Hot Corrosion Behaviour of Austenitic Steel-308 in Chloride Salts

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ABSTRACT

The intensification of process engineering in almost every branch of modern technology, and development of new technologies make increasingly higher requirements for metallic construction materials, especially for their heat and scaling resistance. The increase in operating efficiency of certain installation or plants is generally achieved by the application of higher temperatures and pressures and higher flow velocities of gases and vapors which creates gas corrosion hazard for the construction materials.

The hot corrosion behavior of Austenitic steel-308 in presence of chloride salts at 950° C in a slow current of air for the period of 72 hours has been studied. The Austenitic-308 alloy were severely attacked by calcium- and barium-chlorides due to formation of volatile metallic chlorides. The data have been complemented by oxidation kinetics measurements and morphological structures were analyzed using scanning electron microscope (SEM). The elemental distribution on the alloy surface deposits were characterized by using energy dispersive X-ray analysis (EDAX) techniques. The alkaline earth metal chloride salts have deleterious effect on the protectivity of the scales and rapid degradation of the alloy is noted.

Keywords: *308 Austenitic Steel, $BaCl_2$, $CaCl_2$, hot corrosion, Scales*

Introduction

Corrosion on a metal surface can occur when halide salts contact the surface, because of the differences in electric potential. In environments with high temperature, the surface film of stainless steels break down with sudden increase in scaling causing hot corrosion. Hot corrosion is a widespread problem in various industries such as power generating plants, aerospace and gas turbine, heat treating, chemical processing, refining and petrochemical, pulp and paper, waste incineration, mineral processing and automotive.

Although the largest source of chloride compound is in sea water, but when it is heated or evaporated, chloride compound are found as salt aerosols at the atmosphere. It may strongly influence the corrosion performance of structure and plant. This influence on corrosives reduce proportionately with distance from the seawater surface [1, 2].

Most of corrosion resistant metals rely on an oxide film to provide protection against corrosion. If the oxide is tightly adherent, stable and self-healing, as on many stainless steels, then the metal will be highly resistant or immune to corrosion. If the film is loose, powdery, easily damaged and non-self repairing, such as rust on steel, then corrosion will be unchecked. Even so, the most stable oxides may be attacked when aggressive concentrations of hydrochloric acid are formed in chloride environments [3].

An extensive investigation of the alkali metal chlorides on hot corrosion of austenitic steel has been conducted [4 – 7]. The effect of chloride salts such as $BaCl_2$ and $CaCl_2$ on hot corrosion behavior of austenitic steel-308 steel at 950° C in air and identified the different constituents present in the scales of oxidized alloy.

Materials and Methods

The present study has been carried out using commercially available austenitic steel-308. Its chemical composition as follows: C–0.08%, Mn–2.00%, Si–1.00%, Cr–19.5, Ni–11.0%, P–0.045%, S–0.045% and Fe-remaining. The austenitic steel-308 sheets were cuts into small pieces which was 2.5 x 1.5 x 0.5 cm size. The surface of each specimens were polished mechanically with 180, 320, 600 grit of SiC paper. The specimens were coated with $BaCl_2$ and $CaCl_2$ on the specimen surface in a preheated condition to obtain a layer of salt decomposition [8 & 9]. The coated specimens were weighed and transferred into furnace for heating process for 72 hours at 950° C and recorded the weight changes every 12 hours. Graph of weight changes verses exposure time have been plotted.

The surfaces of certain corroded austenitic steel-308 test specimens have observed by using polarized light microscope and scanning electron microscope (SEM). The elemental distribution on the alloy scales were determined by using Energy dispersive X-ray analysis (EDAX) techniques.

Results

Figure 1 shows the curve of weight changes verses exposure time of austenitic steel-308 coated with calcium- and barium- chlorides, oxidized at 950°C in air. The graph showing the weight changes increase while the exposure times increase up to 48h, followed there is decrease with time. The highest corrosion rate was recorded by alloy that coated with $CaCl_2$ and follow by alloy coated with $BaCl_2$. The greater corrosion rate was recorded at the first 48 hours, followed the trend showing the corrosion rate decreased with the increased of exposure times.

