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# High Temperature Oxidation of Low Carbon Steel with and without an Al Coating in an Atmosphere Containing Burning Ethanol

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**Abstract.** High temperature oxidation of low carbon steel (SAPH440) with and without a hot-dip Al coating in an atmosphere containing burning ethanol, water vapor, and air were studied by isothermal oxidation at 600 °C, 650 °C, 700 °C, and 750 °C over 49 h. The experimental results show that the water vapor and hydrogen produced by ethanol burning in the atmosphere promotes an increase in weight gain and metal loss in the bare steel. The growth of the iron oxide layer is attributed to large amounts of hydrogen dissolved in the iron oxide layer leading to fast oxidation kinetics. The protective Al<sub>2</sub>O<sub>3</sub> layer formed on the surface of aluminide steel can serve as a barrier to hydrogen penetration in the aluminide layer; thus, the oxidation rate of bare steel was significantly slower in the atmosphere containing both water vapor and hydrogen.

## INTRODUCTION

There has been an increase in the use of alternative fuels as replacements for the fossil fuels that have been used since the 20<sup>th</sup> century. Methanol and ethanol have enabled the reduction of fossil fuel consumption and CO emission compared with gasoline. The use of ethanol as substitution as a substitute for gasoline or in diesel fuel blends has been continuously developed for environmental reasons and in the interest of moving toward renewable energy sources [1]. During the past decade, the concentration of ethanol utilized as a bio-additive in petrol in European Union countries has increased to approximately 5 wt.%, and this concentration will have risen to 10 wt.% by the year 2020 [2]. It is well known that ethanol at a high temperature, ethanol can release water vapor and hydrogen in to the atmosphere, which can aggressively corrode steel and its alloys [3-5]. The use of ethanol as an alternative energy source has significantly changed how steel is used to support energy conversion.

Low carbon steel has been widely manufactured for use in gas exhaust systems in the automotive industry due to its lower cost relative to high alloy steels [6]. After use at high temperatures, the formation of very thick, non-protective layers can result in a spallation layer. The spalling of oxide scales is mainly determined by the formation and growth of voids in the scale [7]. Using a hot-dip aluminization procedure is an effective and inexpensive method for modifying the surface of steel to improve the high temperature oxidation resistance of low carbon steel that will be exposed to atmospheres containing ethanol [8]. The aluminide coating is expected to form a protective Al<sub>2</sub>O<sub>3</sub> layer on the surface of the steel during exposure to high temperatures.

It is very important to understand the effects of ethanol on the accelerated oxidation of a plain steel substrate and hot-dip aluminized steel. The aim of the present study was to enhance our understanding of the oxidation mechanism with respect to the oxidation kinetics. The isothermal oxidation of low carbon steel (SAPH440) was studied at 600, 650, 700, and 750 °C in an atmosphere containing burning ethanol, water, and air.

## EXPERIMENTAL SET-UP

The specific composition of the SAPH440 steel is 0.09% C, 0.08% Si, 1.37% Mn, 0.02% P, 0.01% Cr, and 0.01% Ni and Fe-balance (wt.%). Specimens with dimensions of  $20 \times 10 \times 2.5 \text{ mm}^3$  were cut from the material. The bare steel specimens (uncoated specimens) were ground to 2500 grit and then polished using a  $\text{SiO}_2$ -suspension. For the Al-coated specimens, the bare steel was coated by immersion in a molten, pure Al bath at  $700^\circ\text{C}$  for 3 minutes.

The oxidation tests were isothermally performed in a horizontal furnace equipped with an alumina tube 100 mm in diameter. All specimens were oxidized at  $600^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $750^\circ\text{C}$  for various lengths of time (1 h, 9 h, 25 h, and 49 h) in an atmosphere containing burning ethanol, water vapor, and air as the reaction gas. A mini air compressor accompanied by a flow rate controller was used to move the reaction gas (air as the carrier) into the furnace at 200 mL/min. Three specimens were oxidized separately while positioned parallel to the direction of gas flow. Upon starting the oxidation test, the specimens were put in the holder and placed in the furnace tube prior to the start of gas flow.

