, Faculty of Engineering, Universitas Lampung, Bandar Lampung 35145, Indonesia

<sup>2</sup>Department of Physics, Faculty of Mathematics and Natural Science, Universitas Lampung, Bandar Lampung 35145, Indonesia

\*Author for correspondence (mbruddin@eng.unila.ac.id)

MS received 27 August 2018; accepted 10 July 2019

**Abstract.** High-temperature corrosion of aluminized-American Iron and Steel Institute (AISI) 1020 steel with sodium chloride (NaCl) and sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) deposits was studied using isothermal oxidization in a dry air environment at 700°C for 49 h. NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits on the aluminide layer interfered with protective alumina/aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) scale formation on the steel substrate. Chlorine and sulphur gases (Cl<sub>2g</sub> and S<sub>g</sub>, respectively) released into the atmosphere corroded the protective Al<sub>2</sub>O<sub>3</sub> layer. Corrosion of the Al<sub>2</sub>O<sub>3</sub> layer was also due to local formation of iron oxide (Fe<sub>2</sub>O<sub>3</sub>). Fe<sub>2</sub>O<sub>3</sub> growth is attributed to ferric chloride (FeCl<sub>3</sub>) vaporization. S<sub>g</sub> diffusion into the Al<sub>2</sub>O<sub>3</sub> scale via Al<sup>3+</sup> vacancy defects led to the formation of aluminium sulphide on the aluminide layer surface. Cl and S consequently induced hot corrosion of the aluminized steel, thereby increasing cyclic oxychloridation and sulphidation rates at high temperatures.

**Keywords.** Aluminized 1020 steel; hot corrosion; oxychloridation; sulphidation; alumina/aluminium oxide (Al<sub>2</sub>O<sub>3</sub>).

### 1. Introduction

Cold-rolled American Iron and Steel Institute (AISI) 1020 steel is a material suitable for engineering components because of its relatively low cost compared with that of high-alloy steel. This steel is used in heat exchangers, oil gas tanks, high-pressure water pipes and other equipment for fossil fuel power plants. Alkali metal sulphates produced by low-grade fuel combustion react with sodium chloride (NaCl) from ocean breezes at elevated temperatures, forming sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), which severely corrodes the material by oxidation, sulphidation or chloridation, thus rendering it prone to hot corrosion [1–3]. Therefore, the presence of NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits on engineering material components at high temperatures causes rapid degradation of the material [4,5]. In this regard, hot-dipped aluminide steel has great potential in engineering components for harsh environments. Several studies have reported that the aluminium (Al) coating and its alloys can improve carbon steel resistance to oxidation at high temperatures [6–8]. The aluminide layer on steel can supply Al atoms and form a protective aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) layer.

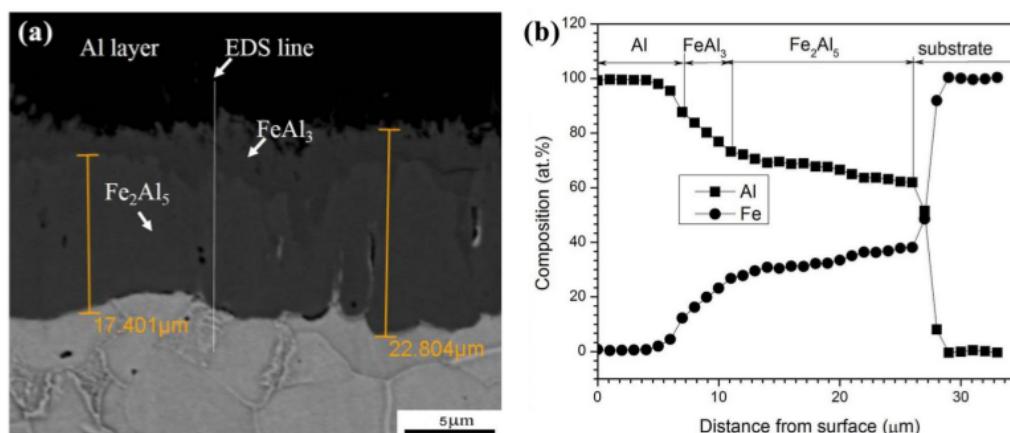
To widen the application range and service life of aluminide steel, hot-corrosion behaviour and its related mechanism must be characterized. Therefore, we studied the effects of NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits on the surfaces of aluminized and bare

steel (AS and BS) by isothermally oxidizing them at 700°C for 49 h in a static-air environment. The corrosion kinetics was analysed to determine the parabolic rate constant of corrosion ( $k_p$ ). Oxidized AS samples were characterized by both optical and scanning electron microscopy (OM and SEM, respectively), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) to determine the possible corrosion causing mechanisms.

### 2. Experimental

#### 2.1 Specimen preparation

A commercial cold-rolled AISI 1020 steel plate with a chemical composition of 0.2C–0.05P–0.05S–0.5Mn (wt%; iron [Fe]-balanced) was cut into specimens with dimensions of 20 × 10 × 2 mm<sup>3</sup>. Before Al deposition, all specimens were ultrasonically cleaned with a solution of 5% sodium hydroxide (NaOH) and 10% phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and then covered with Al welding flux pasta. Commercial 40.5 wt% silicon (Si) was melted in an alumina (Al<sub>2</sub>O<sub>3</sub>) crucible at 700°C, and the specimens were then dipped for 16 s in a molten Al bath. After the aluminizing process, oxide flux deposited on the surface of the aluminized specimens was



**Figure 1.** SEM and EDS results: (a) cross-sectional micrograph and (b) iron (Fe) and aluminium (Al) element line-scan results for aluminized AISI 1020 steel.

cleaned with a solution of nitric acid,  $H_3PO_4$  and water (1:1:1, v/v) at room temperature.

