Research Article

Corrosion Behaviour of AISI409 Stainless Steel with Al Slurry Coating in Molten Salt

Parinya Kongkaoroptham and Mack Boonpensin
Department of Materials and Production Technology Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

Thamrongsin Siripongsakul* and Piyorose Promdirek
High Temperature Corrosion Research Centre, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

* Corresponding author. E-mail: thamrongsin.s@eng.kmutnb.ac.th DOI: 10.14416/j.asep.2021.02.002
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Abstract

A concentrated solar power plant produces electricity by collecting thermal energy from sunlight. Then the thermal energy is stored in the heat transfer fluid (HTF). The most widely used and studied HTF is solar salt (60wt%$NaNO_3$–40wt%KNO_3) that achieves the most requirements of HTF. However, at high temperatures, the corrosion is still violent for most materials, thus the material selection is important. This research aims to investigate the feasibility for application of AISI 409 ferritic stainless steel as containers of the molten salt. AISI 409 is suitable for high temperature usage, and more economical than other grades which have higher chromium. To investigate the corrosion resistance in molten salt, AISI 409 samples were coated by dipping in Al slurry. Then they were heated up to 400°C to remove binders. The coatings with Fe-Al intermetallic and alumina layers were formed after binder removal and subsequently annealing at 700°C for 3 h in the air atmosphere. This research reported the corrosion behaviour of Al coated and uncoated samples which had been treated by immersion in molten salt at 500°C for 100 h with analysis results. The results demonstrated that weight and thickness of uncoated samples were increased due to formation of the oxide layers such as Fe_2O_3 and Fe_3O_4 on the surfaces. For the Al coated samples, the weight and thickness of the coat layers were massively decreased after being immersed in molten salt at the first 1 h due to removal of Al-O, slag or impurity in the coating. Nevertheless, the weight increased gradually until 100 h. The oxidation of the Fe-Al intermetallic layer exhibited about 35% slower oxidation than that of uncoated samples, thus the coating technique has potential to be applied against molten salt.

Keywords: Corrosion, Coating, Molten salt, CSP, AISI 409

1 Introduction

A concentrated solar power plant (CSP) is another future sustainable energy source like fuel cells which produce electrical energy by chemical reactions [1]. While the CSP is the most efficient, reliable, and cost-effective way to store solar power at a large scale for producing clean energy without greenhouse gas emission. The solar heat energy is stored by concentrated sun light which is reflected by mirrors onto a receiver containing molten salt. Molten salt is used as heat storage and also applied as heat transfer fluid (HTF) to deliver the thermal energy to a heat exchanger or an electricity generator to produce electricity. Most requirements of HTF are good thermal stability, low vapor pressure at high temperatures, low corrosion, low viscosity, high thermal conductivity, high heat capacity for energy storage, and low cost. Thus the widely used and studied HTF is solar salt, 60wt% $NaNO_3$:40wt% KNO_3 which achieves most of those requirements. However, at operating temperatures around 200–600°C [2], the corrosion is still violent for steels which are used as containers, pipes or exchangers. According to other researches, the corrosion tests in air atmosphere for 168 and 720 h at 400°C of AISI 1045 medium-carbon steel and AISI 304 austenitic stainless steel which have low content of carbon, and high contents of chromium and nickel, they resulted in better corrosion resistance of AISI 304 than AISI 1045. The improvement in corrosion resistance is due to the contents Cr and Ni in AISI 304 that reacted with oxygen to form a barrier oxide film. On the other hand, AISI 1045 can only form wustite, magnetite and hematite as oxide barriers which are less protective. Thus the steels containing Cr and Ni would be more appropriate for application in such a corrosive environment [3]. However, in the basic environment of molten salt, some amount of Cr can be also corroded and dissolved by alkali oxide [4]. In addition, when steels are exposed in molten salt, $NaFeO_2$ will be formed on surfaces and it is not very adherent to the stainless steel substrate and eventually results in spallation [5]. Thus the corrosion resistance of materials in service is very important.

