High Temperature Cathodic Protection of Fe-Cr Alloy

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Abstract. Power plant industry extensively using ferritic Fe-Cr alloys as boiler materials due to its good resistant to creep, low in thermal shock and thermal expansion. However, the development of new generation of Ultra Supercritical (USC) power plant requires boiler materials to be operate at higher temperature and pressure, thus make it susceptible to high temperature oxidation. The USC power plant successfully reaching the target of working temperature at temperature more than 873K (600°C). By increasing the operating temperature, the efficiency of power plant also increases at the expense of acceleration of high temperature oxidation. This project explored the application of impressed current cathodic protection (ICCP) at 1073 K. At high temperature, gas may dissociates into charged ions that make it possible to conduct electrons. Typical boiler material of T91 was used in high temperature oxidation at 1073K, under Ar-20%O2 mixed gas. The sample is connected to potentiostat with Pt wire to measure the value of corrosion potential (Ecorr), and Icorr. Blank experiment is conducted to determine the presence of reaction by the presence of current conductivity at high temperature in oxygen condition. The weight gain is following parabolic’s rate law, which shows that diffusion is the rate determining step. Blank test shows that as potential induced, current flows from one Pt terminal to another Pt terminal through intermediate mixed gas. Corrosion potential (Ecorr) of the sample show the value is greater than value at room temperature. It is concluded that ICCP is feasible to be conducted for controlling corrosion at high temperature.

1. Introduction

Coal is one of the primary fuel sources that being used in thermal power plant globally. Excessive usage of coal contributes to carbon dioxide emission to the atmosphere. It causes global warming due to the greenhouse effect. The amount of CO₂ released by coal-fired thermal power plant is in the critical state and requires quick action from industrial players [1]. Easiest solution to above problem is by increasing the working temperature of the power plant, thus it will increase energy conversion efficiency proportionately. However, at high temperature, boiler materials is susceptible to accelerated oxidation, particularly with the presence of water vapor [2-6]. Metal oxide formed on the surface of boiler reduces the efficiency of the power plant due to lower heat transfer through oxide scale [7-10]. Ferritic alloys is favourable as boiler tube due to its good thermal conductivity that will minimize the heat loses to the surrounding and maximizing the amount of heat transfer, thus increase the efficiency of the coal combustion. Consequently, controlling oxidation of boiler tube is important from viewpoint of energy generation efficiency and environmental impact. To date, corrosion prevention on boiler tube solely depend on chromium content of its alloys. Chromium is expected to form protective Cr₂O₃ scale at initial stage of operation. However, this scale is subjected to thermal expansion and thermal shock during long operation of boiler. This thermal mismatch always leads to Cr₂O₃ scale cracking, which provides oxygen...
to penetrate the scale and further oxidize the alloys. To the worst case, this repeating processes may cause boiler tube to burst. We hypothesize that at high temperature, gas and water vapor are ionized that make it electronically conductive. Conductive gas then can act as an electrolyte to the system. Impressed current cathodic protection (ICCP) has been employed to low temperature aqueous corrosion successfully. However, to our knowledge the technique has not been reported on high temperature oxidation. This paper intends to investigate the gas conductivity at high temperature and examine the feasibility of ICCP to be used as high temperature corrosion protection. Corrosion rate, corrosion potential, $E_{\text{corr}}$ and $I_{\text{corr}}$ was evaluated and reported in subsequent section.

2. Methodology

2.1 Sample Preparation

T91 alloy, a typical ferritic Fe-Cr alloy for boiler was used as the sample. It was first cut into 8 mm x 6 mm x 2 mm in dimension. The samples were ground by using different grit size of abrasive paper, #800 and then followed by #1000, #1500 and #2000 subsequently. The samples then were polished with 1 μm diamond paste, followed by 0.5 μm and 0.1 μm. After that, the samples were sonicated for 30 minutes.

2.2 Oxidation Experiment

The samples were connected with Pt wire and placed in horizontal tube furnace for oxidation at 1073 K. An R-type thermocouple was located 2 mm from the sample to monitor the temperature. It was set to be in the range of isothermal zone. Another end of Pt wires were connected to potentiostat (Autolab Metrohm). Ar-20%O$_2$ mixed gas was flown into the reaction chamber for oxidation process. The samples were weigh before and after oxidation to evaluate its weight gain. $I-V$ measurements were done during the oxidation at 30 minutes, 1 hour, 2 hours, 12 hours, 24 hours and 48 hours using Nova 2.0 software. The voltage applied within -5 V and +5 V. Corrosion potential, $E_{\text{corr}}$ and $I_{\text{corr}}$ were determined from $I-V$ curve of the respective sample. A blank test was done to evaluate the conductivity of gas at 1073 K. For that purpose, 2 Pt wires were placed 2 mm in mixed gas without contacted each other and without sample, then the $I-V$ measurement was done.

