The Effect of Temperature on the Chromizing Process for Ferritic-Martensitic Steel

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Abstract. The formation of protective Cr₂O₃ layer was usually retarded in the high temperature steam oxidation of boiler tube materials. This condition makes the oxidation rate higher than that in dry condition. Therefore in this work, chromizing process is introduced to diffuse chromium on the surface of boiler steel so that it can act as a reservoir for the formation of Cr₂O₃ layer. The chromizing process was conducted on T91 steel by exposing it into alumina crucible. The crucible was exposed at different temperature (600ºC-1050ºC) under argon environment in the crucible that contains the chromizing mixture powder of masteralloy Cr, activator NH₄Cl and filler Al₂O₃. It was found that Cr diffusion was happened at higher temperature and it formed Cr carbide on the surface. It also clarified that this chromizing process can prevent the retardation of Cr₂O₃ layer.

1. Introduction

The global electricity demand consummation in 2013 to 2040 predicted to be increased by 70% due to the changes of urbanization and economic activity [1, 2]. The increase of electricity leads to the needs of increasing the efficiency at power plant. As stated in Carnot cycle, the easiest way to increase the efficiency is by raising the operating temperature. Currently many developed countries have stated that the operating temperature of future power is targeted to increase above 700°C [3]. Besides, it can increase the efficiency; this improvement will also reduce the greenhouse gasses emission. In the other hand, higher operating temperature may affect the oxidation behaviour of the power plant material, especially the superheater and reheater tubes of boiler, where it exposed to high temperature and high pressure steam [4, 5].

As stated in previous research, the oxidation occurred in steam condition shows worst characteristics morphology compare to the oxidation that occur in dry environment [6-8]. The results show the amount of corrosion product is higher compare to the oxidation in dry condition [9]. The formation of higher corrosion product in steel that exposed to steam condition is due to retardation of protective layer Cr₂O₃ where it cause the formation of non-protective oxide will increase [10].

In order to improve the oxidation resistance, the chromium forming coating or chromizing was conducted to give an idea of the protection for the steel. This idea offers the outer steel is deposited with the chromium and also the chromium diffused into the steel to act as the reservoir to the formation of
Cr$_2$O$_3$ [11, 12]. The steel with this method of chemical vapour deposition (CVD) will be embedded in a crucible full of powder mixture, which is composed of masteralloy, inert filler and activator. The crucible then heated to desired coating temperature with the argon gas loaded into the furnace. The masteralloy will react with the activator forming a gaseous transporting element. This will diffuse through the pack to the steel surface where it allows the masteralloy to be deposited to be penetrated into the steel by solid state diffusion [13, 14]. This also depends on the temperature of the surrounding.

The aim of this work is to diffuse the chromium on T91 steel by chromizing process at different temperature. Morphology of the coating will be investigated by FESEM/ EDX and XRD. It is expected that the diffused chromium become the reservoir for the formation of Cr$_2$O$_3$ layer during high temperature steam oxidation.

2. Experimental Procedure

2.1. Preparation for chromizing process

T91 ferritic-martensitic steel was used as the sample. Powder mixture of NH$_4$Cl, Al$_2$O$_3$ and Cr, was used as activator, inert filler and master alloy, respectively. First, the sample was cut into the required dimension 10 x 10 x 4mm$^3$. The material then were prepared and polished the surface finish up to 2000 grit finish using SiC abrasive papers. It then washed with acetone in an ultrasonic bath to remove its surface from rust and grease. After polished and cleaning process, substrate was put inside alumina crucible together with the powder mixture. Chromizing process was conducted inside horizontal tube furnace with different temperature 600°C, 800°C and 1050°C for 2 hours under argon gas environment. FESEM and EDX was used to characterized the cross sectional image of the sample.

The diffusion coating was assembled in powder pack mixture. For chromizing process, there are four components that will chromizing process complete, they are substrate to be coated, master alloy, activators, and filler. In this research, the master alloy used is chromium (Cr) powder, the activators is NH$_4$Cl powder, and Al$_2$O$_3$ powder as filler. 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 pack cementation is 2 hour at varies temperature 600°C-1050°C with constant flow rate 150 ml/min. The cross sectional image of the chromized steel was investigated by using FESEM and EDX.

Figure 1. Schematic illustration for chromizing process setup.
2.2. Steam oxidation testing

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 which is 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 frit to make sure a good contact between argon and water. For this experiment, the exposure time for oxidation is exposed to 90h. The samples were weighed before and after oxidation to analyze their weight change.