Most of these problems could be solved by the application of high corrosion resistance materials such as Ni-base alloys, which have higher corrosion resistance against molten salts [6]. However, it is not quite cost-effective. On the other hand, using coating can be another solution to expand the service lifetime. An experimental report of NiVAl coating on P91 steel [7] indicated that there was no oxide formation on the coated side but a thick oxide layer had developed on the uncoated side. This is an evidence that properly coated steel can improve corrosion resistance against molten salt even it is a general commercial grade one . Al slurry coating [5], [8], [9] has been shown good corrosion resistance in molten salts as well as Al-Si slurry coating [9] and Al-Ni slurry coating [5]. These coatings can improve corrosion resistance of steels by creating protective layers such as alumina, FeAl, and Fe_2Al_5 to prevent reaction between molten salts with Cr and Fe of the alloy substrates. For Al slurry coating [8], the result has shown that ferritic stainless steels and austenitic stainless steels those coated with Al slurry have the same weight change after exposure in molten salt at 600°C for 2500 h. Thus ferritic stainless steels can be used as an alternative material for this application instead of austenitic stainless steels.

In this experiment, coupons of ferritic stainless steel AISI 409 were used as alternative substrates and coated with Al slurry coating. Then they had been tested in molten salt at 500°C for 100 h because the operation temperature of molten salt is around 200–600°C [2]. The corrosion test at 600°C had been performed before. However, the corrosion of bare AISI 409 samples in molten salt was very violent (blistering and disintegrating) and vey hard for analysing. Thus, in this report the corrosion test was performed at 500°C. The duration of this experiment was 100 h to be sufficient for comparison between coated and uncoated samples. The corrosion should start to be different faster if the temperature is high enough as performed in other experiments [5]–[7], [9]. This experiment aims to study the corrosion of the ferritic stainless steels AISI 409 with and without a Al coating layer to understand the corrosion behaviors which are important to identify suitable coatings for the long service time.

2 Materials and Methods

AISI 409 sheets were obtained from Posco-Thainox Public Company Limited. They were cut into a size of 10×10×1 mm^3. A hole with 2.5 mm in diameter was prepared on the center top of each sample for dangling. All faces of each piece were ground by SiC papers with grit numbers of 200 to 800. The samples were then cleaned with alcohol in ultrasonic bath and finally dried by air. The chemical composition of AISI 409, which can be referred in the Table 1, was investigated by a standard optical emission spectrometer (OES).

Table 1: Optical emission spectrometry of AISI 409

Element	%
Fe	87.847
C	0.014
Cr	10.855
Mn	0.310
Ni	0.054
P	0.182
Si	0.522
S	0.002
Ti	0.215

To prepare the Al coating slurry, pure aluminum powder, sized 325-mesh, was mixed with polyvinylalcohol (PVA) and ethanol. The composition of the slurry was 55%wt Al powder, 28%wt PVA and 17%wt ethanol. The prepared AISI 409 coupons were dipped into slurry mixture and then pulled up. The samples were put in a furnace in air atmosphere at 400°C for 1 h to remove binders then the furnace was heated up to 700°C and held for 3 h to sinter the coating layers. The coated and uncoated samples were characterized by a standard scanning electron microscope (SEM), an energy dispersive x-ray spectrometer (EDX) and an x-ray diffractometer (XRD) with a Cu K α anode.

The corrosion test was performed for both uncoated and Al coated AISI 409 samples under a similar condition. They were immersed in molten salt in the furnace of which the temperature of 500°C had been set for 100 h. The molten salt used in the experiment is the nitrate salt mixed between 60wt% $NaNO_3$ and 40wt% KNO_3. The samples after corrosion test were also analyzed by a standard microscope, SEM, and EDX. A calibrated 6-digit microbalance was used to measure the weight change of all samples.

3 Results and Discussion

3.1 *Characteristics of Al slurry coating*

After the heat treatment process at 700°C, the coating layer produced was dark gray, smooth and homogeneous. The appearance of the AISI 409 coupons without and with Al slurry coating is shown in Figure 1(a) and (b), respectively. In Figure 1(c) and (d) show also the appearance of the respective samples after corrosion test by immersion in the molten salt. The thick black oxide scale and light gray contrast of spallation could be seen on the surfaces of the uncoated samples. On the other hand, the surfaces of Al coated samples were spalled partially. However, the appearance does not show strong contrast as uncoated samples. The results will be discussed in detail later.