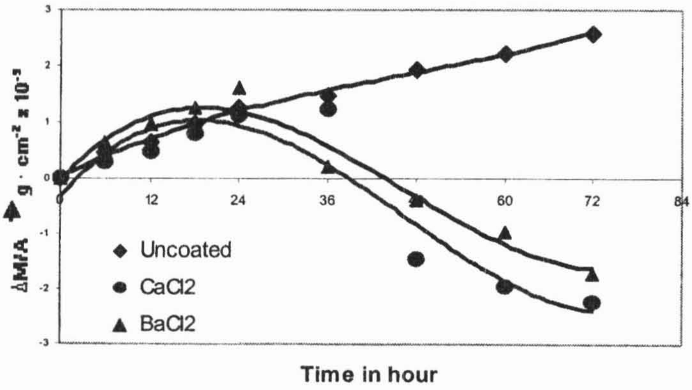
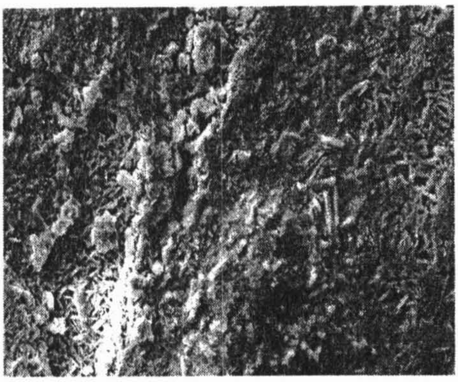
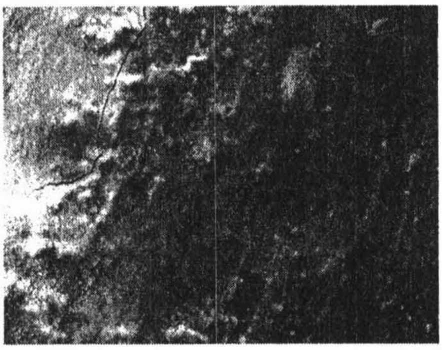


Figure 1. Curve of Weight Change versus Exposure Time of Austenitic Steel-308 Coated with $CaCl_2$ and $BaCl_2$, Oxidized at 950°C in Air.

The spotted area shown in Figure 2 (a) & (b), indicated pitting corrosion seems to be took their place on the metal surface coated with $CaCl_2$ & $BaCl_2$. The SEM micrograph of specimen coated with calcium chloride that exposed at 950°C for 72 hours showing the presence of inter-granular corrosion and pitting corrosion and badly deterioration is observed, exhibiting the breaking of scales.



(a) Coated with $CaCl_2$



(b) Coated with $BaCl_2$

Figure 2: SEM Micrograph of Austenitic Steel-308 Coated with $CaCl_2$ and $BaCl_2$, Oxidized at 950°C for 72 Hours in Air.

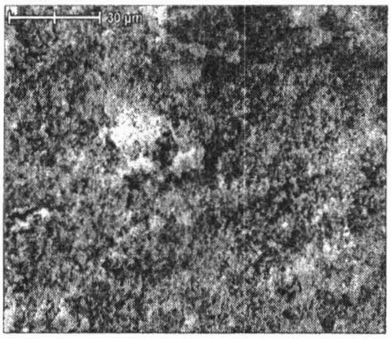
Energy Dispersive X-Ray Analysis (EDAX)

As shown in Figure. 3 and 4, the micrographs and EDAX spectra had verified the content of the elements of the specimen coated with $BaCl_2$ and $CaCl_2$ that exposed at 950°C for 72 hours. The results showed that the surface was mainly composed of chromium (Cr), Nickel (Ni), iron (Fe) and oxygen (O). The results were logically acceptable because austenitic-308 containing Cr-19.50% ; Ni-11.00% and remaining. The oxygen occurs from the air.

