Corrosion Behaviour of Hastelloy C22 in Alkali Salt Environment

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Abstract. Chloride-induced corrosion at elevated temperature is the major drawback of commercialization of biomass fired power generation. The incapability of the biomass-fired boilers to increase the temperature has resulted in a lower efficiency of the power plant. Hastelloy C22 is one of the potential materials for superheater due to the high content of Ni-Cr which provides an excellent corrosion resistance. The aim of this work is to obtain more information on corrosion behaviour of Hastelloy C22 at high temperature in alkali salt environment with the influence of air humidity, hence to justify the suitability of this alloy as a superheater material for higher operating temperature. Corrosion tests were performed in the synthetic salt containing 80 wt% KCl and 20 wt% K₂SO₄ under normal and dry air conditions. The test was conducted at temperature 650°C for 218 hours. The surface morphology, elemental distribution and the corrosion products were characterized using Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive X-ray (EDX). The phase identification was carried out using X-ray Diffraction (XRD) analysis. The results revealed a significant effect of humidity on the corrosion behaviour of the alloy where the presence of air moisture reduces the protective capability of the chromium oxide (Cr₂O₃) scale. A formation of unstable chromium (IV) hydroxide as well as the volatilization of Cr₂O₃ led to the oxide spallation, thus reducing the corrosion resistance of the superalloy.

1. Introduction

Due to the tremendous increase in CO₂ level in the atmosphere that contributes to the global warming, the use of renewable energy has been gaining its importance nowadays. Renewable energy sources that claimed to be CO₂ neutral-like biomass are currently becoming the substitutes for fossil fuel in many power plants. Biomass resources are readily available which make it much more preferable resources compared to others. In real combustion of waste, some types of biomass release high level of salts compounds such as HCl, NaCl and KCl [1]. At high operating temperature in biomass processor, the presence of this complex alkali chloride is subsequently deposited on metallic surface or already-formed oxide layer led to degradation and corrosion damages of construction material which are required a constant repair [2].

Hastelloy C22 is a well-known nickel-based superalloy mostly studied by researchers as a material used for high temperature application [3–7]. The capability of Hastelloy C22 to offer an excellent performance under extreme condition, enables biomass boilers to operate at high temperature which in turns increase the efficiency of biomass fired plants. At elevated temperature, high nickel and
Chromium content of Hastelloy C22 helps it to resist oxidation, carburization sulfidation and halides attack [7-8]. Corrosion resistant of metal alloys depends on the chemical stability, arrangement, compactness, strength, plastic and thermal expansion coefficient of the corrosion product [10]. An oxide layer such as chromia (Cr$_2$O$_3$) is believed to have an ability to protect the alloys by a formation of a stable and dense oxide layer to avoid further corrosive media contact [11].

In this studies, Hastelloy C22 is proposed as a potential material for biomass boilers due to its excellent resistance to corrosion attack [12]. The experimental support is needed to justify the lifetimes and performance of Hastelloy C22. Therefore, the aims of this work are to investigate the influence of humidity on corrosion tendency of Hastelloy C22 and to study the corrosion mechanism of Hastelloy C22 with a presence of synthetic salt in normal and dry conditions.

2. Experimental study

2.1 Sample preparation

The compositions of materials used in this study are given in Table 1. As received Hastelloy C22 were cut into square approximately to 10x10x2 mm. The samples were then ground using silica carbide grinding paper from 300 grit up to 1000 grit, followed by polishing using alumina powder from 1 µm, 0.3 µm and 0.05 µm. Then, all samples were further cleaned in ethanol using ultrasonic bath for 10 minutes and dried to avoid any contamination.

| Element | Ni   | Cr   | Mo   | W | Fe | Co | Si | C | V | Mn | P | S   |
|---------|------|------|------|---|----|----|----|---|---|----|---|-----|
| wt %    | 57.36| 21.20| 13.50| 2.90| 3.80| 0.93| 0.03| 0.003| 0.014| 0.25| 0.007| 0.004 |

2.2 High temperature corrosion test in salt

A mixture of 80% potassium chloride (KCl) and 20% of potassium sulphates (K$_2$SO$_4$) were being used in this research to represent the main corrosive species in superheater tubes for biomass combustion. Experiments were run at 650°C with an exposure time 218 hours for both dry and normal air conditions. Air for dry condition was dried by passing it through an alumina combustion boat containing silica gel. Then, the samples were placed inside a quartz glass tube positioned in the furnace to ensure that the atmosphere remained as dry as possible.

A small amount of synthetic salt was deposited on the surface of each samples by taping it gently with a glass rod. Exposure was carried out in temperature-controlled horizontal quartz glass tube furnace. Samples were raised to the final exposure temperature at a rate of 5°C min$^{-1}$. Under both condition, air flow was fixed at 4 dm$^3$ min$^{-1}$ positioned horizontally, parallel to flow direction. After 28 hours, specimen was withdrawn from the furnace, cooled in air, cleaned with soft brush and washed in boiling water to remove the salt left on the surface. Specimen was then dried in hot air and placed in a desiccator to be ready to undergo characterization.