## 2.2 Corrosion testing and characterization of samples

A saturated NaCl and  $Na_2SO_4$  solution was sprayed onto the largest surface of each specimen placed on a 200°C hot plate to form deposits at a concentration of  $2 \text{ mg cm}^{-2}$ . A salt of NaCl and  $Na_2SO_4$  at a concentration of  $2 \text{ mg cm}^{-2}$  was similar to that reported in the literature [9,10]. All BS and AS specimens with NaCl and  $Na_2SO_4$  coatings were isothermally oxidized at 700°C for 1–49 h. In the present investigation, a temperature of around 700°C is referred to as type-II hot corrosion, which occurs at temperatures below that of salt melting [11].

After a given isothermal oxidation time, the specimens were removed and cooled in air at room temperature. Each data point for corrosion kinetic-related weight gain was obtained from a different specimen. Linear and parabolic plots of the weight gain ( $\text{mg cm}^{-2}$ ) vs. oxidation time (h) were constructed. The aluminide layer thickness and microstructures of aluminized specimens were observed by OM. The phases formed on steel were identified by XRD using monochromatic Cu K $\alpha$  radiation at 40 kV and 100 mA. The surface and cross-sectional morphologies of AS were examined by SEM and EDS, respectively.

## 3. Results and discussion

### 3.1 Examination of the coated specimen

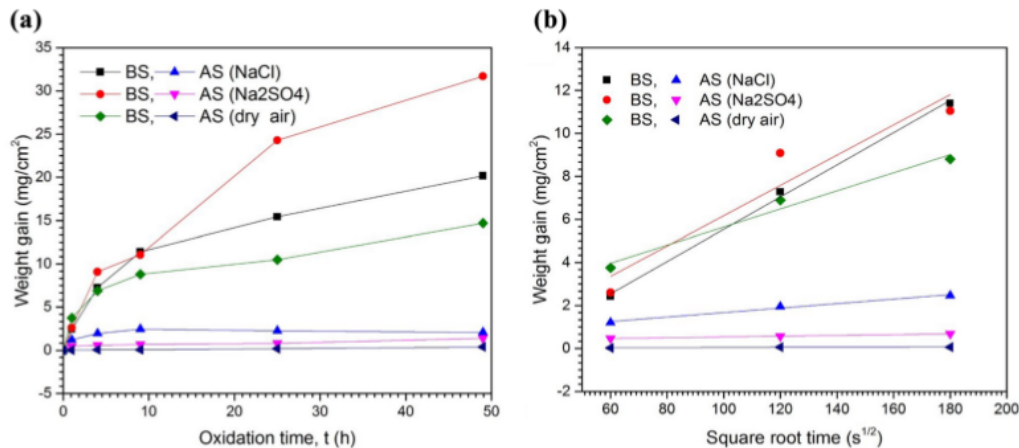
An SEM cross-sectional micrograph and EDS element line scan for the aluminide coating and the steel substrate after the aluminizing process are displayed in figure 1a and b, respectively. When low-carbon steel and molten Al came into contact with each other during the hot-dipping process, a thin

intermetallic compound (IMC) formed between the steel and aluminide layer. However, not all of the IMCs formed during the aluminizing hot-dip coating, except for the  $Fe_2Al_5$  and  $FeAl_3$  phases, could be confirmed [12].

The formation of the IMCs in the Al-rich zone suggests that inward diffusion of Fe and outward diffusion of Al predominantly controlled the phase transformation and formed an aluminide layer on the steel substrate. The thickness of the aluminide layer consisting of the Al and  $FeAl_3/Fe_2Al_5$  intermetallic layers was about 50  $\mu\text{m}$  ( $FeAl_3$ : 5.403  $\mu\text{m}$  and  $Fe_2Al_5$ : 17.401  $\mu\text{m}$ ). This coating layer showed no cracks and voids at the interface between the aluminide layer and steel substrate. In addition, an EDS element line scanning showed that the Fe content of the Al coating was much less than that of the intermetallic layer. This may have been caused by the lower diffusion rate of Fe atoms in molten Al compared with that of Al atoms in Fe [13]. The Al content decreased while the  $FeAl_3$  and  $Fe_2Al_5$  content increased towards the steel substrate after formation of the aluminizing coating by the hot-dip process (figure 1b).

### 3.2 Corrosion kinetics

Figure 2a shows the corrosion kinetics of AS after oxidation at 700°C for 49 h in various environments. Corresponding data for BS are also included for comparison. As seen in figure 2a, BS showed a rapid weight gain for up to 49 h. As weight gain caused by NaCl deposits was slow during the initial corrosion stage (up to 9 h;  $2.5 \text{ mg cm}^{-2}$ ), the rate gradually decreased to  $2.1 \text{ mg cm}^{-2}$  after 49 h of corrosion. Similarly, AS with  $Na_2SO_4$  deposits showed a slow weight gain at  $1.4 \text{ mg cm}^{-2}$  after 49 h of corrosion. AS showed weight gains lower than those of AS specimens with NaCl and  $Na_2SO_4$  deposits oxidized at 700°C in dry air.



**Figure 2.** Corrosion kinetics of BS and aluminized AISI 1020 steel at 700°C: (a) linear plot at 49 h and (b) parabolic plot at 9 h.

Pieraggi [14] suggested that plots of a weight gain ( $\Delta W$ ) vs.  $t^{1/2}$  may be a more useful and accurate analysis for the real effect on the oxidation kinetics of pure metals due to primary oxide scale growth. Therefore, plots of weight gain and square roots of time for all specimens undergoing oxidation for 9 h in the parabolic regime are displayed in figure 2b, and the parabolic rate constant ( $k_p$ ) was determined by linear regression. The  $k_p$  values for BS with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits were  $3.721 \times 10^{-9}$  and  $4.122 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ , respectively; the  $k_p$  value for BS without NaCl or Na<sub>2</sub>SO<sub>4</sub> deposits oxidized in dry air was  $2.735 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ . The  $k_p$  values for AS with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits were  $1.082 \times 10^{-10}$  and  $3.204 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ , respectively, and that for AS in dry air was  $7.517 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ . According to the  $k_p$  values, the aluminide layer on AISI 1020 steel appears to play an important role in forming a protective alumina/aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) scale [8,15]. Consequently,  $k_p$  values for AS with NaCl and Na<sub>2</sub>SO<sub>4</sub> coatings decreased by one and three orders of magnitude, respectively. These reductions are attributed to the growth of an Al<sub>2</sub>O<sub>3</sub> layer, which led to the establishment of a barrier at the Al<sub>2</sub>O<sub>3</sub>/aluminide layer interface [16].

