Accelerates High Temperature Oxidation due to the Change of Schottky’s Barrier Height of Cr₂O₃ Layer in Humid Condition

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Abstract. Development of the new generation of Ultra Supercritical (USC) power plant that has successfully achieved the targeted working temperature of 970 K. Nonetheless, increasing the operating temperature will further accelerate the high temperature oxidation of ferritic alloys of the boiler. Furthermore, water vapour in humid environment will make it easier for the alloy to further oxidize at high temperature. It is hypothesized that water vapour provides hydrogen that dissolves into the ferritic alloy substrate, hence altering their electronic state at the metal-semiconductor (oxide) interface. This study aims to measure Schottky Barrier Height (SBH) in dry and wet environment and relates it with accelerated oxidation behaviour. The Schottky Barrier was prepared by sputtering Cr₂O₃ onto the T91 boiler tube in high vacuum condition of 0.4 Pa, RF power 150W for an hour. The existence of Cr₂O₃ / Fe junction was confirmed by XRD analysis. The junction was then connected with platinum wire to act as the electrode for the current-voltage, I-V and capacitance-voltage, C-V test at high temperature. From the I-V graph, the reversed saturated current, Io was estimated and the SBH was calculated from the results. The SBH increased as the conductivity increased with the increment of temperature. From the C-V plots the value of Vbi was determined and used to calculate the SBH. The SBH increased with the increased of built in voltage. The result obtained from the two method agrees with one another. SBH value in wet condition is higher than that in dry condition. This is explained by the formation of space charge layer at metal/oxide interface due to dissolved hydrogen in metal, thus may change the transport property and accelerate the oxidation rate in water vapor.

1. Introduction
The global carbon dioxide emission in the atmosphere is not just escalating nowadays, it's accelerating, and another potent greenhouse gases, like methane, flourinated gases and nitrous oxide showed a huge spike over the years. The vast increment going utterly in the erroneous direction, with no sign that the planet has the problem under control.

The increasing emissions of CO₂ was mainly contributed by electricity and heat production. As the demand of electricity generation increased with the increased in world population, the burning of coal, natural gas and oil is very much in need to satisfy the demand [1]. Coal-fired power plant shows the most CO₂ emission per electric generating capacity and it is believed that there is no other sources that will outpace the coal, to generate electricity until the year 2035 [2]. In order to reduce the CO₂ emission, an effective measure needs to be taken. One of the way is by increasing the efficiency of electricity generation. Based on the Carnot’s theorem, thermodynamically the efficiency of the
electrical generation can be increased by bringing up the operating temperature of the boiler inside the power plant. Researchers are determined and aiming for higher temperature to attain higher efficiency. The efficiency can be risen up to 47% if the working temperature of the boiler is maintain at 1033 K.

Although the solution has been found, there are still some concern that need to be taken care of before it can be implemented. The ferritic alloy used as the boiler tube are very susceptible to accelerated oxidation at high temperature in water vapour environment. The augmented in the rate of oxidation is due to the presence of water vapour. This phenomenon has been one of the limiting factors to upturn the efficiency of a coal fired power plant and in fact, the long term effect will cause more harm in terms of structural integrity and requires regular maintenance.

It was reported that the oxide scale formed when exposed to high temperature of about 870-970 K in dry environment is a thin compact layer. It is very useful to protect the alloy from oxidation. However, when the alloy is exposed to wet and high temperature environment, the oxide scale formed different with the oxide scale formed in dry environment. The oxide scales are thick and multilayered with high porosity and voids in each layer [3]. This thick, pore-rich oxide scale will only increase the susceptibility towards oxidation at high temperature. F. F. Alia et. al. has shows that chromizing boiler tube is a good alternative to slow down the oxidation in wet condition [9].

The differences in the development of oxide scale and mass gain of the ferritic alloy in dry (absence of water vapour) or wet (presence of water vapour) environments are extensively studied. The phenomena are evidence for the amplified in the oxidation rate of these alloys in such environments. However, the mechanism of the occurrence is still unidentified. It is vital to comprehend the failure of the 9 to 12% of main alloying element Cr to form protective oxide scale in water vapour containing environment despite this type of alloy are specially designed for a long term service environment. Mohd Hanafi B. A. et. al. has discovered that the water vapor might allow hydrogen to dissolve in the ferritic alloy thus enhancing the oxygen permeability and hindering the development of protective external scale by means reducing the lifetime of the boiler tube [4].

This paper aims to study the effect of dissolved hydrogen towards the Schottky Barrier of the Fe/Cr$_2$O$_3$ heterojunction to further understand the oxygen transport during oxidation process. It will explain the mechanism of accelerated oxidation of ferritic alloy in wet condition by the formation of space charge layer at the interface of metal/metal oxide heterojunction.