The characteristics of the coating layers were investigated by SEM and XRD. The Figure 2 shows a cross-sectioned SEM image of a coated sample of which the thickness is 85.25 µm in a pale gray contrast and formed on the bright contrast of the AISI 409 substrate below. The ImageJ software was used to determine the average thicknesses of the coated layers.

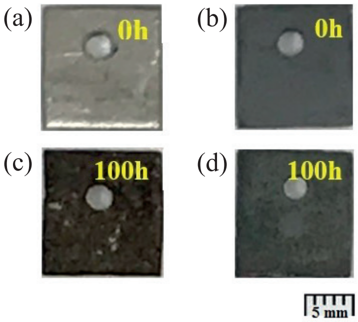

Figure 1: Appearance of the sample surfaces before and after having been immersed in molten salt at 500°C for 100 h. (a) an uncoated sample (b) an Al slurry coating sample (c) an uncoated sample after 100 h in molten salt (d) an Al slurry coating sample after 100 h in molten salt.

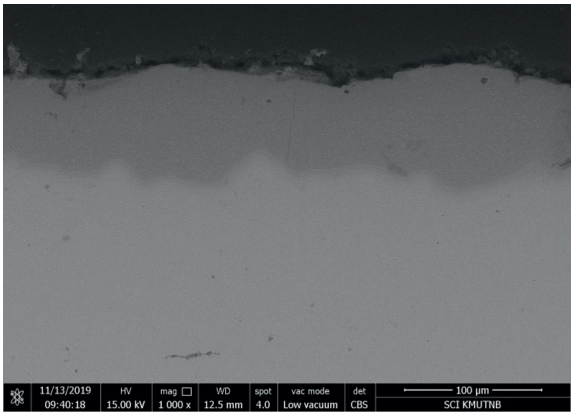

Figure 2: The SEM image of Al coated AISI 409 after sintering at 700°C.

There were slightly thin oxide scales, which are dispersed at the top of the surface. A crack was hardly found, but it could be generated by mismatch between the thermal expansion coefficients of the substrate and the coated layer. To confirm the existing phases in the layer, the XRD was used to analyse. The Figure 3 shows that the Al slurry coating results in the existence of Al and intermetallic (IM) Fe_2Al_5 phases. This result was in good agreement with the growth of Fe_2Al_5 at the interface between the bcc Fe and Al melt although different methods had been used [10].

Al-O could not be detected due to its amorphous structure. However, the existence of Al-O can be identified and discussed later in EDX results. On the other hand,

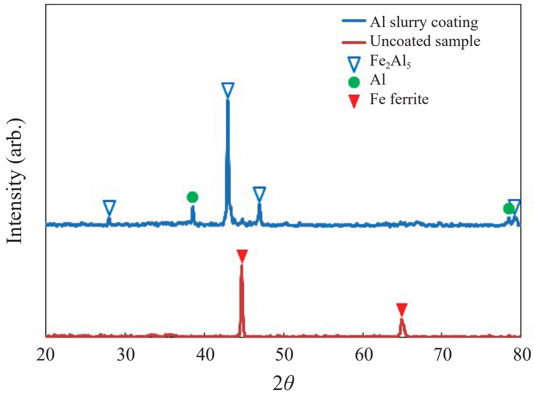

Figure 3: Characterization of the sample after coating. (a) an uncoated sample (b) an Al slurry coating sample.

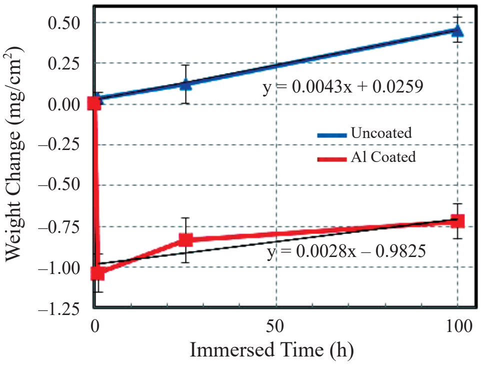

Figure 4: Weight change of uncoated samples and Al slurry coating after immersion in molten salt at 500°C for 100 h.

for the uncoated sample only the XRD peaks of the bcc Fe phase was detected.

