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## The Influence of Molten Salt Deposit in Water Vapor Environment on Corrosion Behaviour of Stainless Steel at High Temperature

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### ABSTRACT

The corrosion behavior of austenitic and martensitic stainless steels exposed in corrosive environment of water vapor only and mixed environment of water vapor and molten Na<sub>2</sub>SO<sub>4</sub>-50%NaCl were investigated at 700°C for 10 h by weight change measurement, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) techniques. The results show that, the corrosion rate of austenitic stainless steel is less than martensitic due to the growth of Cr-rich oxides like Cr<sub>2</sub>O<sub>3</sub>, NiCrO<sub>3</sub> and Cr<sub>1.3</sub>Fe<sub>0.7</sub>O<sub>3</sub> which together act as a protective layer. However, in the presence of molten salt in water vapor environment, the corrosion rate for austenitic stainless steel is higher than martensitic stainless steel. Austenitic stainless steel sample undergoes synergistic effect with less development of oxide scale as we analyzed its cross-sectional morphologies. XRD result also shows that the existing phases exist are FeNi and Cr<sub>2</sub>Ni<sub>3</sub>. The thin and non-protective oxide layer does not prevent the Cl<sup>-</sup> and oxygen from corrosion even though the Cr content is about 16 wt. % as simultaneous presence of water vapor and salt plays a major role in corrosion process. Therefore, the tested stainless steels could withstand corrosion in water vapor environment but not in corrosive environment of water vapor and molten alkali salt especially for austenitic stainless steel.

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## INTRODUCTION

Most industries especially those involving high temperature based operation always face a major problem in their operation which is corrosion. Corrosion at high temperature is much faster than in ordinary condition. Furthermore, for example gas turbines, shipboard and aircraft engines, and boilers of offshore industrial rigs when operated near sea, salt from sea breeze would lead to cause hot corrosion to the alloys. This type of corrosion occurs when alkali salt deposited on the alloys components surface during hot and became a solid salt deposition as it cools down (Zheng *et al.*, 2011). Alkali salt such as sodium chloride (sources from sea breeze) and sodium sulfate are the most studied because there are the common corrosive agents in high temperature application industries. Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) produced from the reaction between sulfur and sodium chloride as described by chemical equation (1) or (2) (S.P.Akbar Hussain, 2013). Sulfur is produced when low grade fuels are used in the operation especially in coal- and oil-fired power generation industries.



Stainless steel is one of the materials that can withstand with this type of corrosion at certain operated temperature due to its elements content. The most important element is chromium. It can develop a thin, dense and continuous passive oxide layer in order to prevent further degradation of alloys at high temperature. Three types of stainless steel which are austenitic, ferritic and martensitic are commonly used in industries due to their specific characteristic. At high temperature, austenitic and martensitic have a good corrosion resistance than

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ferritic. However, in certain cases such as in the presence of water vapor, these stainless steels will undergo corrosion.

Water vapor is one of the corrosion agents that will lead to the deterioration of alloys/metals. It is well known that high temperature oxidation/corrosion had significantly affected in the presence of water vapor. The protective oxide scale is known as to be accelerated loss in the presence of H<sub>2</sub>O or water vapor. This can be directed to a process where is a rapid increase of corrosion rate known as a breakaway and it has several of reaction morphologies depending on chemical composition of alloys. In the case of stainless steel, this associated morphologies evolution is non-uniform, as it involves nucleation, spreading and thickening of oxide nodules on the alloy surface (Gheno *et al.*, 2013). Therefore, in this study, water vapor and alkali salt of NaCl-50%Na<sub>2</sub>SO<sub>4</sub> were combined creating a corrosive environment to be tested on austenitic and martensitic stainless steels to investigate the corrosion behavior of these alloys.