To determine the amount of weight gained by the specimen, they were weighted to 0.1 mg before and after the oxidation tests. The oxidation products were characterized by optical microscopy (OM), SEM with EDS compositional analysis, and XRD analysis. For the metallographic examination, specimens were mounted using resin. Finally, the metallographic specimens were ground to 4000 grits and then polished up to mirror-like finishes using a  $\text{SiO}_2$ -suspension.

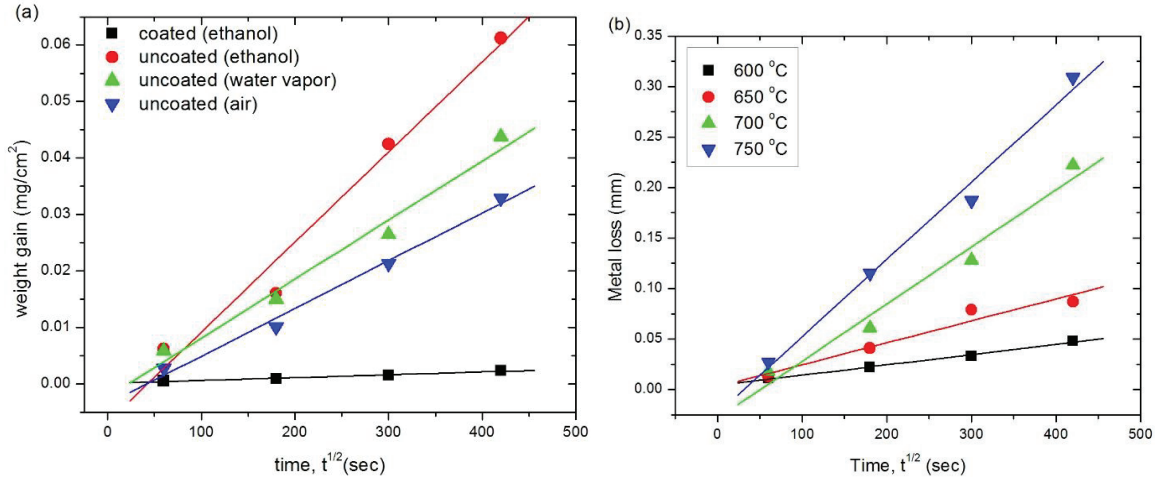
## RESULT AND DISCUSSION

### Oxidation kinetics of the samples with and without an Al-coating

The isothermal oxidation experiments were carried out at  $600^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $750^\circ\text{C}$  under atmospheric pressure in an atmosphere containing burning ethanol, water vapor, and air. The growth rate of the compact layers was typically controlled by the diffusion of a species through the layer itself. A simplified analysis of this situation was carried out to show that controlling the rate by such a process leads to parabolic kinetics [6]. The oxide layer thickens according to parabolic kinetics.

$$(\Delta W/A) = k_p t^{1/2} \quad (1)$$

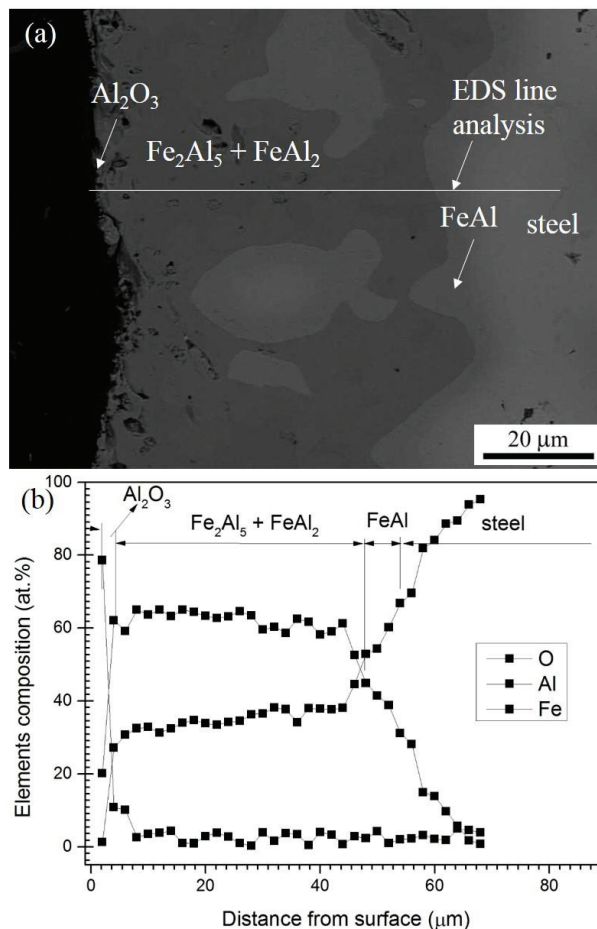
where  $\Delta W/A$  is the weight gain ( $\text{mg cm}^{-2}$ );  $A$  is the surface area ( $\text{cm}^2$ );  $t$  is the oxidation time (sec); and  $k_p$  is the parabolic rate constant ( $\text{mg}^2 \text{cm}^{-4} \text{s}^{-1}$ ).