3.2 *Corrosion test*

The corrosion test had been performed by immersion in molten salts at 500°C for 100 h. Because the coating samples produced by the slurry method after heat treatment at 700°C often present oxide phases, slag or impurity on the surface, which are easily removed at the first period. Thus the weight change had been additionally investigated for 1 h immersion. The Figure 4 shows the corrosion test results of weight have changed of uncoated and Al slurry coated samples after immersion for 100 h. The weight changes of the uncoated samples had been increased after experiencing in molten salt for 1 h then they still tended to increase continuously at 100 h. Even though the oxidation was co-occurred with spallation envisioned, most spalled mass was collected and included in weight change measurement. According to the test, the weight change rate of the uncoated samples was 4.3 . This value was derived from the trend line of the data of 1 h to 100 h immersion. While in case of the Al coated samples, the thickness of the coated layers had been massively decreased after immersed in molten salt for the first 1 h. As previously mentioned that the coating formed by the slurry method may cause some amounts of the Al and Al-O including impurity phases, which are known to be vulnerable to the basic environment, these components are instantly removed at the first period.

However, the increase of weight was very slow after the first hour until the immersion time reached 100 h compared to the uncoated samples. The weight change rate of the Al coated sample was about 2.8 $\mu g/(cm^2 \times h)$. These weight change results exhibited the similar trend as AISI 430 SS reported in the literature [9]. These results showed the higher corrosion resistance of Al coated than that of uncoated samples for both AISI 430 SS and AISI 409 SS. In general, AISI 430 is expected as a stainless steel with a better grade than AISI 409 on corrosion resistance.

Firstly, the increase of mass of each sample could be interpreted that oxidation reaction took part in the corrosion in molten salt. Secondly, in molten salt it could be seen large amount of mass dropped sharply at the first period showing the vulnerability of an oxide scale to the basic environment. The major decrease was caused by sludge formed due to slurry coating.

The SEM images in the Figure 5(a) and (b) show the cross-sectioned surfaces of the uncoated samples before and after the immersion in the molten salt at 500°C for 100 h, respectively. In the images, EDX was used to analyse the composition of elements at the spots specified by number 1, 2, 3, and 4. The results of EDX were collected and shown in the Table 2 which showed the intense oxygen content at the surface and emphasized the oxidation reaction for the uncoated sample as previously mentioned. The average proportion of oxygen increased from 3%wt to 24%wt after immersion. In Figure 5(c) and (d) show the cross-sectioned surfaces of the Al slurry coating samples before and after the immersion test for 100 h, respectively.

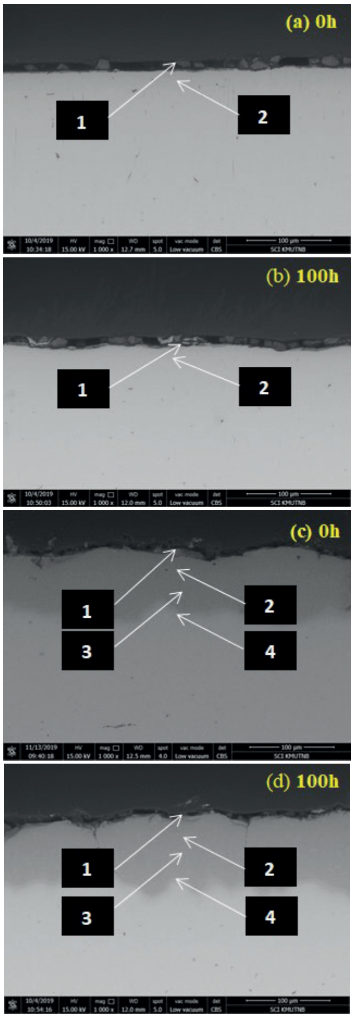

Figure 5: SEM cross-sectioned images of uncoated samples before and after immersion in molten salt at 500°C. (a) and (b) are uncoated samples. (c) and (d) are Al slurry coating samples.