![Figure 2. Schematic illustration for steam oxidation experiment setup.](image)

3. Results and Discussions

The formation of Fe-Cr was detected in XRD which also reveals the presence of Cr and Cr$_7$C$_3$. Eventhough the morphology in low temperature 600ºC do not exhibit chromium, the XRD spectrum shows the differences. A very little amount of Cr peak with only one significant peak Cr reveals on the spectrum image. This can be concluded that the master alloy do react with the activator in the temperature. However, the temperature is not sufficient enough to make the deposition of master alloy and solid state diffusion to occur. In temperature 800ºC, the chromium carbide already formed with a few significant peaks of Chromium. Figure 6 show s the XRD spectrum image for all condition; bare T91 sample, low and high temperature.

From the Figure, XRD analysis reveals the chromium carbide start to form at the temperature 800ºC. Aside of Cr formation detected on the XRD, Cr$_7$C$_3$ also detected on the sample after exposed to lower temperature 800ºC. At lower temperature 600ºC, there are no phase changes in the steel and remain the same as the bare sample of T91. However, at higher temperature 1050ºC the chromium activity is high on the surface where the carbide (Cr$_7$C$_3$, Cr$_5$C$_2$ and Cr$_2$3C$_6$) formation can form at this temperature. The presence of chromium in solid solution cause the large ferrite formed and reduced the amount of carbon in the steel.
Figure 3. XRD spectrum image for T91 steel and chromizing steel in low and high temperature.

The chromizing process was carried out with varies temperature in order to investigate the effect of deposition behavior with temperature. First, the samples were embedded in furnace with temperature 600°C-1050°C. When exposed to this temperature for 2h, morphology from BSE-FESEM image reveals there are no changes of Cr concentration as shown in Figure 4(a). In the image, the steel become cracks after the exposure shows the temperature did give an effect to the changes of the steel. However, due to the low temperature where the activator cannot react with the masteralloy because of the driving force to diffuse the chromium into the steel is not high enough. Therefore the diffusion does not occur in this temperature.

The temperature of the furnace then was increased to 800°C in order to get the deposition and diffusion of chromium. Figure 4(b) show the steel is different as in Figure 4(a). This is because in this image, we can see here are darker region where the darker region is chromium richer part. Besides, the cracks also do not visible in this condition. In this temperature, the chromium was successfully deposited on top of the steel. However, it is too little and not sufficient enough to be used in industry where the steam environment will be in a very long term.
The chromizing then was rested at high temperature 1050°C for 2h. By using this temperature, the chromium diffusion leads to the deposition of Cr rich layer on top of the surface where can be seen in Figure 4(c). At this temperature, the formation of Cr rich layer is gives more homogenous and continuous layer with average thickness 8.509±1.590μm. In this temperature, we can see the presence of pores on this cross section image between 8 and 15 μm under the layer. The pore were observed all along the steels at around the depth. The pore formation is due to the Kirkendall effect as observed previously in chromising effect [15].

This condition has been proved by the EDX analysis with Cr linescan profile and mapping as shown in Figure 5(a), (b) and (c). The linescan profile which measured the concentration of Cr and comparison with Fe was drawn in the EDX software starting from the surface to the substrate of T91 steel. For sample exposed in low temperature 600ºC, the linescan and element mapping profile also show there are no chromium detected either deposited or diffusion in this 600ºC temperature.

Microstructure in Figure 5 (b) is too small to measure their thickness in the BSE FESEM image. So, the spot and linescan analysis in EDX has been used to identify the deposition of chromium on top of the steel. The spot is pointed in EDX line scan profile results the surface thickness of the chromium deposition is around 3μm. However, there were no diffusion of chromium occur in this temperature. This can be seen in Figure 5(b). The mapping of element Cr also shows there is chromium deposited on top of the surface.

Figure 5(c) shows the EDX analysis for linescan and mapping profile of Fe and Cr. In the line scan profile, it shows the diffusion of chromium did occur in this condition. By using the spot analysis, the wt% of chromium been investigated along the line to know the depth of diffusion in the steel. From the spot analysis, the diffusion depth in the image was measured by using the image software where it spotted the chromium diffuse until 41.706μm. The diffusion of chromium is very important in order to make sure during the oxidation occurred, the chromium will act as a reservoir to the formation of Cr₂O₃ to prevent the non-protective iron oxide formed on the steel. The elemental mapping from the EDX analysis also shows the formation of chromium is homogenous and continuous along the surface of the sample.
The satisfying characteristics exhibit from the high temperature chromizing lead to the the sample testing in steam oxidation condition. In this condition, the samples was exposed to 90h with constant flow rate in order to investigate their behaviour. The image in Figure 6 shows the chromium layer on the surface become thinner compare to chromized steel before oxidation. The average surface thickness for chromium rich layer after exposed to oxidation is $4.2012 \pm 1.129 \mu m$.