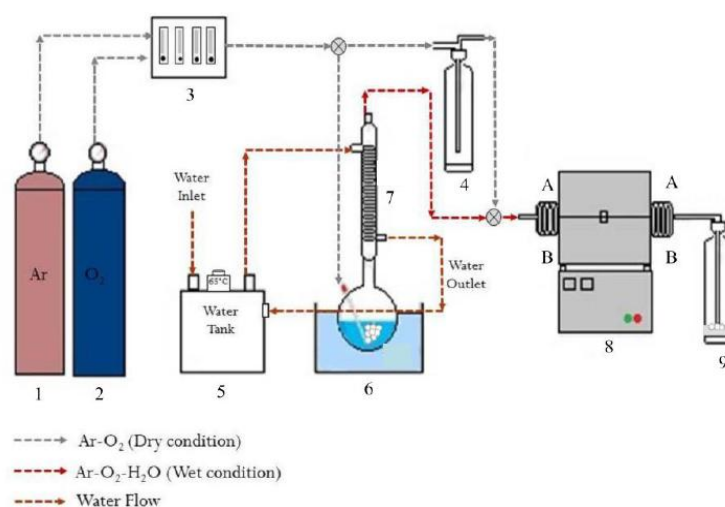
## MATERIALS AND METHODS

In this experiment, two types of stainless steel which are austenitic and martensitic were used. Their chemical composition were analyzed using spark emission spectroscopy was tabulated in Table 1. Specimens were prepared by cutting into dimension of 20mm x 10mm with thickness about 3mm before high temperature corrosion test was carried out. The surface was subsequently grounded using SiC emery paper from 320 to 1200. The sample's edge also curved to reduce the corrosion attack. All samples were washed by acetone, ethanol and rinsed in distilled water via ultrasonicator. They were accurately weighed and measured the dimension to determine the total exposed area in the tested environments.

Two environments were introduced in this experiment; water vapour (Ar-20%O<sub>2</sub>-12%H<sub>2</sub>O) and mixed environments (Na<sub>2</sub>SO<sub>4</sub>-50%NaCl + Ar-20%O<sub>2</sub>-12%H<sub>2</sub>O). The concentration of water vapor was produced by maintaining the temperature of water condenser at 50°C. The details of experimental setup are shown in Figure 1. Specimens were hanged and inserted into tube furnace isothermally for 10 h at 700°C with ramp temperature of 10°C/min. After that, specimens were cooled down to room temperature in the tube furnace with flowing of argon gas. They were reweighed and analyzed using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX). Specimen with deposited of alkali salt was prepared in this manner; pre-heated at 250°C for 30 mins. Then, saturated alkali salt mixture was deposited on specimen's surface with assist of brush. They were put into oven with temperature 120oC to remove excess moisture about 2 h.

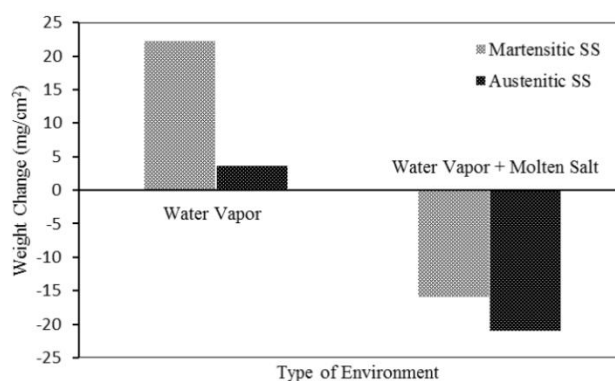
**Table 1:** Chemical composition of tested stainless steel in wt.%.

Elements	Fe	Cr	Ni	C	Mo	Si	Mn	Cu	V
Austenitic (wt.%)	69.00	16.00	12.20	0.04	0.09	0.30	1.78	0.14	0.06
Martensitic (wt.%)	82.80	11.30	2.64	0.26	1.94	0.12	0.38	0.06	0.31



**Fig. 1:** Customized tube furnace for high temperature experimental setup; (1) argon gas, (2) oxygen gas, (3) flow meter, (4) drying tower, (5) water tank, (6) water bath, (7) condenser (8) horizontal tube furnace (9) gas trap, (A) water coolant inlet and (B) water coolant outlet.