2. Methodology

2.1. Sample Preparation

Boiler tube T91 of Cr (9%) and Mo (1%) as the main alloying element was used for the high temperature oxidation. Sample was first cut using using industrial automated saw and then followed by Electrical Discharge Machining into 10 x 8 x 5 mm$^3$ in size. After that, samples were ground and polished by using sand paper with different grit size starting with P60, P800, P1000, P1500, and P2000 flushed with a suitable coolant to remove debris and heat. Different grades particles used in polishing the sample. First start with 1 micron diameter moving on to 0.5 micron diameter and ended with the finest grade, 0.03 micron. Samples were cleaned with ultrasonic in ethanol and acetone. Half of the polished surface was then sputtered with Chromium by using RF magnetron sputtering machine in 0.4 Pa, RF power 150W for an hour. Later, gold (Au) was coated on top of the sputtered part.

2.2. Oxidation Experiment

Platinum wire was attached to the sample and used as electrode and connected to the potentiostat. The sample was placed at the isothermal zone of the furnace as shown in figure 1. At the isothermal zone beside the sample, R-type thermocouple was placed to monitor the temperature. For oxidation in dry environment, the sample was heated from room temperature to, 473, 673, 873, 1073 K and Argon gas (100%) was flown into the furnace. I-V and C-V were conducted at each temperature. Meanwhile for the wet environment oxidation, 95% Argon and 5% Hydrogen gas were flowed inside the vacuumed furnace.
2.3. Determination of Schottky’s Barrier Height (SBH)

After the reaction process, the sample were optically observed. Determination of saturation current and built in voltage from the $I-V$ and $C-V$ test respectively was conducted to calculate the Schottky Barrier Height, SBH of the metal-semiconductor junction using following mathematical treatment. The contact capacity at a high frequency test signal is represented as:

\[
C(V) = A \frac{dQ_{sc}(V)}{dV} = \frac{A}{n_0} \left[ \frac{q\varepsilon N_D}{2[\phi_b(V) - V_0 - \phi_s - V_2]} \right]^{1/2}
\]  

(1)

and the $C^2(V)$ function used for determining the barrier height is denoted by

\[
\frac{1}{C^2(V)} = \frac{2n_0^2}{A^2 q\varepsilon N_D} [\phi_b(V) - \phi_s - V_0 - V_2]
\]

(2)

Here, $A$ is the contact area and $n_0$ is the ideality factor when the capacity is measured at a relatively high frequency test signal. As known, to define the barrier height from the $C-V$ plot, the latter is approximated with a straight line. The value of built in voltage, $V_{in}$ is the voltage intercept at the forward bias region. The approximating line itself can be represented as follows:

\[
\frac{1}{C^2(V)} = \frac{2n_0^2}{A^2 q\varepsilon N_D} [\phi_{bc} - \phi_s - V_2]
\]

(3)

Where by the $\phi_{bc}$ can be denoted by

\[
\phi_{bc} = V_{in} + \phi_s + V_2
\]

(4)

which is the barrier height defined by the voltage intercept $V_{in}$ [5,6].

3. Results and Discussion

3.1. Sample Surface and Phase Identification

Figure 2 shows the T91 samples after oxidation in dry and wet environment. It can be seen that there is changed in color, from shining to greenish colored surface on both sample. The green color is associated with the presence of chromia, Cr$_2$O$_3$.

Figure 2 (c) shows cross sectional part of T91 after undergoes exposure in furnace. Below part shows metallic side, which is covered with thin oxide layer. The average thickness of oxide layer was determined to be 2.4 μm. Figure 3 shows the XRD result of the sample. Few XRD measurements reveal almost similar phase, which is metallic $\alpha$-iron, FeCr$_2$O$_4$ and Cr$_2$O$_3$. Fe has reacted with deposited Cr$_2$O$_3$ to form spinel structure FeCr$_2$O$_4$ which is common phase formed during high temperature oxidation. It is clear that deposition of Cr$_2$O$_3$ has produced an intact Fe/Cr$_2$O$_3$ layer, which has been used for SBH determination.
3.2. Determination of SBH

Figure 4 shows the $I$-$V$ curve of Fe/Cr$_2$O$_3$ heterojunction at potential near zero. It behaves linearly and produced saturated current, $I_s$. This value was used to calculate the SBH. The $I_s$ tend to be decreased as the temperature increased. The value of saturated current in dry environment tends to be larger than the value of $I_s$ in wet condition. It seems that the hydrogen dissolves in chromia and significantly affects the electrical conductivity and thereby the defect structure. As the dependence of the conductivity on the hydrogen activity decrease with increasing temperature, it is furthermore concluded that the hydrogen solubility in chromia decreases with increasing temperature at constant hydrogen activity [7].