For the Al coated samples, it is hard to identify oxide scales at the outmost, but the IM phases (Fe_2Al_5) are clearly detected in gray contrasts at the surfaces. From the XRD results, the Fe_2Al_5 phase, which was equivalent to 45%wtFe–55%wtAl was congruent to the values detected by EDX. The EDX analyzed results for samples before and after immersion, the compositions between Fe and Al were 49%wtFe–51%wtAl and 43%wtFe–57%wtAl respectively. The average values were calculated from analyses of the spots number 2 and 3 of both conditions.

Table 2: EDX results afer immersion in molten salt at 500°C

Sample	Spot No.	Element			
		Al wt%	Fe wt%	Cr wt%	O wt%
Uncoated immersed 0 h	1	-	79.13	14.76	6.11
	2	-	86.68	13.32	0.00
Uncoated immersed 100 h	1	-	54.65	13.52	31.83
	2	-	73.17	9.72	17.11
Al slurry coating immersed 0 h	1	48.94	30.24	8.00	12.81
	2	23.34	18.02	44.13	14.50
	3	44.86	48.13	7.00	0.00
	4	9.56	67.58	11.34	11.53
Al slurry coating immersed 100 h	1	61.07	26.38	5.74	6.81
	2	58.42	37.73	3.86	0.00
	3	49.95	43.27	5.01	1.78
	4	49.55	37.74	12.71	0.00

For the outmost surfaces, EDX spot number 1 in Figure 5(c) shows intense Al and oxygen signals before immersion in the molten salt. The intense oxygen detection became almost lost when it reached the IM layer after immersion. This indicated that the corrosion reaction of Al and Al-O also occurred in the molten salt environment. The EDX results also clarified the existence of Fe and Cr precipitates in the IM layers that were not found in XRD results.

Referred to the SEM images in Figure 5(a)–(d), the change of thicknesses of oxide scales and IM layers includingly were analyzed using the ImageJ Software. It was found that the thicknesses of oxide scales, Fe_2O_3 and Fe_3O_4 (by EDX), increased by 2.8 μg/(cm^2 × h). The increase of oxide scale thickness was also related to the oxidation reaction. In case of immersion of metal (M) in the molten nitrate salt, the sample was experienced in the basic environment that had high amount of alkaline oxide or oxygen ion (O^{2-}) which was decomposed from nitrate ion (NO_3^-) as shown in the reaction 1. And the typical oxidation reaction followed the reaction 2 [9]–[11] [Equations (1) and (2)].

$$NO_3^- + 2e^- \longrightarrow NO_2^- + O^{2-} \tag{1}$$

$$xM^{z+} + yO^{2-} \longrightarrow M_xO_y \tag{2}$$

While the thickness change of Al coated samples demonstrates a different mechanism as shown a rapid drop at the first period in Figure 6. Although the thickness change was slight and less than 1 μm after the first period of immersion, the existence of the Al

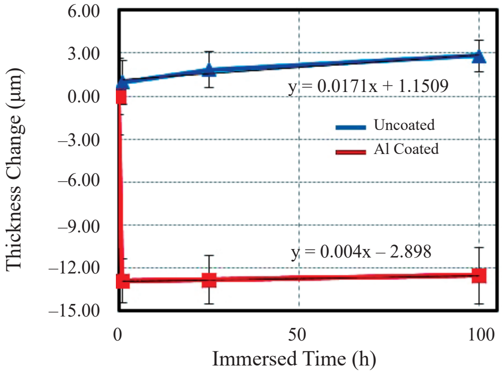

Figure 6: Thickness change of uncoated and Al coated samples after immersion in molten salt at 500°C for 100 h [Equation (3)]

and Al-O including impurity phases, such as sludge, the corrosion occurred. After the Al and Al-O layers were removed, the IM layers functioned as corrosion resistantive layers. In the basic environment, abundant O^{2-} contributed to corrosion of Al and Al-O layers as the following the reaction 3 [11].