## RESULTS AND DISCUSSION



**Fig. 2:** Weight change of tested samples after 10 h exposure in corrosive environments.

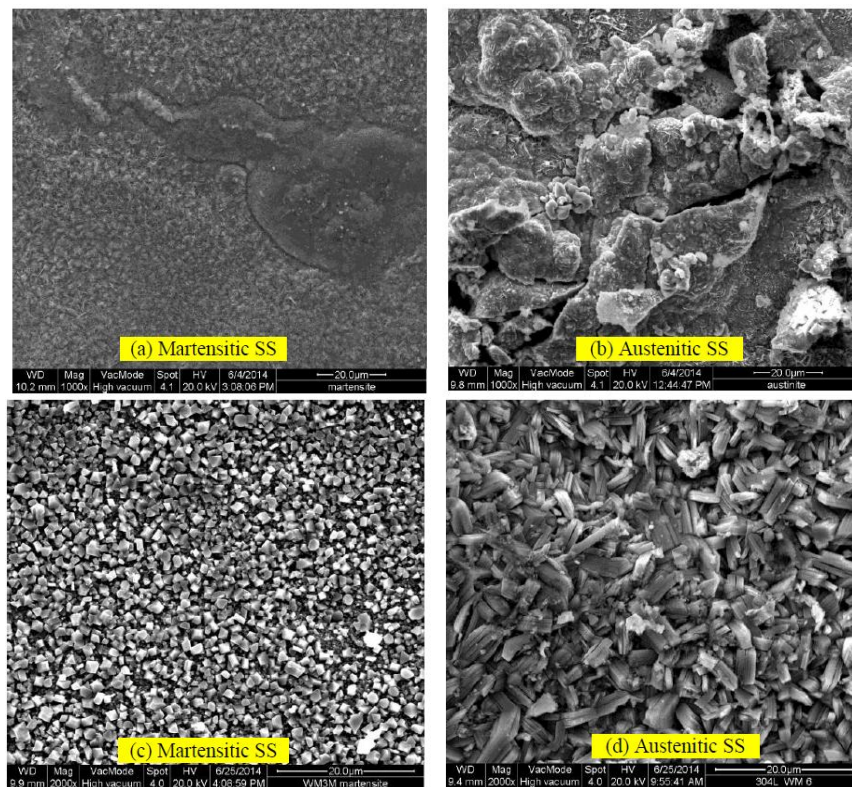
The weight change of martensitic and austenitic stainless steel after exposed in water vapor only and water vapor + molten salt environment at 700°C for 10 h is shown in Figure 2. The weight gain of both samples exposed in water vapor environment is quite significant due to the development of oxide scales. In the presence of both molten salt deposition + water vapor, samples suffered weight loss caused by spallation of oxide scales that was mixed with the deposited salt. It was observed for austenitic stainless steel its corrosion rate in water vapor environment is much less than martensitic sample but, in mixed molten salt + water vapor environment, corrosion rate of austenitic is higher than martensitic. This would be happened because of different element composition in both alloys in different type of corrosive species due to presence of salt.

The surface morphology of all samples after the test is showed in Figure 3. The microstructure of martensitic SS was smooth in wet oxygen/water vapor while in presence of molten salt + water vapor, the cube-like microstructure was developed. Meanwhile, austenitic SS shows rough surface and rectangular-shaped in water vapor and mixed molten salt + water vapor environment respectively.

