

# HIGH TEMPERATURE AND STRESS CORROSION CRACKING OF 310S AUSTENITIC STAINLESS STEEL IN WET CHLORIDE CORROSIVE ENVIRONMENT

Received – Priljeno: 2017-09-04

Accepted – Prihvaćeno: 2017-11-15

Original Scientific Paper – Izvorni znanstveni rad

High temperature corrosion and stress corrosion cracking of 310S austenitic stainless steel in wet chloride environment at a high temperature was investigated. The result showed that high temperature corrosion products mostly consisted of ferrous oxides and chromium oxides. Chloride ions attacked a chromium passive film and strongly reacted with iron and chromium. As a result of metal chlorides being volatilized, tunnel of pores inside corrosion layer existed. Intergranular stress corrosion cracking was observed. The oxide originated on surface could act as a crack initiator and a crack propagation would progress along grain boundaries and particularly along tunnel of pores.

*Key words:* high temperature corrosion, stress corrosion cracking, austenitic stainless steel, chloride environment, x-ray methods

## INTRODUCTION

Stress corrosion cracking (SCC) is a phenomenon which occurs under the combined influence of a corrosive environment and mechanical loading. The SCC is particularly dangerous, since no effective detection system is installed and advanced non-destructive testing (NDT) technique is employed. SCC of austenitic stainless steel (ASS) especially in a chloride environment has been an active research for many years because this problem is very important. The main factors affecting SCC of ASS in a specific chloride environment are involved stress, production conditions, and chloride environment conditions of ASS [1,2].

High temperature corrosion (HTC) of ASS has been examined by several scholars. A crucial phenomenon at high temperature is oxidation which its properties play a critical role in determining the oxidation resistance of ASS in a specific environment. The Cr quantity is a principal factor to affect corrosion resistance of ASS in many environments. The methods to enhance performance of a high temperature oxide film is to increase the quantity of Cr, Al, or Si in order to alternatively form more stabilized passive oxides at the high temperature [1,3].

In many industries, oxidation does not solely occur. The occurrence of HTC caused by contaminants are also presented in the atmosphere. Those contaminants accelerate HTC due to a strong synergistic effect with

oxidation [4–6]. Chlorides or chlorines contribute to HTC and cause corrosion acceleration resulting in increased oxidation, metal wastage, internal attack, and void formation [7–9].

The objective of this research is to characterize and discuss the SCC of 310S at 900 °C in chloride containing environment.

## MATERIAL AND METHOD

In this study, wrought SUS 310S ASS was selected for investigation. Specimens in rectangular coupons with 140 mm × 30 mm × 4 mm (length × width × thickness) were prepared. Table 1 displays chemical compositions of 310S analyzed by X-ray fluorescence technique (XRF).

Table 1 **Chemical composition of 310S/ wt.%**

C	Cr	Ni	Si	Mn
0,08	24,58	19,13	0,59	1,85

In order to apply an external stress to specimens, the specimen is bent into U-shape. The applied stress could be calculated by using bending theory and flow curve of the material.

A HTC test shown in Figure 1 was carried out within ceramic tube chamber. The solution was prepared by mixing HCl solution and distilled water with ratio 6:1 by mole. The final concentration of such solution was 6 M. The total volume of fed solution was about 1,098 ml. Then, the solution was boiled to generate vapor and go through nozzle into the chamber and creates wet acidic chloride corrosive environment. The chamber was heated up from room temperature to 900 °C for about 3

T. Pornpibunsompop, P. Thanakijkasem, Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, Thailand, Email, tosaporn.p@dti.or.th, purit.tha@kmutt.ac.th

hours, held on for 210 hours, and cooled down to room temperature showed the Time –temperature (TT) diagram in Figure 2. The acidic vapor was fed and kept within closed chamber for 210 hours.

## RESULTS AND DISCUSSION

### High temperature corrosion (HTC)

Two sets of 310S ASS samples were tested with difference bending radii. The HTC product layer, built up on the ASS, would be categorized into three sub-layers; (1) Broken up scale, (2) External corrosion product layer, and (3) Internal corrosion product layer as illustrated in Figure 3. The broken up layer was examined by X-ray diffraction technique (XRD).