Figure 5 shows the relationship between saturation current, $I_s$ and reaction temperature. From equation (2), it is easy to deduct that the relationship between the SBH and the $I_s$ is inversely proportional to one another. The larger the value of $I_s$, the smaller value of SBH was obtained. As the value of $I_s$ decreased along the increasing of temperature, the value of SBH increased. It also can be seen from figure 5 that the value of SBH in wet is higher than that in dry environment, with percentage difference around 1.56%.

Figure 2. Surface appearance of T91 sample exposed in (a) dry and (b) wet condition. (c) Cross section SEM micrograph of T91 sputtered with Cr$_2$O$_3$

Figure 3. XRD result of T91 after deposited with Cr$_2$O$_3$ and reacted at high temperature
Figure 4. I-V curve of Fe/Cr$_2$O$_3$ heterojunction near zero potential

Figure 5. Temperature dependency of saturate current (above), and calculated value of SBH at various temperature in dry and wet condition (below)

In the same manner, SBH could be determined through C-V test. The built in voltage, $V_{bi}$ can be determine by extrapolating the graph and used to calculate SBH. The x-intercept for $1/C^2$ versus $V$ will give the value of $V_{bi}$. Figure 6 shows the $V_{bi}$ against temperature, which indicates linear correlation in agreement of figure 5. Again, SBH in wet show increment from dry condition. At high temperature, wet condition containing water vapor which dissociates into H$^+$ and OH$^-$. H$^+$ is suspected to dissolved into Cr$_2$O$_3$ film and change its electronic behavior due to its higher affinity to any solid matters.

The change in saturated current / built in potential reflects the electronic property if Cr$_2$O$_3$ film close to interface, because when the applied potential is first increased, the region close to interface is depleted in electrons. This suggest that T91/Cr$_2$O$_3$ region has an uniform donor density. Cr$_2$O$_3$ is reported to exhibits p-type electrical behavior with small deviation from stoichiometry [10]. This study has shown that humid condition somehow change the electrical behavior probably due to increase of Cr vacancy. Hence, it increases the Cr self-diffusivity, $D_{Cr}$. C. Greskovich [10] has reported the dependency of Cr diffusivity, $D_{Cr}$ with oxygen partial pressure $P_{O_2}$ by the defect equation

$$8\text{Cr}_{Cr} + \frac{3}{2}\text{O}_2(g) = 2\text{V}^{--}_{Cr} + 6\text{Cr}^{4+}_{Cr} + \text{Cr}_2\text{O}_3$$

Where Cr$_{Cr}$ is a trivalent chromium ion on its regular lattice site, V$^{--}_{Cr}$ is triply negatively ionized vacancy of a regular chromium ion, Cr$^{4+}_{Cr}$ is a Cr$^{4+}$ ion or a positive hole on regular chromium site. Point defect model (PDM) describes the dynamic and steady-state properties of a passive film in term
of electrochemical reactions \[11,12\]. During the film growth, vacancies are produced at oxide/gas interface but annihilated at the metal/oxide interface. The PDM predicts the thickness of barrier layer vary linearly with voltage at steady state. The flux of chromium ions through Cr$_2$O$_3$ passive film may written as

$$J_{Cr} = -D_{Cr}(\frac{\partial C_{Cr}}{\partial x}) - 2KD_{Cr}C_{Cr}$$

(6)

Where $K = \frac{\gamma e}{\varepsilon}$, $\varepsilon$ is the mean electric field strength, $\gamma = \frac{F}{RT}$ and $D_{Cr}$ is the diffusion coefficient of Cr ions. Accordingly, with a presence of humidity when mean electric field strength increase, the flux of chromium ions also increase proportionately. This will accelerate the oxidation of chromium.

Figure 6. Correlation of $V_{bi}$ against temperature for both condition wet and dry of T91/Cr$_2$O$_3$ interface

4. Conclusions
The $I-V$ and $C-V$ measurement of T91/Cr$_2$O$_3$ layer was performed to evaluate the SBH on metal/oxide interface. The samples were exposed in dry and humid condition at high temperature to investigate the accelerated oxidation in humid condition. It was found that saturated current and built in potential varies accordingly at respective temperature. Hence, SBH increase in the presence of humidity/water vapor. These changes reflect the change in electronic property of Cr$_2$O$_3$ scale at near interface. The change of electronic property of passive Cr$_2$O$_3$ layer was discussed from perspective of point defect model (PDM) and ionic diffusivity. H$^+$ ions dissociates from water vapor / humidity affect the diffusivity in Cr$_2$O$_3$ layer by increasing the flux of Cr, thus promotes accelerated oxidation of T91 boiler material in humid condition.

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