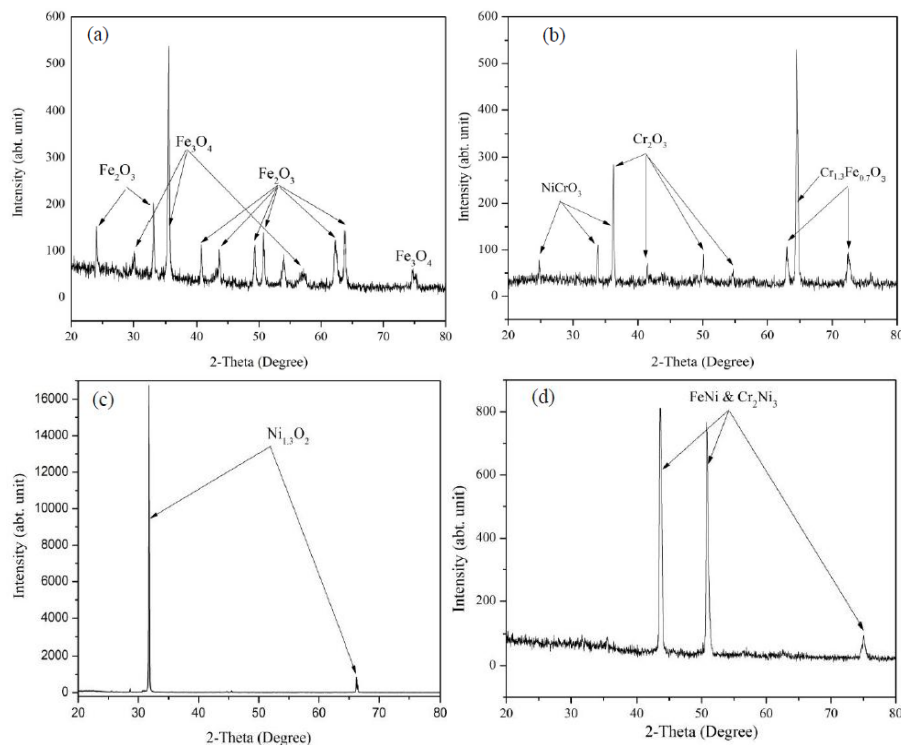
All samples were then were analyzed using XRD technique to determine the developed phases and shows in Figure 4. Oxide scales of martensitic and austenitic samples consist of Fe-rich oxide and Cr-rich oxide respectively. The Cr-rich oxides which are  $\text{Cr}_2\text{O}_3$ ,  $\text{NiCrO}_3$  and  $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$  developed on the surface of austenitic in water vapor environment. These oxide scales prevented further degradation of sample, thus the corrosion rate was low compared to martensitic sample that covered by non-protective Fe-rich oxide which are magnetite ( $\text{Fe}_3\text{O}_4$ ) and ( $\text{Fe}_2\text{O}_3$ ) oxides. Meanwhile, for sample exposed in environment of molten salt + water vapor, the identified phases for martensitic and austenitic SS consist of  $\text{Ni}_{1.3}\text{O}_2$  and FeNi and  $\text{Cr}_5\text{Ni}_3$  respectively.

Based on the Figure 5, the cross-sectioned samples showed the development of oxide scales. Both samples exposed in 12% of water vapor exhibited two layers of thick oxide scales. The outer layer was porous and non-adherent in contrast with the inner oxide scales layer which is continuous, dense and adherent with the stainless steel. In addition, there are some voids between the outer and inner layer of oxide scales. The voids occurred due to the formation of volatile species and gaseous such as  $\text{CrCl}_3$ , HCl and  $\text{Cl}_2$  (Wang and Shu, 2003) while internal voids were caused by a countercurrent flow of vacancies left by the outward diffusion of iron and/or chromium (Seybolt, 1970). Besides that, the growth of oxide scales on martensitic SS is much thicker than austenitic SS. This result corresponds with weight change result in Figure 2, where the weighed gained of martensitic SS is higher than austenitic SS due to the different thickness of oxide scales. Thus, this indicates that, the corrosion rate of martensitic SS is lower than austenitic SS in water vapor environment. However, samples exposed in temperature of 700°C in the presence of both molten salt + water vapor experienced a porous and non-adherent and loose growth of oxide scales. Sample of Fe-Cr exposed in water vapor and NaCl studied by Wang and Shu (2003) does not form any oxide scales. These stainless steels failed to withstand the degradation due to synergistic effect of corrosive environment within the duration of 10 h. Investigation done by (Shu *et al.*, 2000) on pure Cr, the influence of NaCl in water vapor damaged the protectiveness of the  $\text{Cr}_2\text{O}_3$  scale after it had formed and thus further corrosion occurred.

