

# A Study on Aggressiveness of KCl to Steel Material in High Temperature in Biomass Boilers

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**Abstract**—Aggressiveness of KCl in high temperature was studied in this article. Electrochemical experiments in hot molten KCl and corrosion experiments in high temperature were conducted for analysis of possible reaction. Comprehensive analysis indicated that aggressiveness mechanisms of KCl in high temperature were controlled by four-step processes. The final step was activation oxidation process, which can lead to higher stress and result in oxide scale exfoliation.

**Keywords**—chemical property; aggressiveness; high temperature reaction; activation oxidation process

## I. INTRODUCTION

With the depletion of coal, oil and other non-renewable resource and the deterioration of the environment, It is imperative to develop and utilize the low pollution, high environmental protection, renewable new energy [1]. This makes the research of biomass energy become an important direction.

There exists serious molten salt corrosion for superheater material at high temperature in the flue gas side of biomass boilers due to high concentration of KCl salts in biomass fuels [2]. Alkali chlorides are aggressive and can react with the steel surface at high temperature, which may enhance local oxidation. It has been shown that high-temperature corrosion of stainless steels is greatly enhanced by the presence of KCl, especially for large power capacity of biomass power plant with steam temperature higher than 540 C [3,4].

Potassium chloride is a colorless cubic crystal or white crystalline powder with small granules. KCl looks like salt, odorless non-toxic. The density of KCl is 1.987g/cm<sup>3</sup>. Melting point is 773 C.

Solubility of KCl in water increased rapidly with the increase of temperature. Its solubility in 20 C is 34.4g/100mL water [5,6]. Its solubility in 100 C is 56.7g/100mL water. Basic properties of KCl are similar with sodium chloride. KCl can be used as industrial raw material for preparation of potassium metal according to reaction ( $KCl + Na \rightarrow K + NaCl$ ) in 850 C. This is a reversible reaction. The thermodynamics nature is in favor of the reaction. When the temperature reaches 773 C, potassium in KCl would exist in vapor state. It is conducive to the direction of the reaction.

KCl can deposit on the surface of the heat pipe wall. It can react with metal or metal oxide, and the low melting point

eutectic can also be formed on the surface of the tube. When the temperature of the tube wall reaches the crystal melting point, chlorine salt can transform into liquid phase in the ash/metal interface. Due to the ferroelectric with molten metal chloride, the aggressiveness of KCl will significantly accelerate the corrosion of pipes, which is quicker than the metal in the solid or gaseous metal corrosion in chloride medium speed. Table 1 list the typical chloride compounds and the formation of the eutectic chemicals with lower melting points in biomass power plants.

In this paper, super-heater tube material T91, usually used in biomass boiler [7], was selected as the object of study. Electrochemical experiments in hot molten KCl and high-temperature corrosion experiments were employed to study the corrosion properties of KCl to T91 material. According to chemistry analysis and discussion, aggressiveness of KCl in high temperature and performance evaluation of T91 has been conducted in detailed.

## II. EXPERIMENTAL METHODS

In order to analyze the aggressiveness of KCl in high temperature in biomass power plants, evaluation methods include electrochemical experiments and corrosion experiments in high temperature. T91 material was selected as samples with size of 50×25×2mm. The surface of each sample was treated in turn by the metallurgical sandpaper with different grades, ethanol, acetone solution cleaning. Then each sample was treated with the sandpaper and placed in a drying box at 150°C for 2 hours. Weighing and measuring the length/width and thickness, micro-structure characterization was carried out before the experiment.

The experimental temperature was set at 600°C, 650°C and 700°C. The exposure time was set to 30 hours. During experimental process, samples would be taken out in different time, such as 1,4,7,10,20 and 30 hours. Each sample would be checked and measured for observation of their morphology change and massive change. The corrosion kinetic curves and oxidation kinetic curves can be drawn according to weight changes data from experimental time.

### III. RESULTS

#### A. Molten Electrochemical Experiments in High Temperature

Electrochemical experiments must be carried in hot molten KCl electrolyte. It is necessary to monitor the signal of current and potential in such molten salt system. The open circuit potential (OCP), i.e.  $E_{corr}$ , is a thermodynamic parameters, which can characterize the tendency towards material corrosion. The more negative  $E_{corr}$  is, the higher tendency the metal material may corrode. Linear polarization resistance,  $R_p$  value, is inversely proportional to the corrosion current density. When  $R_p$  value increases, the corrosion current density would decrease, the anti-corrosion performance of such material is improved. So the OCP and  $R_p$  values of T91 must be measured in high temperature. Figure 1 showed the change process of OCP and  $R_p$  value with corrosion time for T91 material in 800°C molten KCl.