The oxidation rates for AS with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits were three and one order(s), respectively, of magnitude higher than those of AS in dry air (figure 2b). This enhancement is attributed to the presence of gaseous chlorine (Cl<sub>2</sub>) and sulphur (S<sub>2</sub>) from NaCl and Na<sub>2</sub>SO<sub>4</sub> decomposition [1,5,7,17,18] via the metal-oxide reaction with Cl and S particles, which led to an active corrosion phenomenon at the Al<sub>2</sub>O<sub>3</sub>/aluminide coating interface. The weight gain of AS containing NaCl deposits decreased slowly at oxidation times ranging from 9 to 49 h. This slow decrease may have been due to disruption of Al<sub>2</sub>O<sub>3</sub> scale growth by Cl via cyclic oxychlorination, which forms volatile metal chlorides [7,9,19].

### 3.3 Hot-corrosion mechanisms in AS

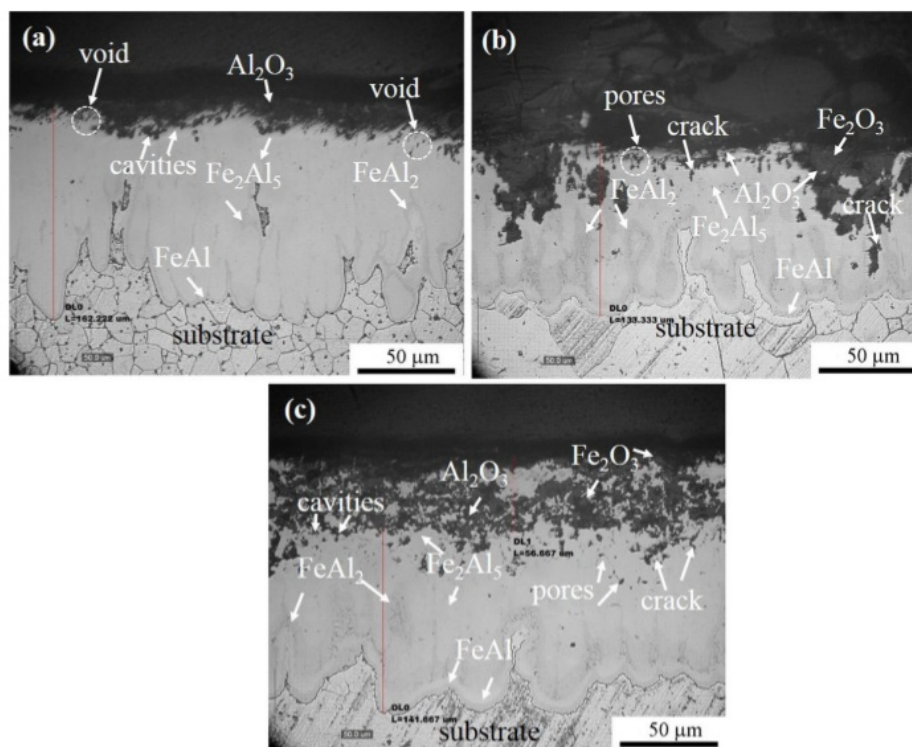
To elucidate the hot-corrosion behaviour and phase transformation in the aluminide layer, saturated NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions were deposited on AS specimen surfaces, which were then isothermally oxidized at 700°C for 1–49 h. In the present study, we speculated that during the initial stages of oxidation, the kinetics was controlled by oxidation of the aluminide coating with oxygen to form Al<sub>2</sub>O<sub>3</sub>. In further stages of oxidation, hot corrosion occurs in which Al<sub>2</sub>O<sub>3</sub> later reacts with the salt deposits and forms a mixture of salts having a lower-melting point than the original salts. The melting points of NaCl and Na<sub>2</sub>SO<sub>4</sub> salts were 801 and 884°C [20], respectively. The NaCl hot-corrosion mechanisms at a 700°C appeared to be similar to those reported by Ciszak *et al* [18] and Godlewska *et al* [21]. Furthermore, the Na<sub>2</sub>SO<sub>4</sub> hot-corrosion mechanisms at 700°C appear to be similar to those reported by Shi [17] and Yan *et al* [19]. Thermodynamic data for the reaction kinetics of Fe and Al in the formation of metal chlorides and sulphates were determined based on Gibbs free energy change ( $\Delta G$ ) calculations [22].  $\Delta G$  values at 700°C are tabulated in table 1. Table 1 shows a detailed summary of the possible chemical reactions for accelerating hot-corrosion processes of aluminide layers with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits.

The cross-sectional morphologies of AS specimens with NaCl deposits hot corroded at 700°C for 1, 9 and 25 h are presented in figure 3. After 1 h of oxidation, an Fe<sub>2</sub>Al<sub>5</sub>/FeAl<sub>2</sub> layer and a thin FeAl layer formed on the steel substrate (figure 3a). The thickness of the aluminide layer depended on the diffusional processing at high temperatures between Al atoms from the aluminide coating and Fe atoms from the steel substrate [13], in which the diffusion coefficient of Fe into Al was  $53 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (520–1050°C) [23], which was larger than that of Al into Fe,  $1.8 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (730–1400°C) [24].