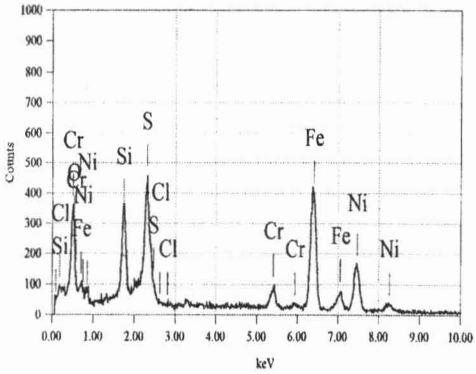
Table 1 and 2 showing the elemental analysis results of specimen coated by barium- and calcium- chloride that exposed at 950°C for 72 hours from EDAX. According to the results in Table 1, iron oxide, FeO, was the main oxide products, it appearance as the site product while corrosion occur. Iron oxide formed when iron (Fe), reacting with oxygen in air, the equation shown as below:

$$2Fe + O_2 \text{ à } 2FeO$$

Besides that, Cr_2O_3 also occur in great quantities as the protective films for the stainless steel. In addition, the surface also accompanied with other oxides such as BaO, CaO, SO_3, and SiO_2 with small composition. Those were components in austenitic steel-308 that formed oxides while the alloy is deteriorated.

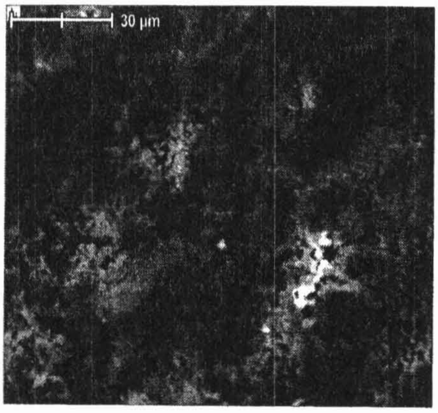


(a) Micrograph

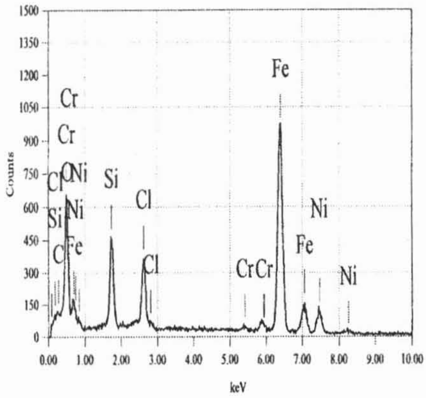


(b) Spectra

Figure 3: Micrograph and EDAX Spectra of the Elements and Compounds of the Specimen Coated with $CaCl_2$, Oxidized at 950°C for 72 Hours.



(a) Micrograph



(b) Spectra

Figure 4: Micrograph and EDAX Spectra of the Elements and Compounds of the Specimen Coated with $BaCl_2$, Oxidized at 950°C for 72 Hours.

Table1: Elemental Analysis Results of Specimen Coated with $CaCl_2$. Oxidized at 950°C for 72 Hours from EDAX.

Element	Mass (%)	Compound	Mass (%)
O	30.63		
Si	5.46	SiO_2	9.68
S	4.79	SO_3	11.96
Cl	0.36	Cl	0.36
Mn	1.57	MnO	2.10
Cr	3.63	Cr_2O_3	5.31
Fe	37.50	FeO	50.10
Ni	16.10	NiO	20.49
Total	**100**		**100**

Table 2. Elemental Analysis Results of Specimen Coated with $BaCl_2$. Oxidized at 950°C for 72 Hours from EDAX.

Element	Mass (%)	Compound	Mass (%)
O	23.69		
Si	4.24	SiO_2	7.08
S	1.96	SO_3	2.20
Cl	4.21	Cl	4.21
Mn	2.07	MnO	1.80
Cr	2.63	Cr_2O_3	2.31
Fe	52.50	FeO	47.10
Ni	9.39	NiO	11.94
Total	**100**		**100**