**FIGURE 1.** (a) The parabolic plot of weight gain curves of the specimens being oxidized at  $750^\circ\text{C}$  for 49 h, (b) metal loss vs. the square root of the time the bare steel was exposed to the burning ethanol atmosphere at an elevated temperature.

Figure-1a shows that the weight gain of specimens exposed to burning ethanol is higher than those of specimens exposed to just water vapor and air, but the oxidation resistance of the bare steel in the burning ethanol atmosphere

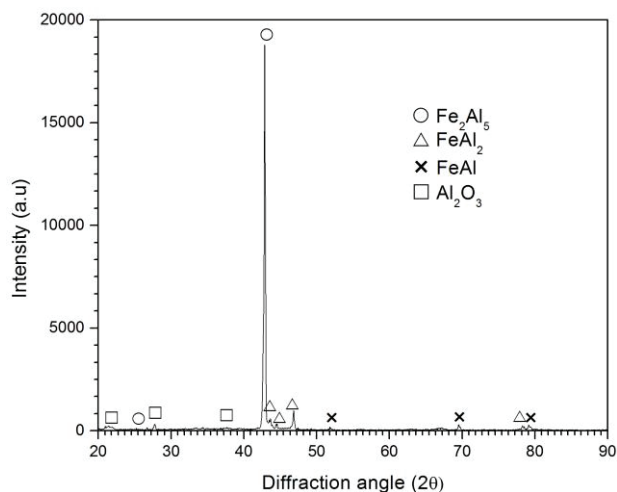
can be enhanced by the addition of an aluminum coating by the hot-dipping procedure. The total depth of the corrosion, known as metal loss, for bare steel during isothermal exposure at 750 °C showed that the metal loss in the atmosphere containing ethanol is higher than that in the atmospheres containing water vapor and air, as shown in Figure-1b.



**FIGURE 2.** (a) SEM morphology of a cross-sectional image and (b) EDS line profile of the aluminized steel after oxidation in the burning ethanol atmosphere at 700 °C for 25 h

The increase of metal loss in the atmosphere containing ethanol is consistent with the increased weight gain. An increase in the oxide thickness occurs because of an increase in surface area due to the significant increase in the defects caused by the rapid oxide growth, which potentially provides myriad of sites for the adsorption of oxidation gas and hence leads to fast oxidation kinetics. A large increase in the rate of oxidation of the base steel in an atmosphere containing water vapor was supported by significant diffusion paths of iron ions from the bulk steel at high temperatures [9]. This can be seen in the increase in the thickness of the oxide layer as time and temperature of exposure are increased, Figure-1b. At 750 °C, ethanol burning produces water vapor and hydrogen, and therefore the amount of water vapor and hydrogen in the atmosphere are increased. Moreover, decomposition of water vapor produced a large amount of hydrogen, which leads to an increase in the oxidation rate of the steel [10]. As reported by Rahmel and Tobolski [11], the addition of water vapor can enhance the formation of the oxide due to a dissociation reaction in the pores of oxide containing  $\text{H}_2\text{O}$  and  $\text{H}_2$ . They also reported that at 750 °C, water vapor had no effect on the oxidation rate, but the highest concentration of water had a significant effect on oxidation at 950 °C. The formation of micro-cracks generated by the diffusion of Fe cations in the grain boundary [12] will allow water vapor and hydrogen to easily penetrate the oxide layer. The oxide layer formed on outer layer of the steel becomes loose and porous relative to the inner layer because of dissolved hydrogen in the oxide layer. The growth of the oxide layer occurs at the outer edge of the pore with the oxidation of either the metal or the oxide at the inner surface, and this process transfers oxygen in toward the metal and accelerates the oxidation reaction. This

mechanism is necessary for either water or hydrogen to penetrate the layer and then enter the pore. Consequently, ethanol in the atmosphere would clearly increase the rate of oxidation of steel because it produces additional hydrogen, Figure-1b.