**Table 1.** Gibbs free energy change ( $\Delta G$ ) of reaction [22].

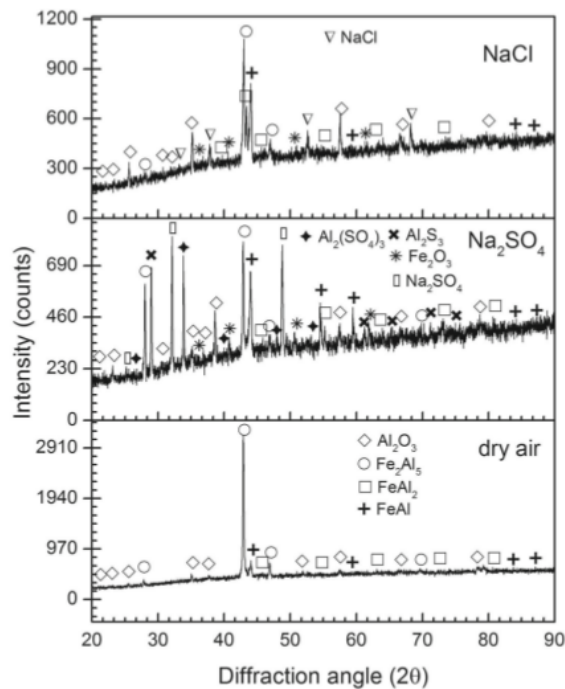
	$\Delta G_{700}$ (kJ)
NaCl hot corrosion	
$2\text{Al}_{(s)} + 2\text{NaCl}_{(s)} + 2\text{O}_{2(g)} \rightarrow \text{Al}_2\text{O}_{3(s)} + \text{Na}_2\text{O}_{(s)} + \text{Cl}_{2(g)}$	-1010.4
$2\text{Al} + 3\text{Cl}_{2(g)} \rightarrow 2\text{AlCl}_{3(s)}$	-471.6
$4\text{AlCl}_{3(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{Al}_2\text{O}_{3(s)} + 6\text{Cl}_{2(g)}$	-592.4
$2\text{Fe} + 3\text{Cl}_{2(g)} \rightarrow 2\text{FeCl}_{3(s)}$	-157.6
$4\text{FeCl}_{3(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{Fe}_2\text{O}_3 + 6\text{Cl}_{2(g)}$	-109.3
$2\text{Al}_{(s)} + 3/2\text{O}_{2(g)} \rightarrow \text{Al}_2\text{O}_{3(s)}$	-1383.1
Na <sub>2</sub> SO <sub>4</sub> hot corrosion	
$2\text{Al}_{(s)} + 3\text{SO}_{3(s)} + 3\text{O}_{2(g)} \rightarrow \text{Al}_2(\text{SO}_4)_3$	-807.0
$9\text{Al}_{(s)} + 3/2\text{S}_{(s)} \rightarrow \text{Al}_2\text{S}_3$	-676.5
$\text{Fe}_{(s)} + \text{SO}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{FeSO}_{4(s)}$	-275.6
$\text{FeSO}_4 \rightarrow 1/2\text{Fe}_2\text{O}_3 + \text{SO}_2 + 1/4\text{O}_{2(g)}$	-7.2
$\text{SO}_{2(g)} + 1/2\text{O}_{2(g)} \rightarrow \text{SO}_{3(g)}$	-7.6



**Figure 3.** OM cross-sectional micrographs of AS with NaCl deposits oxidized at 700°C for (a) 1 h, (b) 9 h and (c) 25 h.

Therefore, the thickness of an aluminide layer was 162  $\mu\text{m}$  and consisted of  $\text{Fe}_2\text{Al}_5$ ,  $\text{FeAl}_2$  and  $\text{FeAl}$  layers and a thin  $\text{Al}_2\text{O}_3$  scale (figure 3a). In addition, some voids could be observed in the outer part of the aluminide layer (figure 3a) as a result of outward diffusion of Al atoms to form the  $\text{Al}_2\text{O}_3$  scale, which presented thin and dense characteristics and consisted of an adherent  $\text{Al}_2\text{O}_3$  layer on the aluminide layer.

As the oxidation time increased to 9 and 25 h, the thickness of the  $\text{Fe}_2\text{Al}_5/\text{FeAl}_2$  intermetallic layer decreased due to hot-corrosion attack in the aluminide coating (figure 3b and c). Some coarse voids and cavities formed in the outer part were filled with a mixture of oxides beneath the  $\text{Al}_2\text{O}_3$  scale as shown in figure 3b and c. XRD examination indicated that identical intermetallic phases ( $\text{Fe}_2\text{Al}_5$ ,  $\text{FeAl}_2$  and

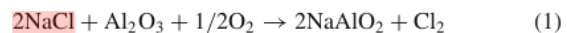


**Figure 4.** XRD patterns of AS specimens oxidized at 700°C for 9 h in three different environments.

FeAl) formed in the aluminide layer after oxidation of the AS specimens containing NaCl and Na<sub>2</sub>SO<sub>4</sub> at 700°C during oxidation progress in an air atmosphere (figure 4). As oxidation time increased, void formation due to outward/inward Al transport predominantly formed pores in the outer part and in the aluminide layer, which is known as the Kirkendall effect [25]. Later, an interconnection of coalescing pores generated crack paths and allowed oxygen (O), Cl<sub>2g</sub> and S<sub>g</sub> penetration into the aluminide layer, forming the internal oxides (figure 3b and c). The protective Al<sub>2</sub>O<sub>3</sub> layer formed during the early stages could protect the aluminide layer that was directly in contact with NaCl. However, after 25 h of corrosion, the Fe<sub>2</sub>Al<sub>5</sub>/FeAl<sub>2</sub> layer was severely degraded (figure 3c). This result implies that the NaCl deposit plays an important role in the hot-corrosion behaviour of the aluminide layer over long periods.

Figure 4 displays the XRD results for the AS with and without NaCl and Na<sub>2</sub>SO<sub>4</sub> salt deposits, which confirmed the presence of the oxidation product, Al<sub>2</sub>O<sub>3</sub> scale, together with some iron oxide (Fe<sub>2</sub>O<sub>3</sub>) scales. The low-intensity diffraction peaks of Al<sub>2</sub>O<sub>3</sub> seen in the XRD spectrum in figure 4 were due to the thin Al<sub>2</sub>O<sub>3</sub> scale on the AS specimens oxidized in air. The intensities of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> peaks for AS specimens with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits increased, indicating that the corrosion layer thickened. It may be argued that Fe<sub>2</sub>Al<sub>5</sub>, FeAl<sub>2</sub> and FeAl can behave as Al reservoirs that maintain the growth of the Al<sub>2</sub>O<sub>3</sub> scale during long-term oxidation.