Disscusion

The corrosive environment of calcium chloride and barium chloride effect onto the hot corrosion behavior of austenitic steel-308 at 950°C has been studied. $CaCl_2$ coated in the stainless steel surface, breakdown the protection film of stainless steel caused the formation of a volatile, CrO_2Cl_2. The reaction can be described as follows [7]:

$$CaCl_2 + Cr_2O_3 + 3/2\ O_2\ \text{à}\ CrO_2Cl_2 + CaCrO_4$$

The formation of volatile products such as CrO_2Cl_2 and $CaCrO_4$, exert sufficient vapour pressure to break the passivation of oxides on austenitic steel-308. Once the passive film breakdown, the molten $CaCl_2$ further attacks the stainless steel and lead to corrosion. The equation was:

$$2Fe + 2CaCl_2 + O_2\ \text{à}\ 2CaO + 2FeCl_2$$
$$2Cr + 3CaCl_2 + 3/2O_2\ \text{à}\ 2CrCl_3 + 3CaO$$
$$Cr + CaCl_2 + 3/2\ O_2\ \text{à}\ CrO_2Cl_2 + CaO$$

The chlorides formed such as CrO_2Cl_2 and $CrCl_3$ were released at the salt interface and get oxidized to release chlorine gas:

$$4CrCl_3 + 3O_2\ \text{à}\ 2CrO_3 + 6Cl_2$$
$$CrO_2Cl_2\ \text{à}\ 2CrO_3 + O_2 + 4Cl_2$$

The chloride might be entrapped between inner oxide layers of the alloy and get condensed on cooling and appear as distinct and discrete phase in the scales [5]. $BaCl_2$ has undergone the same reaction as $CaCl_2$.

High chloride containing solutions will increase the rate of corrosion over less chloride containing solutions. Instead of Fe^{2+} reacting with only hydroxyl ions it can now react with chloride ions. All common metals are very soluble in chloride form and so the reaction is increased. The presence of chloride ions in the electrolytic solution affects nearly every aspect of the corrosion behavior. The oxide layer that protects the steel breaks down in the presence of chloride, causing pits to form. This type of corrosion can lead to structural failures [10].

Temperature is a factor in activation controlled corrosion. Raising the time will also increase the corrosion rate as the activation energy decreases with temperature. Increasing solution temperature increased the susceptibility to both pitting and active dissolution [11].

The corrosion rate of each test was decrease with the increasing of exposure times. It is because the decrease of the concentration of the chloride ions with times, most of the chloride ions that leads to corrosion has reacted to breakdown of the chromium film protecting the surface of the steel and activates the unprotected surface [7]. This determined the concentrations of chloride solution would affect the corrosion rate. The chemical reactions of chloride ions are:

$$Fe^{2+} + 2Cl^-\ \text{à}\ FeCl_2$$
$$FeCl_2 + 2H_2O\ \text{à}\ Fe(OH)_2 + 2HCl$$

From the SEM micrographs analyses, the alloy coated with $CaCl_2$ that exposed to 950°C undergone a seriously corrosion than the alloy coated with $BaCl_2$. It determined ionic salts also affect the corrosion rate. Increasing the time and high temperature, exhibiting the susceptibility to both pitting and active dissolution. Higher temperatures resulted in increased corrosion current densities and peak current densities [10].

Conclusion

The results of the study shown the increased chloride content, the easily the passive region shrinks and simultaneously with the formation of corrosion.

From the study of the effect of different temperature on austenitic steel-308 , the patterns of the graphs follow the kinetic theory of reaction where the reactions rates were directly proportional to the increasing of time. It means as the high temperature, the time require in initiating corrosion attack is decreased. The oxidation rates of stainless steel in presence of $BaCl_2$ and $CaCl_2$ salts were studied. $CaCl_2$ coated stainless steel shown higher weight changes than the coated specimens by $BaCl_2$. This shows the aggressiveness of these corrosion agents in decreasing manner is calcium chloride follow by barium chloride.

The corrosion rate was highly affected by the concentration of chloride ions and temperature. The trend showing the corrosion rate decreased with the increased of exposure times. This is because the concentration of the chloride ions decreases with times. Besides that, temperatures also affect the corrosion rate.

Pitting corrosion, intergranular corrosion and stress corrosion cracking were the commonest corrosion found in austenitic steel-308.

From the results of EDAX, iron oxide, FeO, Cr_2O_3 & NiO occur in great quantities on the corroded stainless steel surface. There were also other oxides such as BaO, CaO, SO_3, and SiO_2 with small composition.

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