High temperature oxidation in boiler environment of chromized steel

F F Alia¹, T Kurniawan*, Y P Asmara¹, M H B Ani² and A B D Nandiyanto³

¹Structural and Material Degradation Focus Group, Faculty of Mechanical Engineering, University Malaysia Pahang, 26600 Pekan, Pahang, Malaysia.
²Department of Manufacturing and Materials, Faculty of Engineering, International Islamic University Malaysia, PO Box 10, 50728 Kuala Lumpur, Malaysia.
³Department of Chemistry, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudhi No. 229, Bandung 40154, Indonesia.

*Corresponding author: tedikurniawan@ump.edu.my

Abstract. The demand for increasing efficiency has led to the development and construction of higher operating temperature power plant. This condition may lead to more severe thickness losses in boiler tubes due to excessive corrosion process. Hence, the research to improve the corrosion resistance of the current operated material is needed so that it can be applied for higher temperature application. In this research, the effect of chromizing process on the oxidation behaviour of T91 steel was investigated under steam condition. In order to deposit chromium, mixture of chromium (Cr) powder as master alloy, halide salt (NH₄Cl) powder as activator and alumina (Al₂O₃) powder as inert filler were inserted into alumina retort together with the steel sample and heated inside furnace at 1050°C for ten hours under argon gas environment. Furthermore, for the oxidation process, steels were exposed at 700°C at different oxidation time (6h-24h) under steam condition. From FESEM/EDX analysis, it was found that oxidation rate of pack cemented steel was lower than the un-packed steel. These results show that Cr from chromizing process was able to become reservoir for the formation of Cr₂O₃ in high temperature steam oxidation, and its existence can be used for a longer oxidation time.

1. Introduction

The demand to increase the efficiency of the development advance power plant such as supercritical (SC) and ultra-supercritical (USC) is becoming an important issue. This is because by increasing the efficiency of the power plant, it would reduce the environmental impact caused by the greenhouse gasses emission [1]. The easiest way to increase the efficiency of the power plant is to increase their operating temperature as stated in Carnot cycle [2, 3]. Currently, the maximum operated temperature is about 650°C, and targeted operating temperature for future power plant is above 700°C [1, 4]. However, by increasing the temperature of the power plant, the operating conditions of the plant component will become more severe for oxidation resistance of the material [5-6]. Therefore, further study to improve corrosion resistant of the current operated material is needed so that it can be applied for higher temperature application.

In the superheaters and reheater of boiler in power plant, the inside part is exposed to high temperature and high pressure steam (steam side) and the outer part is exposed to combustion gases (fire side). These steam condition gives the higher rate of oxide growth and produced the corrosion product. Many report clarified in their research the oxidation in steam condition is more severe than in dry condition [7-9]. The expected protective chromia (Cr₂O₃) that will be formed on the surface will
be retarded in steam condition due to the growth of duplex scale, which consists of magnetite as the outer scale and Fe-Cr spinel as the inner scale. Galerie [9] in their study stated 15-18% Cr ferritic steels in environment containing water vapour at 800ºC-1000ºC, the failure for the formation of protective Cr₂O₃ will cause the iron oxide to form, and the initial oxide (Fe, Cr)₃O₄ shows the growth with oxidation time. The mass gain on the surface of the tube will cause the thickness loss and may lower the thermal conductivity, lead to premature creep failure [10]. Furthermore, the exfoliated scale may accumulate inside the bends tube and cause blockage to the tube. If the oxide particles enter the steam turbine, erosion blades and nozzles may occur.

The aim of the present work is to improve the oxidation behavior of the steel in steam condition. The surface of steel is enriched by chromium in the form of diffusion coating by the chromizing process (pack cementation process). The result for steam exposure test was done by comparing the weight gain for oxidation after chromizing and also the steel that does not undergo the chromizing process. The same process has been conducted for the P11 steel [11]. In this work, the test was carried out with pure water vapor at ambient pressure and 700ºC with different exposure time.

2. Experimental procedure

2.1. Chromizing process

The ferritic-martensitic steel T91 was used as a substrate material to apply the diffusion coatings. The chemical composition of this material is summarized in Table 1. The samples were cut into the required dimension 10 x 10 x 4mm³. The material then was prepared and polished their surface finishing up to 2000 grit finish using SiC abrasive papers and washed with acetone in an ultrasonic bath to remove its surface from rust and grease.

| Alloy | Composition wt.% |
|-------|------------------|
| C     | 0.11             |
| Mn    | 0.47             |
| Si    | 0.30             |
| Nb    | 0.08             |
| Mo    | 0.96             |
| V     | 0.23             |
| N     | 0.05             |
| Cr    | 9.26             |
| Fe    | Balance          |

The chromizing process was assembled as illustrated in the Figure 1. For chromizing, there are four component that will make the chromizing process complete, they are substrate to be coated, master alloy, activators, and filler. For this chromizing process, the master alloy used was chromium (Cr) powder, the activator is NH₄Cl powder, and Al₂O₃ powder as filler. The pack powders for chromizing process were set up for 20wt.% Cr; 20wt.% NH₄Cl; balance, Al₂O₃. Powder pack mixture was homogenized by using a porcelain mortar for one hour. Samples and powder then embedded in the alumina crucible with lid glued by alumina cement. The crucible then was put into a horizontal tube furnace and loaded with argon gas. The exposure time for chromizing process was 10 hours at temperature 1050ºC with constant flow rate 150 ml/min. The samples were allowed to cool naturally in the crucible at room temperature. Lastly, the samples were taken out from the crucible and the surfaces were cleaned again by using ultrasonic cleaning. The cross sectional image of the chromized steel was investigated by using FESEM/EDX.
2.2. Oxidation tests in steam condition