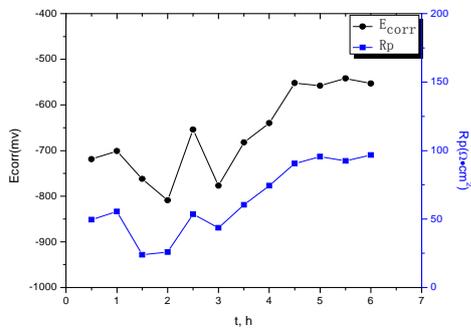


FIGURE I. THE CHANGE PROCESS OF OCP AND B VALUE WITH CORROSION TIME FOR T91 MATERIAL

Because there is high temperature in molten salt, the process of metal ionization and transfer of charged particle are faster. The corrosion rate is mainly controlled by the oxidant diffusion in molten salt or diffusion of charged particle in the oxide film. Figure 2 showed electrochemical impedance spectroscopy (Nyquist) respectively for T91 material in molten KCl system.

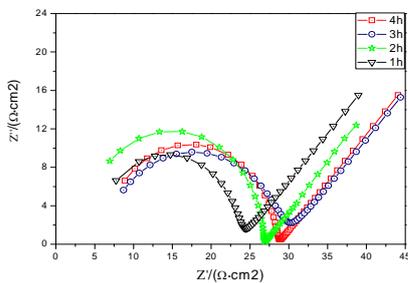


FIGURE II. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR T91 MATERIAL

#### B. Exposure Corrosion Experiments in High Temperature

Figure 3 showed high temperature chlorination corrosion kinetics curves of T91 under different temperatures. It showed

that different temperature, different time presented different curve law. At the temperature of 600°C and 650°C, the initial corrosion kinetic curves were logarithmic. The later stage was negative logarithmic. At the temperature of 700°C, corrosion kinetic curves were first parabolic law, then the linear rule.

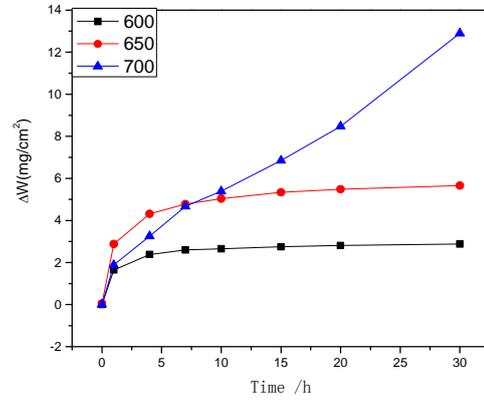


FIGURE III. HIGH TEMPERATURE CORROSION KINETICS CURVES OF T91

#### C. Materials Characterization Tests

XRD analysis of products of hot corrosion in molten salts for 4h and 8h was showed in Figure 4. XRD results showed that corrosion products formed on the surface of 4 hours were  $Fe_2O_3$  and  $K_2Fe_4O_7$ . At the late stage (8h) of corrosion, corrosion products were  $Fe_3O_4$ ,  $K_2Cr_2O_7$  and  $K_2Fe_4O_7$ . Because T91 materials contain a certain amount (9%) of Cr, the formation of  $FeCr_2O_4$  protective film has a higher solubility with spinel type composites.

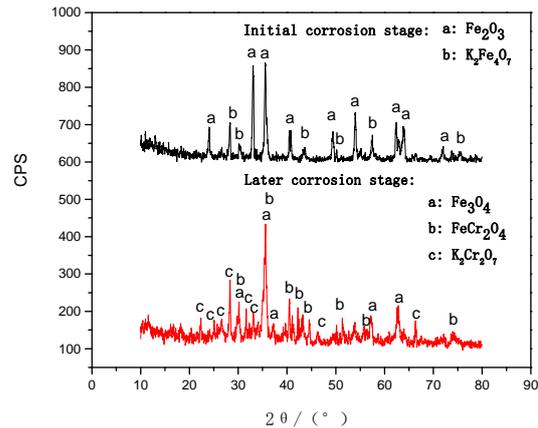


FIGURE IV. XRD ANALYSIS OF PRODUCTS OF HOT CORROSION IN MOLTEN SALTS FOR DIFFERENT TIME

Figure 5 showed the microscopic morphology of T91 under 700°C corrosive hot KCl for 8 hours. The sample surface was smooth. There were a lot of bulges. Small amounts of bulges were broken. EDS analysis showed atomic

percentages for elements were Fe (43.20%), O (40.00%), Cr(9.55%), Cl (0.21%) and K:0.11%. According to the atomic percentage, the main composition of bulges is dense FeO and Cr<sub>2</sub>O<sub>3</sub>. At the same time, the exist of Cl element showed that the bulge forming has close relationship with KCl.