3. Results and Discussion

3.1 X-ray diffraction analysis (XRD)

Figure 1 shows the XRD pattern of T91 sample. Cr is solute solution into iron, thus the result confirmed that the samples are in single phase of α-Fe solid solution. The figure shows that the highest peak at diffraction angle of $2\theta = 44.691^\circ$ with crystal plane of (110). The other plotted peaks show diffraction angle of $2\theta = 65.023^\circ$ with crystal plane of (200).

![Figure 1. XRD result of T91 alloy](image-url)
3.2. Oxidation Kinetics

Table 1 shows weight gain of the samples after oxidized at respective interval time. The resultant weight difference is then used to calculate weight gain per unit area of the sample. Samples weight gain plot over oxidation time is shown in Figure 2. The oxidation of T91 alloy is following parabolic’s rate law, which signifies diffusion of ion is the rate-determining step in the oxidation process. The weight gain is then used to calculate the oxidation rate of Fe-Cr alloy at 1073 K, which may be represented by a parabolic equation:

\[(\Delta W)^2 = k_p t\]  \hspace{1cm} (1)

Where \(\Delta W\) is gain in weight in g/cm² of a sample oxidized for \(t\) seconds; \(k_p\) is the parabolic rate constant (g²/cm⁴ sec⁻¹). The parabolic’s rate constant, \(k_p\) of the sample at temperature 1073 K is 2.94 x 10⁻⁸ g²cm⁻⁴sec⁻¹.

| No. | Sample       | Weight difference (mg) | Surface area (cm²) | Weight gain (mg/cm²) |
|-----|--------------|------------------------|--------------------|----------------------|
| 1.  | 30 minutes   | 2.0                    | 1.392              | 1.44                 |
| 2.  | 1 hour       | 11.8                   | 1.344              | 8.78                 |
| 3.  | 2 hours      | 18.9                   | 1.311              | 14.42                |
| 4.  | 12 hours     | 57.6                   | 1.464              | 39.34                |
| 5.  | 24 hours     | 85.8                   | 1.319              | 65.05                |
| 6.  | 48-hour      | 87.9                   | 1.296              | 67.82                |

![Figure 2. Weight gain of T91 alloy at respective oxidation time](image)

3.3. Gas conductivity at 1072 K

Figure 3 shows the I-V results of blank experiment. It is interesting to note that without terminal contact, presence of current conductivity was observed when voltage from -5 V to +5 V were applied at temperature of 1073 K with different interval time of 12 hours and 48 hours. It can be seen that there is slight change of slope when the interval time is increased. This proved that the gas is conductive at flow rate at 50 sccm. Presence of current conductivity justifies the presence of oxygen plasma at high temperature where the charged particles of oxygen species provides medium for corrosion to occur.
3.4. Corrosion Potential Measurement of Fe-Cr Alloy at 1072 K

Figure 4 shows the I-V plot of the sample at 1073 K. The value of current is increased linearly as the potential is increased. Interestingly, the slope is increased as the exposure time increased. The obtained graph shows that the longer the time taken at 1073 K, the greater the reaction will be between the sample with the oxygen gas.

Corrosion potential of the sample is then measured by plotting logarithmic value of the current versus potential or tafel plot. Figure 5 shows the tafel plot obtained when the sample is exposed to oxygen at temperature 1073 K. Each graph is then extrapolated to linear sections to obtain the value of $E_{\text{corr}}$ and $I_{\text{corr}}$. The value of $E_{\text{corr}}$ and $I_{\text{corr}}$ is tabulated in Table 2. The value is decreased as the oxidation time increased.

The value of $E_{\text{corr}}$ and $I_{\text{corr}}$ is compared with literature value at room temperature as shown in Figure 6. The value of $I_{\text{corr}}$ at room temperature condition is $0.21201 \, \mu\text{A cm}^{-2}$ [5]. It is notably that the value of $I_{\text{corr}}$ at 1073 K is one magnitude order of the value at 25 K. While the electrolytes are different, it is still can serve as benchmark value due to lack of literature. The corrosion potential value at other temperature is currently under progress.

Figure 3. Ar-20%O$_2$ mixed gas conductivity at 1073 K

Figure 4. I-V curve of the sample at 1073 K, respective time (left), and change of slope over exposure time (right)
4. Conclusions
A blank experiment and corrosion potential measurement of T91 boiler tube was done at 1073 K in Ar-20%O₂ mixed gas. The oxidation is following parabolic’s rate law. The mixed gas is conductive in nature and act as the electrolyte for oxidation process. $E_{corr}$ and $I_{corr}$ has been determined successfully, shows large deviation from room temperature. It can be serve as benchmark value for further study and high temperature ICCP development.
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