The schematic illustration for experimental setup which was used in this experiment is illustrated in Figure 2. The temperature for steam oxidation tests was 700ºC with constant flow rate at 150 ml/min of high purity argon was used as a carrier gas. The distilled water was set at a constant value at the mantle heater. The argon gas was carried in the glass grit to make sure a good contact between argon and water. For this experiment, the exposure time for oxidation is exposed to 6h, 12h and 24h for chromized steel and non-chromized steel. The samples were weighing before and after oxidation to check their weight change.
3. Results and discussion

Figure 3(a) and 3(b) shows the image of as polished steel, chromized steel respectively, while Figure 3(c) and 3(d) shows the steel exposed to steam condition for chromized and non-chromized steel in 12h exposure. It can be seen that in Figure 3(b) shows the changes happened when Cr diffused in the steel. The colour changes were observed as soon as the steel taken out from the crucible. This happened because of the reaction of content in pack mixture during chromizing process. The exposed steel in steam condition for 12h in Figure 3(d) shows a very bad condition due to the formation of iron oxide which is coincide with previous work stated that steel that exposed in water vapour existence will cause severe exfoliation and spallation to the steel. However, the chromized steel in Figure 3(c) does not formed iron oxide when exposed in the same condition. This results show the formation of iron oxide can be reduced by using the suitable parameters for chromizing process.

![Figure 3](image.png)

Figure 3. The image for (a) as polished steel; (b) the steel after chromizing process; (c) chromized steel after 12h oxidation; (d) non-chromized steel after exposed to 12h oxidation.

This result was strengthened by surface morphologies investigated in FESEM/EDX in Figure 4. The results show that the content of Cr increase whiles the content of Fe decrease in 10h chromizing time at 1050°C. This suggests the Cr content in the steel prevents the diffusion of Fe into the coating from steel substrate. In order to determine the thickness of obtained coating, the back scattered electron (BSE) image of the cross section were measured as shown in Figure 4. It is found that chromized layer was diffuse into the steel until 15 µm. The continuous and homogenous coating are composed of Cr-rich layer and diffusion rich layer which both determine the effective of the chromizing process. One of the parameters to increase the thickness of Cr-rich layer is the diffusion time. The relatively short diffusion time cause the Cr has less time to diffuse inside the coating layer. The using of 10h exposure time is suitable for the formation of higher and stable Cr-rich layer.
The increase in the mass gain of the non-chromized steel after exposed to steam condition lead to the test of chromized steel in steam condition. The morphology of the cross section image is shown in Figure 5. The results exposed in 6h does not have much changes from the chromized steel. The exposure time for 6h is too short for the oxidation to occur. Hence, the image in Figure 5 shows the BSE image for steel exposed in steam condition for 12h. From the cross sectional image, we can see the Cr-rich layer was formed on top of the steel. By using the spot analysis in EDX analysis, the element depth of the diffusion was measured as 20 µm. After the exposure, there are small amount of Fe was present in the layer. There was interdiffusion zone between inner layer, outer layer and steel substrate as can be seen in the image. The interdiffusion zone is not visible on the EDX graph, but can recognized on the Cr and Fe concentration measured by EDX spot analysis. Cr atoms that diffused across the Cr-rich layer enabled the growth of the interdiffusion zone.

The diffusion depth for chromized steel exposed in 24h also show the same behaviour with 12h exposure time. From the results, authors suggested to extend the time exposure in future work. The image for 24h exposure can be seen in Figure 6. In this condition, the wt.% of Cr is higher compare to Cr wt.% in steel exposed in 12h steam condition with value 84.8wt.% and 79.9wt.% respectively.
Figure 6. BSE cross sectional image after exposed to 24h in steam condition.

The graph of mass change versus time for after oxidation time was plotted in Figure 7. It showed that lower mass gains were observed for the chromized steels when it compared to the non-chromized steels. It is assumed that for the non-chromized steel, the chromium content was not enough to form continuous protective Cr₂O₃ layer when it is exposed to high temperature steam. The difference for weight after exposure was divided with total area of the sample to obtain the total mass gain of the sample. The difference of mass gain between chromized steel and non-chromized steel suggests that the chromized steel able to slow down the formation of iron oxide when oxidation occur. Meanwhile, for the chromized steel, the Cr reservoir can maintain the formation of Cr₂O₃, so that when the oxidation process occur, the formation iron oxide in the steel can be prevented.

Figure 7. Graph for mass gain versus exposure time.

4. Conclusions
Chromizing process at 1050°C for 10 hours has successfully diffuse Cr and formed Cr-rich layer in the surface of T91 steel. The diffused Cr able to become chrome reservoir for the formation of protective Cr₂O₃ layer during high temperature steam oxidation at 700°C and reduce corrosion rate of the steel.
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