Figure 4 showed XRD patterns of broken up scale corrosion products between 310S which was compared by 304 in order to illustrate the effect of chemical composition on characteristics of corrosion product. The main

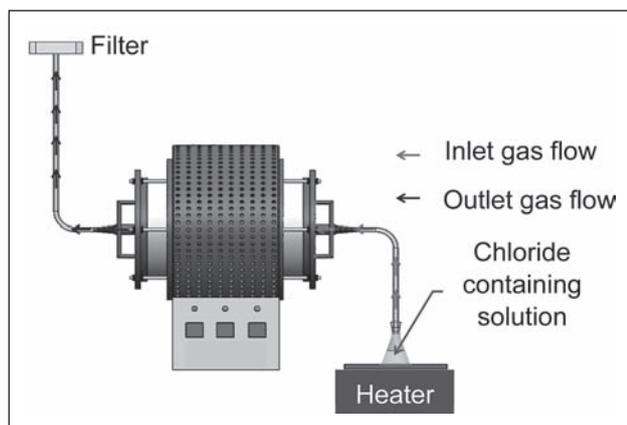


Figure 1 Schematic representation of corrosion testing chamber

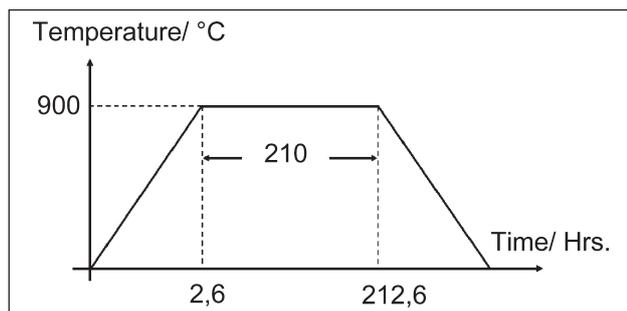


Figure 2 TT Diagram of corrosion test

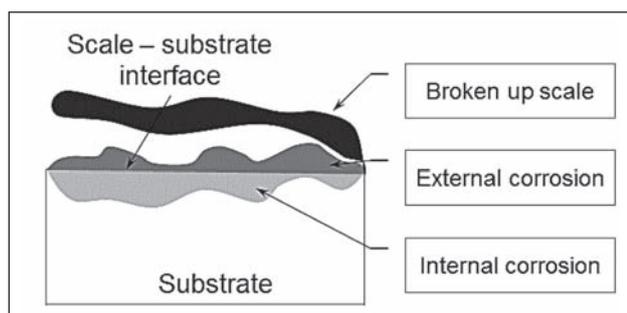


Figure 3 Sub-layers of corrosion product after HTC test of ASS

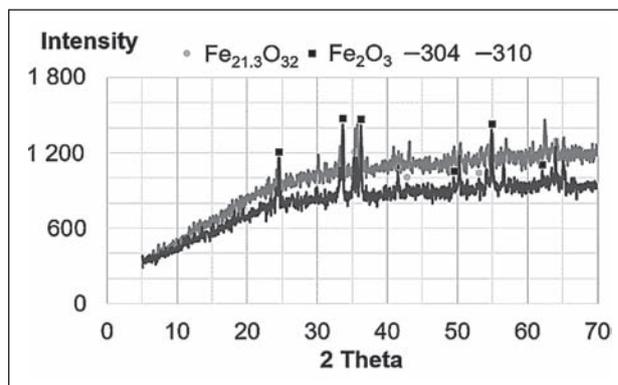


Figure 4 X-ray diffraction pattern of broken – up scale exposed to chloride environment at 900 °C

constituents of corrosion products caused by a high temperature chloride environment in both cases of 304 and 310S were  $Fe_2O_3$  and  $Fe_{21.3}O_{32}$  ferrous oxide because  $Fe_2O_3$  needs a large content of  $O_2$  to exist.  $Fe_{21.3}O_{32}$  was the result of the chlorination-oxidation process [3–5].

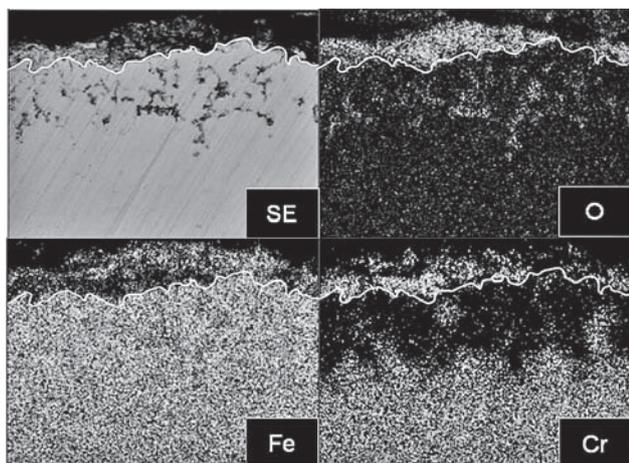
The thickness of broken up scale was relatively studied and found that scale of 304 was thicker than 310S as shown in Figure 5. This phenomenon was expected because 304 contained lower quantity of Cr than 310S. So that 304 is more susceptible to attack by corrosive environment because of lower re-passivation capability, and launched massive oxide scale.