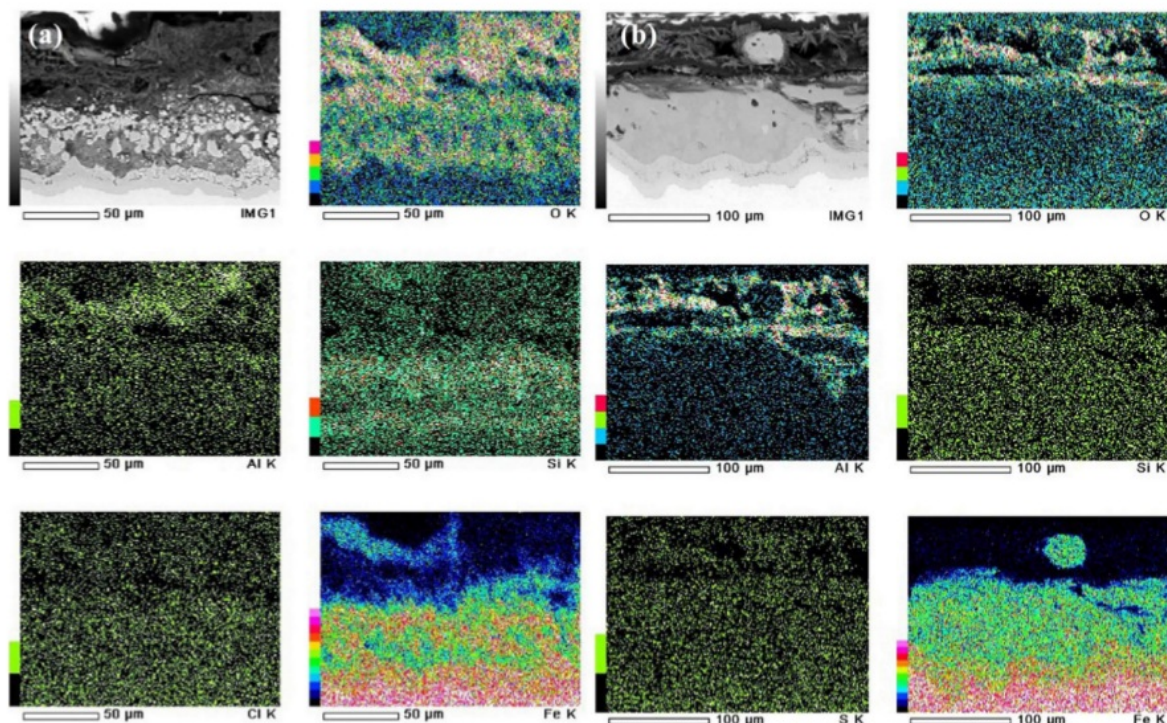
As mentioned above, some pores became interconnected and resulted in crack features in which oxidant and corrosive gases consisting of O<sub>2g</sub>, Cl<sub>2g</sub> and sulphur trioxide (SO<sub>3g</sub>) penetrated into the aluminide layer through the pores and crack paths [25]. The relative decrease in weight gains of the NaCl-deposited AS specimens during a longer oxidation time (9 h) of exposure is believed to be caused by reactions involving metal, NaCl and O, which prevented the formation of a protective oxide scale. As reported by Ciszak *et al* [18], Cl<sub>2g</sub> is the first major gaseous species that forms during the reaction of Na-Ti oxides at 560°C. In the present study, the Al<sub>2</sub>O<sub>3</sub> formed during the early stage could further react with NaCl and O in the gas atmosphere according to the following reaction [21]:



Cl<sub>2g</sub> was generated by the reaction among Al<sub>2</sub>O<sub>3</sub>, NaCl(s) and O<sub>2g</sub> in which Na–Al oxides that readily penetrated the Fe<sub>2</sub>Al<sub>5</sub>/FeAl<sub>2</sub> layer through crack paths generated during oxidation were also formed. The Cl<sub>2g</sub> caused corrosion of the aluminide layer, thereby forming the metal chlorides, ferric chloride (FeCl<sub>3</sub>) and AlCl<sub>3</sub>. Both Fe and Al were the driving forces behind metal-chloride formation in the aluminide layer during the initial stages of the reaction [7]. Furthermore, Fe and Al could have dissolved in the molten salt and volatilized or reacted with O. The melting points of AlCl<sub>3</sub> and FeCl<sub>3</sub> were 182 and 304°C, respectively [20], and their thermodynamic equilibrium Gibbs free energies at 700°C ( $\Delta G_{700}$ ) were about −471.6 and −157.6 kJ (table 1), respectively. The negative values of  $\Delta G_{700}$  for the metal chlorides suggest that degradation of the aluminide layer was caused by the formation of Fe and Al chlorides, which are similar findings to those reported by Li *et al* [7] and Tsaur *et al* [25]. In addition, FeCl<sub>3</sub> formation was dependent on the activity of Al atoms in the aluminide layer, in which they reach lower concentrations because of their inward diffusion into the steel substrate. Metal chlorides resulted from the reaction of both Al and Fe atoms with Cl<sub>2g</sub> at 700°C in the aluminide layer, thereby increasing the partial pressure of metal chlorides and forcing AlCl<sub>3</sub> and FeCl<sub>3</sub> to move towards O at high-partial pressures [7]. At the same time, Fe atoms in Fe<sub>2</sub>Al<sub>5</sub> and FeAl<sub>2</sub> diffused outwards and reacted with Cl to form FeCl<sub>3</sub>. Subsequently, FeCl<sub>3</sub> moved towards O at high-partial pressure, reacting again with O to form Fe<sub>2</sub>O<sub>3</sub>. These results are observed in the XRD scan and the SEM/EDS elemental maps (figures 4 and 5a, respectively).