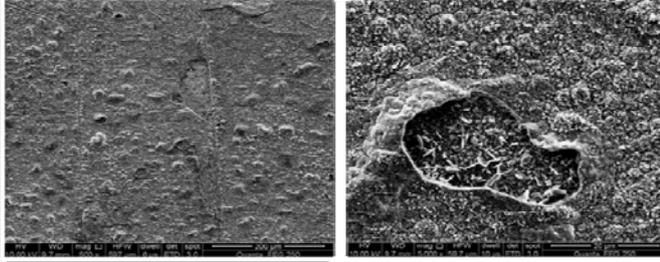


FIGURE V. SEM OF T91 AFTER 700 C CORROSION EXPERIMENT

#### IV. ANALYSIS OF AGGRESSIVENESS OF KCL IN HIGH TEMPERATURE

##### A. Analysis of Electrochemical Experiments

Figure 1 showed that E<sub>corr</sub> of T91 in the molten KCl declined sharply in the early stage of corrosion process. The decline range reached as high as 150mV. At the same time, linear polarization resistance R<sub>p</sub> decreased. After 1 hour of corrosion stage, E<sub>corr</sub> tended to increase little higher, R<sub>p</sub> tended to increase. These indicated that a relatively stable oxide film formed after 1 hour of exposure, which resulted in abnormal change of E<sub>corr</sub> and R<sub>p</sub>.

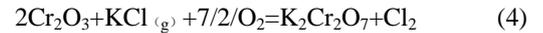
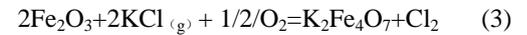
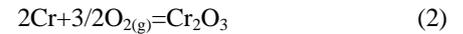
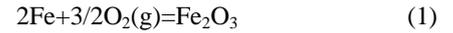
Figure 2 showed that T91 materials represent two kinds of impedance characteristics spectroscopy in different corrosion time. At the early stage of the corrosion process, impedance Nyquist spectroscopy showed typical Warburg impedance characteristics. There is a circular arc shape in high frequency and almost one slope linear in low frequency. This kind of impedance spectroscopy featured the diffusion control of oxidant at the early stage of the corrosion process. In the late stage of corrosion, impedance Nyquist spectroscopy showed the characteristics of two capacitance arcs. Therefore, corrosion rate is mainly controlled by the transfer rate of charged particle in the oxide film in later stage.

##### B. Analysis of the Corrosion Process on the Steel Surface

According to EDS analysis, chlorine gas with strong permeability can be formed on the steel surface by reaction between KCl with oxides. Chlorine gas, Cl<sub>2</sub>, can pass through the oxide film and accumulate at the junction between the metal matrix with lower oxygen potential and protective film. Metal chlorides of Fe and Cr may be generated at this place. Then gaseous metal chloride can volatilize outward, there would be a gradual growth of strain stress by penetration process of Cl<sub>2</sub>. Finally, KCl in high temperature destroyed oxide film and lead to state change on the surface of T91 material.

##### C. Aggressiveness Mechanisms of KCl

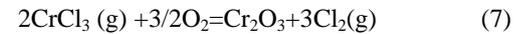
At the beginning of the high temperature chlorination corrosion experiments, oxide film can be formed quickly on the surface of T91 material, as shown in Equation (1) and (2). Then, KCl steam with gaseous state in high temperature can contact the oxide film and react as Equation (3),(4). These reactions produced K<sub>2</sub>Fe<sub>4</sub>O<sub>7</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with low melting point and the protective oxide film on the surface of steel was destroyed. Then chlorine gas will be generated with large quantities. The products include K<sub>2</sub>Fe<sub>4</sub>O<sub>7</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with low melting points and Cl<sub>2</sub>. This can be proved by XRD test results.



Part of Cl<sub>2</sub> may penetrate oxide film with progress of the corrosion process. There were large quantities of pores in oxide layers, which lead to quick chlorination corrosion. With the gradual decrease of oxygen partial pressures inside of oxide layers, the partial pressure of chlorine gas in the oxide film increased gradually. Finally, metal chloride could be formed as Equation (5), (6).



Metal chlorides have relatively low melting point (T=677 C) and high volatility. When large quantities of metal chlorides were formed, they would diffusion outward and reached regions with higher oxygen potential. Then Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and Cl<sub>2</sub> were produced by the oxidation process, as shown in Equation (7), (8).



Chlorine gas would react again in the interface between oxide film and metal matrix, which caused phenomenon 'activation oxidation'. Activation oxidation can lead to higher stress between the metal substrate and the oxide film, which resulted in oxide scale exfoliation. Therefore, such process made small concentration of metal chloride in the corrosion layer because of activation oxidation. This was proved by EDS test results.

## V. CONCLUSION

According to analysis of all experiments for evaluating aggressiveness of KCl in high temperature, four-step processes are aggressiveness mechanism of KCl. ① KCl, in gaseous state in high temperature, can react with oxide film on the surface of steel material and form metal salts and chlorine gas. ② Metal chloride can be formed due to penetration of  $\text{Cl}_2$  through the oxide layer. ③ Because of relatively low melting point, metal chloride may volatilize and produce metal oxide and chlorine gas again. ④ Activation oxidation process can lead to higher stress between the metal substrate and the oxide film, which resulted in oxide scale exfoliation.

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