External and internal corrosion layer analysis of 310S was characterized by Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM/EDS) as shown in Figure 6. The significant composition of corrosion scales on 310S consisted of Fe, Cr, and O elements. The Fe was quantitatively detected both above and under specimen surface, in contrast with chromium and oxygen which were mostly detected at specimen surface only. The distribution of such elements would be explained in detailed as follows:

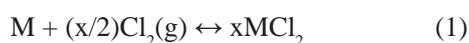
When HCl stream was fed into the chamber, HCl would oxidize within chamber and resulted  $Cl_2$  gas.  $Cl_2$  will diffuse and penetrate through passive film and chemically react with metal element forming metal chloride as follows Eq. (1). So that, passive film was strongly destroyed by wet chloride ambient leading to decrease corrosion resistance of the  $Cr_2O_3$  passive film.



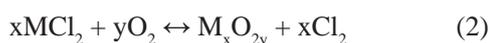
Figure 5 Test specimen after exposed to 210 hrs. 6 mol/l chloride environment at 900 °C



**Figure 6** SEM/EDS mapping micrograph of 310S stainless steel in chloride atmosphere during 210 hrs.



Furthermore,  $O_2$  would be extracted from a wet condition within the chamber and, then, oxidized with metal chlorides to form metal oxides [5–8]. The oxidation reaction can be described according to Eq. (2).



Because chromium chlorides need a lower concentration of  $O_2$  to form chromium oxides than ferrous chlorides and free energy of chromium chlorides formation is more negative than ferrous chlorides so that it will be formed adjacent to the interface between external and internal layer. The concentration of oxide compounds on external and internal corrosion layer was identified and recognized as insignificant corrosion products.

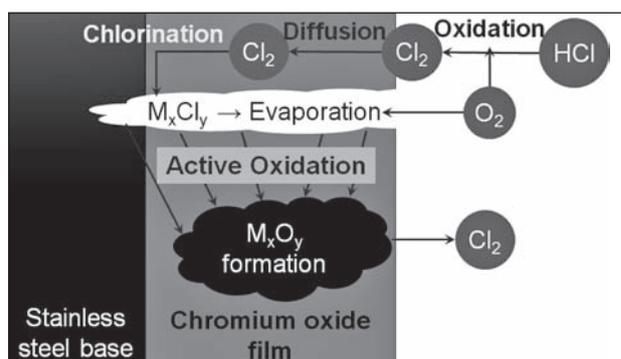
This chlorination – oxidation process will be occurred in repeat character and can be visualized in Figure 7.

### Stress corrosion cracking (SCC)

Intergranular cracks caused by a HTC and an applied stress were microscopically characterized. The results were illustrated in Figure 7. The maximum crack depth measured from the interface to the bottom of cracks can also be observed in Figure 8. It was noticed that, in case of 310S, the maximum crack depth of 12 mm bending radius specimen is deeper than that of 24 mm bending radius specimen because of a higher level of applied stress. Moreover, metal oxides built up on the interface were obtained and might performed as crack initiator. Additionally, tunnel of porous below corroded surface caused by evaporation of metal chlorides would accelerate crack propagation because pores are weak areas and cannot retard crack branching.