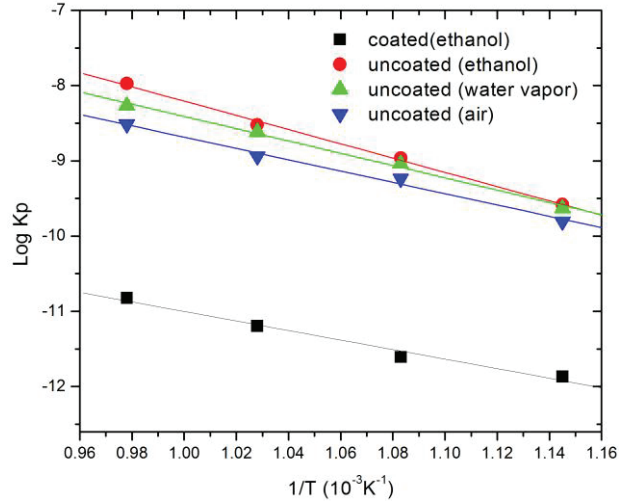
**FIGURE 3.** X-RD diffraction patterns of the aluminized steel after oxidation in a burning ethanol atmosphere at 700 °C for 49 h

As illustrated in Figure-1a and Figure-1b, weight gain and the total depth of corrosion for the steel oxidized in burning ethanol is more severe than what is seen in steel oxidized in water vapor and air. The increase in the rate of oxidation causes rapid growth of the oxide layer, which leads to an increase in the weight gain and metal loss. However, the hot-dipped aluminized steel exhibits excellent corrosion resistance compared to bare steel. The aluminum coating formed on the bare steel is beneficial for improving of the high temperature corrosion resistance in the burning ethanol atmosphere because it forms a protective  $\text{Al}_2\text{O}_3$  layer. The aluminide coating on the steel substrate has two important roles; one is the outward diffusion of Al to form the  $\text{Al}_2\text{O}_3$  layer and the other is inward diffusion of Al towards the steel substrate to form intermetallic compounds [6,8]. The aluminum oxide coating ( $\text{Al}_2\text{O}_3$ ) formed on the aluminide layer will provide a significant reduction in hydrogen permeation compared to the bare steel [13,14]. The weight gain versus the square root of exposure time for the aluminized specimen oxidized at 750 °C is shown in Figure-1a. The data presented in Figure-1a show an approximately 62% in reduction of in the rate of oxidation of the Al-coated steel was achieved compared to the bare steel. This suggests that the aluminide coating is able to provide steam oxidation resistance to steel substrates through the formation of a protective oxide scale ( $\text{Al}_2\text{O}_3$ ).

An SEM cross-sectional micrograph of an aluminized specimen oxidized at 700 °C for 25 h and its corresponding to EDX line profiles of the distributions of Al and Fe across the coating layer are depicted in Figure-2a and Figure-2b, and they show the intermetallic phase formed in the aluminide layer. These three distinct phases can be confirmed by XRD examination, Figure-3; moving from the outer aluminide layer to steel substrate the layers are  $\text{Fe}_2\text{Al}_5$ ,  $\text{FeAl}_2$ , and  $\text{FeAl}$ , respectively, Figure-2a. The outer layer consists of a thin  $\text{Al}_2\text{O}_3$  layer since a protective layer provides better oxidation resistance during exposure to the burning ethanol atmosphere, Figure-1a

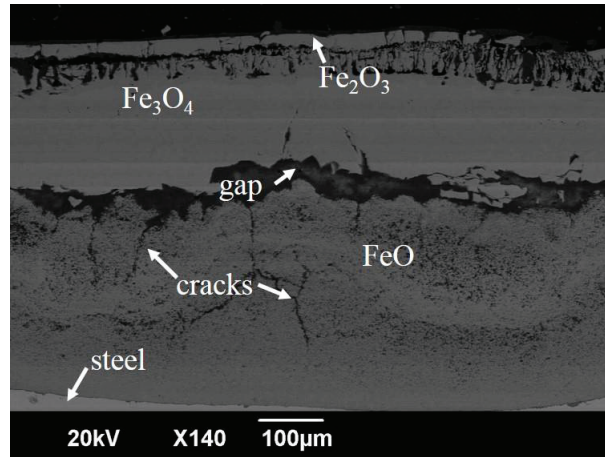
### The effect of the gaseous atmosphere on the oxide layer growth