2.3 Characterization

The surface morphology of corroded samples after exposure in synthetic salt was observed by Scanning Electron Microscope (SEM) in Secondary Electron (SE) mode. Chemical compositions were determined by Energy Dispersive X-ray Spectroscopy (EDX). Phase identification of the corrosion product was conducted by X-ray Diffraction (XRD) meter with Cu Kα incident radiation ($\lambda = 0.15406$) operating at 2θ from 10° - 90°.
3. Results and discussion
3.1 Oxidation behaviour of Hastelloy C22 in normal and dry atmosphere

The oxidation behavior of Hastelloy C22 at temperature 650°C has been discussed according to the type of atmosphere they were being exposed. Under the corrosive condition, Hastelloy C22 was commonly coated with oxide films which formed as a result of interaction between Hastelloy and molten salt mixture. Fig 1 shows the SEM micrograph of corroded Hastelloy C22 specimen in chloride salt under dry and normal atmospheres at different magnifications. Corrosion product of the specimen under normal air appears to be much colloid-like tiny structure and granular-like structure on the surface area (Fig 1 (a)). While the corrosion product appears under dry air specimen seems to be an agglomeration of granular-like structure (Fig 1 (c)). The corrosion products formed under dry air condition is relatively more uniform and spread evenly across the specimen surface as compared to normal air condition.

![SEM micrograph with elemental analysis of corrosion product](image)

**Fig. 1** SEM micrograph with elemental analysis of corrosion product after exposure in synthetic salt for 218 h with normal atmosphere at magnification of (a) 2000x (surface area), (b)2000x (cross section), dry atmosphere at magnification of (c) 2000x (surface area) (d) 10000x (cross section) and (e) Spallation of the sample under normal air at 1000x magnification

At certain area, specimen under normal air shows a spallation (Fig 1 (a) and (e)) due to bad adhesion between the oxide layer and the substrate. This scenario mostly happened when the corrosion
products on the surface are not thermodynamically stable. Corrosion layer are fragile and alloy will be further exposed to the corrosion media and oxide started to form again. The corrosion occurs and the cycle continues until the grains being exposed.

Thickness of the oxides formed were measured by cross sectional morphology of the specimen. Corrosion layer of a specimen under normal air is thick (61.13 µm) and porous (Fig 1 (b)) compared to the specimen under dry air which is very thin (2.87 µm) and dense (Fig 1 (d)). This is due to the presence of air moisture and synthetic salt at high testing temperature that accelerates the corrosion reaction [13]. Thus, the oxide growth thicker for a specimen under normal air condition compared to dry air condition. However, a porous structure formed under normal air condition is unstable and cannot provide a protection to the alloy.

EDX result reveals that the corrosion product formed is constituted of Ni, Cr, Mo-rich oxides (Fig 1). However, the results from XRD data only reveals the main peaks of NiCr and protective Cr$_2$O$_3$ peaks (Fig 2). The phases might be difficult to be detected due to the low crystallinity and low amount of oxide formed on the specimens. The peaks of protective Cr$_2$O$_3$ is slightly lower for the normal atmosphere due to the dissolution and volatilization of some Cr-rich oxides in the outer layer under presence of air moisture [12]. Hence, the oxide spallation occurs and XRD detected mostly the newly exposed substrate on the surface layer of the normal specimen. It has been proved by EDX data of the exposed grain boundary (Fig 1 (e)), which composed of lack amount of oxygen and high amount of nickel followed by chromium, molybdenum and others alloying elements.

| Specimen | Phase          |
|----------|----------------|
| Normal air | NiCr, Cr$_2$O$_3$ |
| Dry air   | NiCr, Cr$_2$O$_3$ |
| Raw C22   | NiCr          |

Fig 2 XRD pattern of corroded Hastelloy C22 in comparison with raw Hastelloy

3.2 Corrosion mechanism

The reaction between Cr$_2$O$_3$ layer with water vapour and oxygen at temperature above 400˚C formed a volatile species of Cr(VI) hydroxide as shown in Eq. 1 which causes the loss of protective properties of the specimen under normal condition [6,11]. This phenomenon led to the chromium depletion of the oxide and in the alloy substrate, hence causing the breakdown of protective chromium-rich corundum type oxide. The present study is in accordance with the previous work [13-14], indicating that vaporization of Cr(VI) hydroxide does take place in oxygen with air and water environment, resulting in the depletion of the oxide in chromium.

The important features that contributes to the corrosion resistance of a certain material is its ability to form a stable protective oxide scales [7]. However, under chlorine-containing environment and a presence of water vapour, corrosion process is very likely to be accelerated. This resulting in increased oxidation and loose non-adherent scales that weaken and destroy the protective oxide scales. The corrosion scales are dominated by KCl due to its high corrosivity. Meanwhile, K$_2$SO$_4$ was believed to
preserve the protective character of oxide scale, by avoiding the diffusion of gaseous chloride species to the metal surface and preventing the depletion of chromium within the oxide layer [15-16].