SEM observation and EDS elemental mapping of the aluminide layer (figure 5a) clearly show that Cl<sub>2g</sub> resulted from oxychlorination, which destroyed the protective Al<sub>2</sub>O<sub>3</sub> scale on the aluminide layer [15]. Almost all of the Fe<sub>2</sub>O<sub>3</sub> scales formed on the FeAl layer, and only a small portion of FeAl<sub>2</sub> remained in the aluminide layer. Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> formed together above the FeAl layer as shown in figure 5a. The Al<sub>2</sub>O<sub>3</sub> scale that grew was loose. During oxidation for





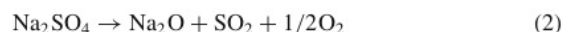
**Figure 5.** SEM and EDS elemental maps of AS specimens with (a) NaCl deposits and (b) Na<sub>2</sub>SO<sub>4</sub> deposits, oxidized at 700°C for 49 h.

49 h, the FeAl layer replaced the Fe<sub>2</sub>Al<sub>5</sub> and FeAl<sub>2</sub> layers, supplying Al atoms that formed the protective Al<sub>2</sub>O<sub>3</sub> scale.

Furthermore, the presence of Na<sub>2</sub>SO<sub>4</sub> deposits on the AS specimens oxidized at 700°C for 49 h had a considerable effect on the corrosion kinetics when compared with AS specimens oxidized in dry air (figure 1a). In the present study, the experimental temperature was lower than the melting point of Na<sub>2</sub>SO<sub>4</sub> (884°C) [20], and the increase in weight gain was about 3.5 times that of AS oxidized in dry air (figure 1a). XRD measurements (figure 4) showed that the intermetallic phases that formed Fe<sub>2</sub>Al<sub>5</sub>, FeAl<sub>2</sub> and FeAl are the same in various environments. In addition, Al<sub>2</sub>O<sub>3</sub> formed during the early stages of oxidation acted as a barrier to S<sub>g</sub>, which could penetrate the aluminide layer in the reaction over short periods. Na<sub>2</sub>SO<sub>4</sub> remained on the specimen surface after corrosion testing (figure 4).

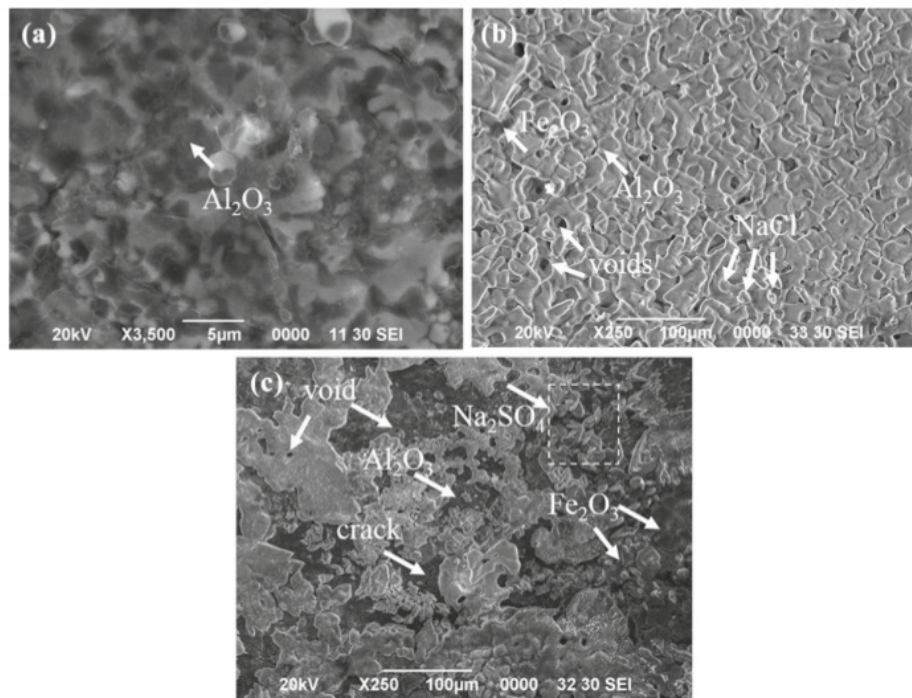
As reported by Shi [17], accelerated oxidation of Fe with Na<sub>2</sub>SO<sub>4</sub> deposits at 750°C may be attributed to a Na<sub>2</sub>O/Na<sub>2</sub>SO<sub>4</sub> eutectic-melt formation on the surface of the specimen. The salt decomposes when the local partial pressure of O in the environment is lower than that at equilibrium with the Na<sub>2</sub>O/Na<sub>2</sub>SO<sub>4</sub> eutectic mixture [26]. The partial pressure of O decreased because of O consumption during Al<sub>2</sub>O<sub>3</sub> formation in the early stages. When the Na<sub>2</sub>SO<sub>4</sub> salt that is deposited on the surface of the specimens does not

melt, the following reaction tends to occur on the alumina scale [19]:



Subsequently, the formed Na<sub>2</sub>O<sub>(s)</sub> dissolved in Na<sub>2</sub>SO<sub>4</sub>, reaching equilibrium with the Na<sub>2</sub>O/Na<sub>2</sub>SO<sub>4</sub> eutectic mixture [17]. The lower temperature of the eutectic mixture (550°C) [17] is strongly believed to support the formation of aluminium sulphide (Al<sub>2</sub>S<sub>3</sub>) in the aluminide layer by allowing the release of SO<sub>3g</sub> into the atmosphere. Because Na<sub>2</sub>SO<sub>4</sub> was still found on the aluminide layer surface after it was oxidized for 9 h (figure 4), the decomposition is believed to supply S that forms Al<sub>2</sub>S<sub>3</sub> on the Fe<sub>2</sub>Al<sub>5</sub>/FeAl<sub>2</sub> layer.