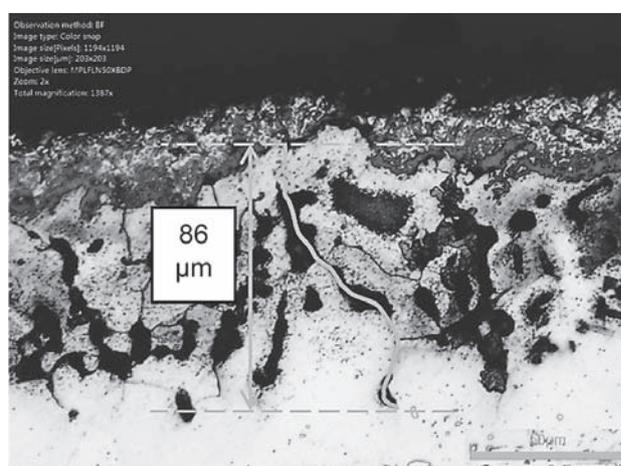
### CONCLUSION

HTC and SCC of ASS in high temperature chloride environment was investigated and major conclusions are as follows:

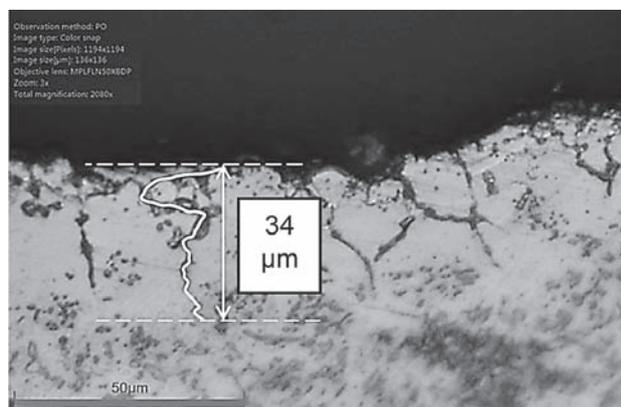


**Figure 7** Cyclic chlorination – oxidation process

- Broken up scale composed of 2 types of ferrous oxides:  $Fe_2O_3$  and  $Fe_{21.3}O_{32}$ . The thickness of 304 scale was larger than 310S and it had the ratio of  $Fe_2O_3$  to  $Fe_{21.3}O_{32}$  almost at 1.0. 310S had the ratio less than 1.0 because of weaker corrosion resistance of 304 than 310S due to lower content of Cr.
- HTC product contained ferrous and chromium oxides which did not perform as a passive film.  $Cl_2$ , which was derived from HCl, destroyed passive film and reacted with Fe and Cr to form evaporated metal chlorides and, then, flowed out leaving pores within the passive film and specimen. Finally, oxidation of metal chlorides was occurred and transformed to metal oxides built up on scale – substrate interface.



a)



b)

**Figure 8** Optical microscopic images of 310S stainless steel varying bending radii (a) 12 mm (b) 24 mm

– Intergranular SCC was revealed. Crack initiation happened at scale-substrate interface and propagated progressively along grain boundaries via tunnel of pores. Crack depth of each stainless steel was also studied and found that a high applied stress level could cause a deeper crack.

## REFERENCES

- [1] L.Colombier et al, *Stainless steel*, UGINE s.a., 1993, pp. 331-333.
- [2] K. H. Lo, C. H. Shrek, J. K. L. Lai, Recent development in austenitic stainless steels, *Material science and engineering R*, 39 (2009), 39-104.
- [3] A. S. Khanna, *Introduction to high temperature oxidation and corrosion*. ASM international, 2002, pp. 5-10.
- [4] Y. N. Chang, F. I. Wei, High temperature chlorine corrosion of metals and alloys, *Material science*, 26 (1991), 3693-3698.
- [5] A. Zahs, M. Spiegel, H. J. Grabke, Chloridation and oxidation of iron, chromium, nickel and their alloys in chloridizing and oxidizing atmospheres at 400-700 °C, *Corrosion science*, 42 (2000), 1093-1122.
- [6] C. J. Wang, C. C. Li, The high temperature corrosion of austenitic stainless steel with a NaCl deposit at 850 °C, *Oxidation of metal*, 61 (2004), 485-505.
- [7] H. P. Nielsen, F. J. Frandsen, K. D. Johansen, L. L. Baxter, The implications of chlorine-associated corrosion on the operation of biomass-fired boilers, *Progress in energy and combustion science*, 26 (2000), 283-298.
- [8] M. A. Uusitalo, P. M. J. Vuoristo, T. A. Mantyla, High temperature corrosion of coatings and boiler steels below chlorine-containing salt deposits, *Corrosion science*, 46 (2004), 1311-1331.
- [9] K. A. Habib, M. S. Damra, J. J. Carpio, I. Cervera, J. J. Saura, Performance of NiCrAlY Coatings Deposited by Oxyfuel Thermal Spraying in High Temperature Chlorine Environment, *Material engineering performance*, 23 (2014), 3511-3522.

**Note:** The responsible for English language is the lecturer from University