EDX analysis shows the line and mapping profile for Cr, Fe and O. The linescan profile exhibit the presence of oxygen. However, the oxygen react with chromium to form $Cr_2O_3$ on the surface. However,
the chromium diffusion from the chromizing process is still diffuse in the steel with the increasing diffusion depth with 51.185 μm compared to before exposed to oxidation. After exposed in that time, the formation of non-protective oxide Fe₂O₃ and Fe₃O₄ was not detected in the steel. The EDX analysis for samples exposed in steam condition for 90h at high temperature 1050°C can be seen in Figure 7.

In order to identify the formation of chromium and chromia after doing chromizing and steam oxidation, the XRD analysis was carried out to analyze the spectrum, as shown in Figure 8. The formation of Cr₂O₃ can be detected in the XRD. Beside of chromium carbide, the Fe-Cr spinel also formed in the steel when exposed to steam oxidation. Both in chromizing process and corrosion testing the chromium carbide (Cr₃C₂ and Cr₇C₃) coming from the Cr rich layer that react with steel was present during the exposure of chromizing and steam oxidation.

![Figure 7. EDX analysis for sample exposed in high temperature 1050°C.](image)

![Figure 8. XRD spectrum image for T91 sample after exposed to steam oxidation.](image)
4. Conclusions
The chromium was successfully diffused at temperature above 800°C. At higher temperature 1050°C, carbon from the steel also diffuse to the surface and form chromium carbide. The diffusion is essential to become reservoir for the formation of Cr₂O₃ during high temperature steam oxidation as shown by the oxidation result at 700°C.

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References
[1] Parker JD. International perspectives on plant life assessment. Materials at high temperatures. 2002;19(2):47-57.
[2] Bromhead A, Alessandro Blasi, Ikeyama S. Southeast Asia Energy Outlook 2015. France: International Energy Agency, 2015.
[3] Tominaga A, Wakazono O, Nakajima M, Fujikawa T, Sato S, Sugitani T. Mitsubishi heavy industry 2003.
[4] Viswanathan R, Romanosky R, Rao U, Purget R, Johnson H, editors. Boiler materials for USC plant. 17th annual conference on fossil energy materials; 2003.
[5] Kurniawan T, Fauzi FAB, Asmara YP. High-temperature Oxidation of Fe-Cr Steels in Steam Condition—A Review. Indonesian Journal of Science and Technology. 2016;1(1):107-14.
[6] Zurek J, Quadakkers WJ. Effect of Surface Condition on Steam Oxidation of Martensitic Steels and Nickel-Based Alloys. Corrosion-US. 2015;71(11):1342-59.
[7] Fujii C, Meussner R. The Mechanism of the High-Temperature Oxidation of Iron-Chromium Alloys in Water Vapor. Journal of the Electrochemical Society. 1964;111(11):1215-21.
[8] E. Essuman GHM, J. Zurek, M. Hansel, W. J. Quadakkers. The Effect of Water Vapor on Selective Oxidation of Fe-Cr Alloys. Oxidation of Metals. 2008;69(3-4):143-62.
[9] Fauzi F, Kurniawan T, Asmara Y, Ani M, Aziz M. Oxidation behavior of pack-cemented P91 steel in steam condition. Oxidation behavior of pack-cemented P91 steel in steam condition. 2016.
[10] Lepingle V, Louis G, Petelot D, Lefebvre B, Vaillant J, editors. High temperature corrosion behaviour of some boiler steels in pure water vapour. Materials science forum; 2001: Trans Tech Publ.
[11] Bose S. High Temperature Coatings. 2007;1:73-154.
[12] Fauzi F, Kurniawan T, Salwani M, Bin Y, Harun W, editors. Chromium Enrichment on P11 Ferritic Steel by Pack Cementation. MATEC Web of Conferences; 2016: EDP Sciences.
[13] Geib FD, Rapp RA. Simultaneous chromizing—Aluminizing coating of low-alloy steels by a halide-activated, pack-cementation process. Oxidation of Metals. 1993;40(3-4):213-28.
[14] Kung S, Rapp RA. Kinetic study of aluminization of iron by using the pack cementation technique. Journal of the Electrochemical Society. 1988;135(3):731-41.
[15] Fan HJ, Gösele U, Zacharias M. Formation of nanotubes and hollow nanoparticles based on Kirkendall and diffusion processes: a review. small. 2007;3(10):1660-71.