Examination of the SEM cross-sectional micrographs and EDS elemental maps of O, Fe, Al, Cl and S clearly shows the difference between the effects of NaCl [15] and Na<sub>2</sub>SO<sub>4</sub> deposits on AS with respect to acceleration of oxidation and corrosion (figure 5a and b). The micrograph of the corroded sample clearly shows that the aluminide Fe<sub>2</sub>Al<sub>5</sub>/FeAl<sub>2</sub> layer formed on the FeAl layer (figure 5b). Elemental mapping of this scale (figure 5b) suggests that the corrosion products consisted mainly of Al<sub>2</sub>O<sub>3</sub> and some Fe<sub>2</sub>O<sub>3</sub> scales. In the early stage of corrosion, an Al<sub>2</sub>O<sub>3</sub> scale was quickly formed by unmelted Na<sub>2</sub>SO<sub>4</sub> on the surface of the specimens.



**Figure 6.** SEM images of the surface morphologies of AS oxidized at 700°C for 49 h (a) in dry air, (b) in a NaCl environment and (c) in a Na<sub>2</sub>SO<sub>4</sub> environment.

SEM observation of the AS surface after oxidation in dry air at 700°C for 49 h (figure 6a) indicates that the Al<sub>2</sub>O<sub>3</sub> scale on the aluminide coating is compact. In contrast, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> grew together on AS with NaCl deposits (figure 6b). Furthermore, EDS analysis of the oxide scale (figure 6c) indicated that a sulphur concentration of 10.02 wt% was sufficient to increase the high ratio of the partial pressure of S<sub>g</sub> to the partial pressure of O<sub>2g</sub> [27]. SO<sub>3</sub> thus released into the atmosphere and use and dissolve in the Al<sub>2</sub>O<sub>3</sub> scale, forming Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as confirmed by XRD (figure 4). The sulphate particles in this scale combine with the oxide matrix in the reaction over long periods. According to the Gibbs free energy ( $\Delta G_{700} = -807$  kJ) given in table 1, the chemical reaction is spontaneous when sulphur ions dissolved in the aluminium oxide matrix Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> diffuse into Al<sub>2</sub>O<sub>3</sub> via Al<sup>3+</sup> vacancy defects, eventually coming into contact with Al ions diffusing from the aluminide layer. When the activities of both ions were high enough [5], Al<sub>2</sub>S<sub>3</sub> forms as shown in the XRD results in figure 4. This result supports the hypothesis that Na<sub>2</sub>SO<sub>4</sub> decomposition supplies S for the direct formation of trace amounts of Al<sub>2</sub>S<sub>3</sub> in the oxide scale at low temperatures (such as during Na<sub>2</sub>SO<sub>4</sub> melting).

EDS examination of the surface of the corroded sample (figure 6c) showed the composition in wt% in which Fe (28.17 wt%) was higher than that of Al (13.65 wt%). The composition of Al decreased because Al atoms diffused outwards to react first with oxygen, forming the Al<sub>2</sub>O<sub>3</sub> scale

and then diffused inwards into the steel substrate. Consequently, Al activity was decreased to a lower concentration, and the rest of the Fe reacted with the rest of the S<sub>g</sub> remaining in the atmosphere. This result explains why SO<sub>3g</sub> and O<sub>2g</sub> in the atmosphere also diffused into the aluminide layer to form FeSO<sub>4</sub> in which the Fe atom activity was high. The low-formation energy of FeSO<sub>4</sub> ( $\Delta G_{700} = -7.2$  kJ) facilitated FeSO<sub>4</sub> dissociation to Fe<sub>2</sub>O<sub>3</sub> and subsequent release of SO<sub>2</sub> into the atmosphere. The reaction of sulphur gas (as SO<sub>2</sub>) with O<sub>2g</sub> in the atmosphere also produced SO<sub>3</sub> gas. These reactions continued cyclically, forming an Fe-rich oxide (figure 6c) and Al<sub>2</sub>S<sub>3</sub> as confirmed by XRD measurements (figure 4). Consequently, Al<sub>2</sub>O<sub>3</sub> failed to protect the aluminide layer and the steel substrate at 700°C during corrosion over long periods.

#### 4. Conclusions

The presence of NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits on the surface of AISI 1020 steel can accelerate oxidation and corrosion. However, the aluminizing coating on the steel could cause a one to three orders of magnitude reduction in  $k_p$  for oxidation at 700°C for 49 h in an environment containing Cl<sub>2</sub> and S<sub>g</sub>, relative to that of steel without the coating. During the early stages of hot corrosion, a thin and dense Al<sub>2</sub>O<sub>3</sub> scale was created. During the subsequent corrosion, this Al<sub>2</sub>O<sub>3</sub> layer



facilitate the formation of a porous  $\text{Fe}_2\text{O}_3$  scale on itself, which allowed Cl and S penetration into the aluminide layer and enhanced the corrosion kinetics. Vaporization of  $\text{Al}_2\text{Cl}_3$  and  $\text{Fe}_2\text{Cl}_3$  is believed to strongly affect the corrosion kinetics of AS with NaCl deposits, contributing to the decrease in weight gain after oxidation for 9 h. In contrast, from  $\text{Na}_2\text{SO}_4$  decomposition degraded the protective  $\text{Al}_2\text{Cl}_3$  scale, allowing to easily penetrate the oxide scale and form  $\text{Al}_2\text{S}_3$ . The consequent and appreciable increase in the penetration depth of S appears to have resulted in the precipitation of sulphide particles and growth of  $\text{Fe}_2\text{O}_3$ .

# **Acknowledgements**

The authors thank the Ministry of Research, Technology, and Higher Education of the Republic of Indonesia for financial support via the Incentive Research System of National Innovation and the National Strategy Research grant under contract number 529/UN26/8/LPPM/2016–2017.