At high temperature around 650°C - 750°C, the synthetic salt are partially melted. The corrosion process is dominated by electrochemical corrosion as the liquid phase formed acts as a pathway for ionic transport. Furthermore, corrosion may be further enhanced when the protective surface oxide scale is dissolved by molten salt that are partially in liquid. Acceleration corrosion happened for oxygen as well as other aggressive corrosion species can get in and diffuse to the alloy substrate. Destruction of oxides at splat boundaries by chloride and the diffusion of chlorine along grain boundaries became the main factors that contributes to the failures of the Hastelloy. Consider the reactions in Eq. 2:

\[
2Cr_2O_3(s) + 3O_2 + 4H_2O (g) \rightarrow 4CrO_2(OH)_2 \quad \text{Eq. 1}
\]

\[
2RCl (s, l) + \frac{1}{2}Cr_2O_3(s) + \frac{5}{4}O_2 (g) \rightarrow R_2CrO_4(s, l) + Cl_2 \quad \text{Eq. 2}
\]

Where RCl corresponds to KCl in this studies. Alkali chloride also can react with other chlorides to form low temperature melting eutectic compounds. For instance, KCl-CrCl\(_2\) = 462-475°C, KCl-FeCl\(_2\) = 340-393°C, KCl-FeCl\(_3\) = 202-220°C [19]. The compounds tend to volatile easily and help to transfer the alloy outwards which in turns accelerates the corrosion. Cr is the main protector for high temperature corrosion by forming a protective Cr\(_2\)O\(_3\) layer. However it has lost its advantages when facing the water vapour and molten chloride salts. Meanwhile, NiO is not liable to be dissolved as compared to Cr\(_2\)O\(_3\). This is mainly associated with the preferential dissolution of Cr\(_2\)O\(_3\) that consumes oxygen and inhibits the dissolution of NiO. This preferential dissolution happens to Mo\(_2\)O\(_3\) as well which leave a NiO skeleton in the corrosion product [18]. This explains the occurrence of high amount of nickel and oxygen after the corrosion test.

4. Conclusion

The high temperature corrosion of Hastelloy C22 was studied at temperature 650°C in synthetic salt under two different atmospheres for 218 hours. The corrosion under normal air conditions was more severe than dry air. High test temperature with a presence of air moisture and synthetic salt aggravated the corrosion via preferential dissolution and formation of volatile hydroxide species. This volatile species converts the protective chromium oxide into a poorly protective oxide, hence reducing its protective capability.

The comparison of corrosion behaviour between normal and dry air conditions reveals that the presence of air moisture at high temperature increases the corrosion attack. However, a dense oxide structure that remains on dry air specimen proves that the Hastelloy C22 has a tendency to form a protective oxide layer. In future studies, attention should be drawn to the development of protective oxide layer prior to the corrosion test in order to improve the corrosion resistance of the alloy in molten salt at high temperature.

References

[1] Y. S. Li et al. 2014 Corros. Sci. 2014 64
[2] F. Abe, H. Kutsumi, H. Haruyama, and H. Okubo 2016 Corros. Sci. 114 1
[3] A. C. Lloyd, J. J. Noël, N. S. McIntyre, and D. W. Shoesmith 2005 JOM 31
[4] M. A. Rodriguez and R. M. Carranza 2011 J. Electrochem. Soc. 158 C221
[5] O. Hedayati, N. Korei, M. Adeli, and M. Etehminabhakhsh 2017 J. Alloys Compd. 712 172
[6] Q. Wang, Y. Zhang, S. Bai, and Z. Liu 2013 J. Alloys Compd. 553 253
[7] A. Fattah-alhosseini, A. Jalali, and S. Felegari 2015 Arab. J. Sci. Eng. 40 2985
[8] M. A. Rodriguez, R. M. Carranza, and R. B. Rebak 2005 Metall. Mater. Trans. A 36 1179
[9] W. Luo, Z. Liu, Y. Wang, and R. Yang 2012 36 212
[10] X. Tang, S. Wang, D. Xu, Y. Gong, J. Zhang, and Y. Wang 2013 Ind. Eng. Chem. Res. 52 18241
[11] S. Tuzi, H. Lai, K. Goransson, M. Thuvander, and K. Stiller 2017 J. Nucl. Mater. 486 350
[12] S. Liu, Z. Liu, Y. Wang, and J. Tang 2014 Corros. Sci. 83 396
[13] M. P. Brady et al. 2017 Energy Sustain. Dev. 37 20
[14] N. K. Othman, J. Zhang, and D. J. Young 2010 Corros. Sci. 52 2827
[15] E. J. Opila et al. 2007 2 1971
[16] X. Zhang and D. W. Shoesmith 2013 Corros. Sci. 76 424
[17] R. Altobelli, M. Cristina, and L. De Oliveira 2013 Corros. Sci. 76 6
[18] J. Pettersson, H. Asteman, J. E. Svensson, and L. G. Johansson 2005 Oxid. Met. 64 23
[19] G. J. Janz, C. B. Allen, J. R. J. Downey, And R. P. T. Tomkins 1978 Chem. Informationsd. 9 16