$$M_xO_y + zO^{2-} \longrightarrow M_xO^{2-}_{y+z} \quad (3)$$

Metal oxides were still corroded with O^{2-}, and became metal oxide ions ($M_xO^{2-}_{y+z}$) that brought along the decreased weight in Al slurry coated samples because Al-O compounds were not stable and got corroded violently. However, this corrosion mechanism also occurred in the uncoated samples of which oxide scales were FeO and Fe_2O_3 as the following reactions [11] [Equations (4)–(6)].

$$Fe + O^{2-} \longrightarrow FeO + 2e^- \quad (4)$$

$$3FeO + O^{2-} \longrightarrow Fe_3O_4 + 2e^- \quad (5)$$

$$2Fe_3O_4 + O^{2-} \longrightarrow 3Fe_2O_3 + 2e^- \quad (6)$$

Thus, after 1 hour immersion, the mass gains of the uncoated samples were increasing gradually due to the co-existence of oxidation and corrosion reactions. The corrosion behavior of the uncoated sample can be illustrated as shown in Figure 7(a). The oxide scale can be formed by O^{2-} at the surface same as EDX result that shows amount of O increases after the corrosion test. After being formed by an oxide layer, the corrosion mechanism is taken place.

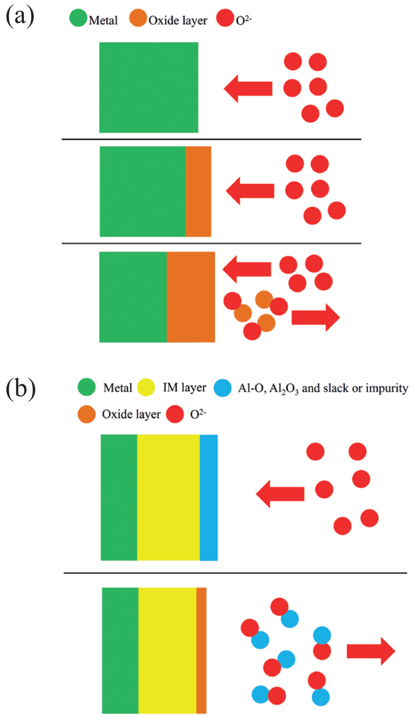

Figure 7: Corrosion mechanism of an uncoated AISI 409 (a) and of the Al slurry coating AISI 409 (b).

On the other hand, Al and Al-O with oxygen depletion can be immediately corroded at the first period when an IM layer is exploded to the molten salt. Then the corrosion mechanism is slower and tends to be stable due to the existence of a protective IM layer of Fe_2Al_5. The same as Table 2 that shows EDX result of Al coated sample after corrosion test has lower amount of O but Al is still rich. The oxidation reaction is still occurring due to Fe and Cr precipitated in the layer that related to EDX result that shows Al coated sample which has lower amount of Fe and Cr contain after it had been exposed to molten salt for 100 h, following with the corrosion of the oxide scales which were formed. This mechanism is illustrated in Figure 7(b).

4 Conclusions

The ferritic stainless steels AISI 409 can be improved operation lifetime due to an IM protective layer of Fe_2Al_5 which is formed by Al slurry coating technique.

The Fe_2Al_5 layer is created in the air atmosphere at 700°C and can reduce the corrosion rate of AISI 409 about 35% against molten salt compared to uncoated ones. The corrosion behavior of uncoated samples in molten salt at 500°C starts with oxidation reaction of metallic elements with alkaline oxide or oxygen ion O^{2-}. The metal oxide layer reacts again with O^{2-} and corroded in form of metal oxide ion. While, the corrosion behavior of Al coated samples in molten salt at 500°C starts with corrosion of Al and Al-O compounds by O^{2-}. Then the reaction to form the Fe_2Al_5 IM layer tends to slower oxidation reaction. This results in better corrosion resistance against molten nitrate salt of the Fe_2Al_5 IM layer.

Acknowledgments

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