# **References**

- [1] Subhash K, Jayaganthan R and Prakash S 2010 *Bull. Mater. Sci.* **33** 299
- [2] Safadoost A, Davoodi M and Mansoori S A A 2014 *J. Nat. Gas Sci. Eng.* **19** 105
- [3] Mishra N K and Mishra S B 2015 *Bull. Mater. Sci.* **38** 1679
- [4] Lindberg D, Niemi J, Engblom M, Yrjas P, Lauren T and Hupa M 2016 *Fuel Process. Technol.* **141** 285
- [5] Badaruddin M, Risano A Y E, Wardono H and Asmi D 2017 *AIP Conf. Proc.* **1788** 030066
- [6] Sen M, Balasubramaniam R and Kumar A V R 2000 *Bull. Mater. Sci.* **23** 399
- [7] Liu H H, Cheng W J and Wang C J 2011 *Appl. Surf. Sci.* **257** 10645
- [8] Badaruddin M, Wang C J, Wardono H, Tarkono and Asmi D 2016 *AIP Conf. Proc.* **1711** 040002
- [9] Wang C J and Li C C 2004 *Surf. Coat. Technol.* **177–178** 37
- [10] Wang C J, Lee J W and Twu T H 2003 *Surf. Coat. Technol.* **163–164** 37
- [11] Bose S 2018 High-temperature corrosion in *High temperature coating*, chapter 5, 2nd edn (Butterworth-Heinemann: Elsevier) 74. <https://doi.org/10.1016/C2015-0-01316-8>
- [12] Yajiang L, Juan W, Yonglan Z and Holly X 2002 *Bull. Mater. Sci.* **25** 635
- [13] Bouche K, Barbier F and Coulet A 1998 *Mater. Sci. Eng. A* **249** 167
- [14] Pieraggi B 1987 *Oxid. Met.* **27** 177
- [15] Badaruddin M and Sugiyanto 2013 *Adv. Mater. Res.* **789** 463
- [16] Koech P K and Wang C J 2018 *Oxid. Met.* **90** 713
- [17] Shi L 1993 *Oxid. Met.* **40** 197
- [18] Ciszak C, Popa I, Brossard J M, Monceau D and Chevalier S 2016 *Corros. Sci.* **110** 91
- [19] Yan Y F, Xu X Q, Zhou D Q, Wang H, Wu Y, Liu X J et al 2013 *Corros. Sci.* **77** 202
- [20] Speight J G 2002 *Lange's handbook of chemistry* 16th edn (New York: McGraw-Hill)
- [21] Godlewska E, Mitoraj M and Leszczynska K 2014 *Corros. Sci.* **78** 63
- [22] Knacke O, Kubaschewski O and Hesselmann K 1977 *Thermochemical properties of inorganic substance* (Berlin: Springer) 91. <https://doi.org/10.1007/978-3-662-02293-1>
- [23] Neumann G 1990 in *Diffusion in solid metals and alloys, numerical data and functional relationships in science and technology* H Mehrer (ed) (Springer-Verlag, Berlin) vol. 26, p 152
- [24] Le Claire A D 1990 in *Diffusion in solid metals and alloys, numerical data and functional relationship in science and technology* H Mehrer (ed) (Springer-Verlag, Berlin) vol. 26, p 129
- [25] Tsaur C C, Rock J C, Wang C J and Su Y H 2005 *Mater. Chem. Phys.* **89** 445
- [26] Buscaglia V, Nanni P and Bottino C 1990 *Corros. Sci.* **30** 327
- [27] Lee W H and Lin R Y 1999 *Mater. Chem. Phys.* **58** 231

# High-temperature corrosion of aluminized-AISI 1020 steel with NaCl and Na<sub>2</sub>SO<sub>4</sub> deposits

ORIGINALITY REPORT

80%

SIMILARITY INDEX

PRIMARY SOURCES

- 1

[link.springer.com](https://link.springer.com)  
Internet

3350 words — 77%
- 2

Y.F. Yan, X.Q. Xu, D.Q. Zhou, H. Wang, Y. Wu, X.J. Liu, Z.P. Lu. "Hot corrosion behaviour and its mechanism of a new alumina-forming austenitic stainless steel in molten sodium sulphate", Corrosion Science, 2013  
Crossref

37 words — 1%
- 3

Onkar Mangla, Savita Roy, S Annapoorni, K Asokan. "A study on defect annealing in GaAs nanostructures by ion beam irradiation", Bulletin of Materials Science, 2020  
Crossref

36 words — 1%
- 4

[repository.lppm.unila.ac.id](https://repository.lppm.unila.ac.id)  
Internet

13 words — < 1%
- 5

Susan Immanuel, R Sivasubramanian. "Fabrication of two-dimensional chemically reduced graphene oxide nanosheets for the electrochemical determination of epinephrine", Bulletin of Materials Science, 2020  
Crossref

13 words — < 1%
- 6

[www.kemija.org](https://www.kemija.org)  
Internet

10 words — < 1%
- 7

Singh, H.. "Characterization of oxide scales to evaluate high temperature oxidation behavior of Ni-20Cr coated superalloys", Materials Science & Engineering A, 20070825  
Crossref

9 words — < 1%

9

Rodrigo Cardoso Costa, Michel Volpato Dacoreggio, Norton Zanette Kejelin, Franco Wronski Comeli.

8 words — &lt; 1%

"Avaliação da resistência a corrosão de revestimentos metálicos depositados por aspersão térmica a arco: uma aplicação em trocadores de calor", Soldagem & Inspeção, 2014

Crossref

10

M. Reza Bateni, Stephanie Shaw, Ping Wei, Anthony Petric. "Deposition of Fe–Al Intermetallic Coatings on Solid Oxide Fuel Cell (SOFC) Interconnects by Pack Cementation", Materials and Manufacturing Processes, 2009

8 words — &lt; 1%

Crossref

11

Mohammad Badaruddin, Chaur Jeng Wang, Yudhistyra Saputra, Abu Khalid Rivai. "High Temperature Corrosion of Aluminized AISI 4130 Steel with the Different Composition of NaCl/Na<sub>2</sub>SO<sub>4</sub> Deposits", Makara Journal of Technology, 2015

6 words — &lt; 1%

Crossref

EXCLUDE QUOTES

ON

EXCLUDE MATCHES

OFF

EXCLUDE

ON

BIBLIOGRAPHY