As reported by (Johnson *et al.*, 1975), alloys with high chromium content could be attacked when NaCl present in the mixture of NaCl-Na<sub>2</sub>SO<sub>4</sub>. In addition, small amount of NaCl for about 10% in Na<sub>2</sub>SO<sub>4</sub> was enough to crack the protective oxide layer,  $\text{Cr}_2\text{O}_3$  and increase the amount of sulfur incorporated into the alloys, thus induced the corrosive attack. The hot corrosion of 310 SS at 750°C in 25%NaCl or more of NaCl- Na<sub>2</sub>SO<sub>4</sub> mixture show unstable weight change growth rate and much severe than in 100% Na<sub>2</sub>SO<sub>4</sub> and simple oxidation (Tsaur *et al.*, 2005).

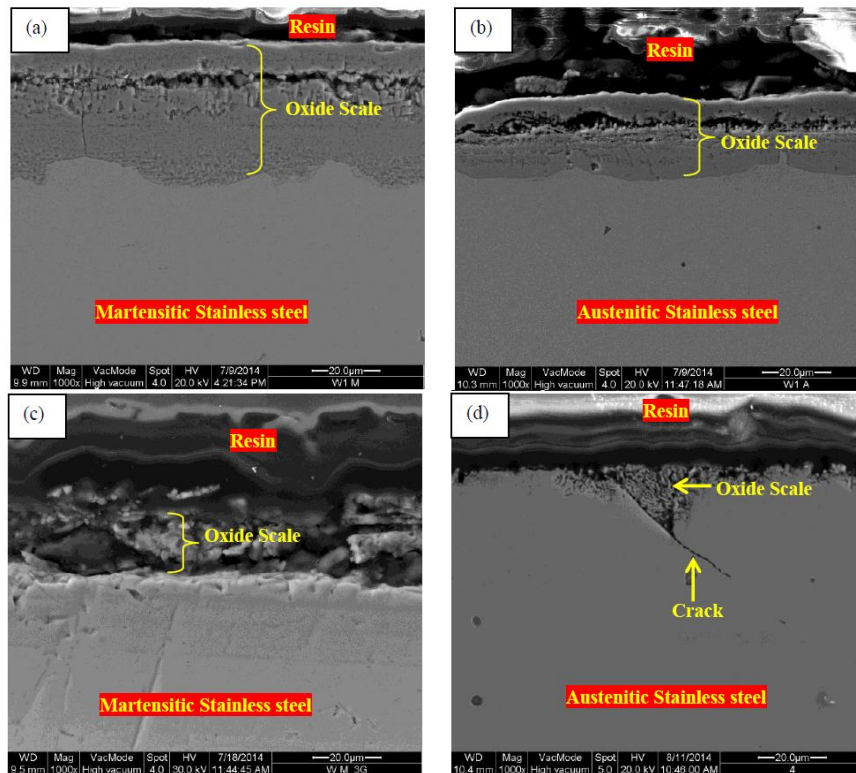


**Fig. 3:** SEM micrograph of martensitic and austenitic stainless steel surface exposed in (a-b) water vapor environment with 1000× mag and (c-d) molten salt in water vapor respectively with 2000× magnification.



**Fig. 4:** XRD spectrum of the tested sample (a) martensitic SS (b) austenitic SS in water vapor environment and (c) martensitic SS (d) austenitic SS in molten salt + water vapor environment.





**Fig. 5:** SEM micrograph of cross-sectioned samples with 1000 $\times$  mag of martensitic SS in (a) water vapor (c) molten salt + water vapor and austenitic SS in (b) water vapor (d) molten salt + water vapor.

#### Conclusion:

Martensitic and austenitic stainless steels were exposed in tube furnace at 700 $^{\circ}$ C for 10 h in corrosive environment of water vapor only and mixed water vapor + molten  $\text{Na}_2\text{SO}_4$ -NaCl. The corrosion rate of stainless steel in water vapor environment was low compared to that in the environment of water vapor + molten  $\text{Na}_2\text{SO}_4$ -NaCl. The presence of salt induced the corrosion rate of stainless that undergoes spallation and weight loss. For austenitic stainless steel the protective Cr-rich oxides developed and prevent the further degradation of sample in water vapor environment only. However, the synergistic effect of water vapor + molten salt was significantly aggravated due to the deterioration of protective and any developed oxide scale even though the content of Cr for austenitic stainless steel is about 16wt.%.

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