The oxide layer on bare steel grows more quickly in an atmosphere with burning ethanol than in an atmosphere containing just water vapor and air. Therefore, it is important to understand the oxide layer growth to design and control low carbon steel for high temperature applications. Figure-4 shows the linear relationships between  $\log k_p$  and the reciprocal of the absolute temperature,  $1/T$ . The slope of the straight line was obtained by the curve fitting method, and that value allowed us to calculate the activation energy,  $Q$ , for the growth of each specimen's oxide layer. The activation energies for bare steel oxidized in the burning ethanol atmosphere, water vapor, and air are  $Q_{(\text{ethanol})} = 181.03$ ,  $Q_{(\text{water vapor})} = 155.96$ , and  $Q_{(\text{air})} = 143.65$   $\text{kJ mol}^{-1}$ , respectively. For the aluminized steel, the activation energy is approximately 121.11  $\text{kJ mol}^{-1}$ .



**FIGURE 4.** Relationship between  $\log k_p$  and  $1/T$  for the SAPH440 steel under isothermal oxidation conditions in the different atmospheres

The activation energy for the growth of the oxide layer on bare steel in the burning ethanol atmosphere is the highest of the activation energies determined here. The significant difference in the activation energies comes from the large amount of hydrogen in the atmosphere between the surface of the oxide layer and the oxide layer/alloy interface. Increased amounts of hydrogen in the alloy, which are injected into the steel during steam oxidation, can increase oxygen permeability and thus enhance the ability of the steel to promote fast growth of the iron oxide scales [15]. This result shows that hydrogen easily permeates into the steel at high temperatures.



**FIGURE 5.** SEM of cross sectional morphology of SAPH440 oxidized at 750 °C for 49 h in the burning ethanol atmosphere

As shown in Figure-5, cracks can be observed in the FeO layer. The increase in the partial pressure of hydrogen is a possible cause for increased oxidation rate. The increase in pressure leads to increases in solid state diffusion within this oxide scale and is quantifiable and accounts for the increase in scale thickness. In the present study, we suggest that the growth of the iron oxide layer is strongly affected by the large amount of hydrogen dissolved in the oxide layer, which then enhances the growth of the iron oxide layer by providing an additional source and sinks for the generation of pores and the formation of micro-channels.

### Examination of oxide morphology and phase compositions

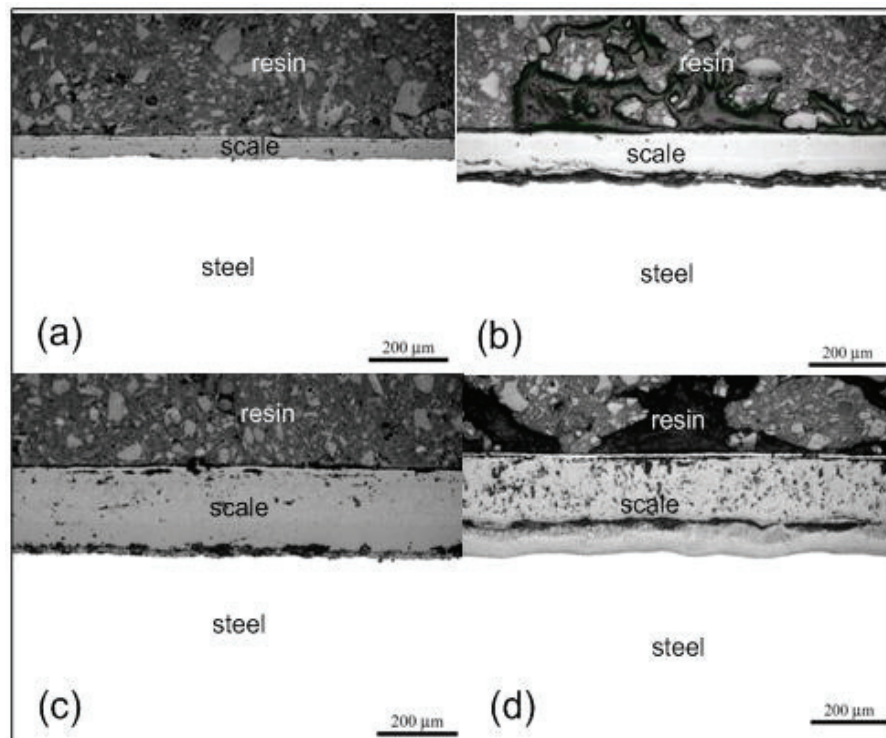
General observations have indicated that the iron oxide scales, which form on the steam-side surface of the carbon steel, generally consist of multilayered scales [16]. The composition of the scales is predominantly hematite



( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and wustite ( $\text{FeO}$ ). The typical surface morphologies of the steel after high temperature oxidation are shown in Figure-6. The experimental results show that the temperature and the atmospheric conditions (hydrogen and oxygen content) had substantial influences on the characteristics of the oxidized steel. The typical characteristics of the iron oxide scale significantly affected by several alloying elements in the steel [17].

The inward transportation of oxygen by water vapor ( $\text{H}_2\text{O}$ ) and hydrogen ( $\text{H}_2$ ) from the outer edge of the pores of the oxide layer could heal the gap, as shown in Figure-5. The formation of the gap might be caused by vacancy condensation due to the rapid growth rate of the inner edge magnetite layer.

Hydrogen diffusing from the metal/oxide interface outward may form water molecules where it encounters a sufficient oxygen potential, such as in voids in the scale, which can trigger dissociation of the scale and enlarge the voids. The growth of the layer depends to large extent on the transport processes within this gap [15] providing a mechanism for transporting water from the dissociation reaction into the layer. In voids containing both hydrogen and water vapor, the Hydrogen diffusing from the metal/oxide interface outward may form water molecules where it encounters a sufficient oxygen potential, such as in voids in the scale, which can trigger dissociation of the scale and enlarge the voids. The growth of the layer depends to large extent on the transport processes within this gap [15] providing a mechanism for transporting water from the dissociation reaction into the layer. In voids containing both hydrogen and water vapor, the oxidation of the surface nearest the metal will occur by the reaction with water to form a new oxide and generate hydrogen as a product. This mechanism facilitates the rapid inward diffusion of oxygen while the void gradually moves outwards from the metal/oxide interface to the oxide/gas interface. Accordingly, the oxidation rate depends not only on both  $p\text{O}_2$  and  $p\text{H}_2\text{O}$  but also on the structure of the oxidation products and the amount of hydrogen dissolved in the layer.



**FIGURE 6.** Cross-sectional morphologies of SAPH440 steel oxidized at (a) 600 °C, (b) 650 °C, (c) 700 °C, and (d) 750 °C for 25 h in a burning ethanol atmosphere

The wustite phase,  $\text{FeO}$ , is a  $p$ -type electron-deficit semiconductor. The presence of a large number of defects can promote the mobility of iron ions migrating outwards through the  $\text{FeO}$  layer. Therefore, the  $\text{FeO}$  layer enables this layer to become much thicker than the  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  layers, Figure-5. The constituents of the layers in this study reveal that the corrosion activities were dominated by oxygen and water vapor oxidation, and the amount of hydrogen dissolved was highest in the oxide layer.

## CONCLUSION

Burning ethanol produces water vapor and hydrogen, and at 750 °C, this process can add a large amount of hydrogen to the atmosphere, thus the hydrogen dissolution in the oxide layer leads to rapid oxidation of steel. A crack formed in the inner oxide layer will facilitate water vapor and hydrogen penetration into the iron oxide layer. Therefore, the partial pressure of oxygen, water vapor, and hydrogen will increase in the oxide scale, and fast transport of Fe-ions in the inner oxide leads to a faster oxidation rate for SAPH440 steel. The high temperature oxidation resistance of the SAPH440 steel in water vapor and hydrogen atmospheres can be improved by the hot-dipped aluminum coating. The better performance of the aluminized steel is attributed to the formation of a protective Al<sub>2</sub>O<sub>3</sub> layer on the surface of the bare steel during exposure to high temperatures.

## ACKNOWLEDGEMENT

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