ABSTRACT

Reactions between potassium chloride (KCl) and chromium oxide (Cr₂O₃) as well as pure chromium (Cr) have been studied as model reactions for high temperature corrosion. The compounds have been used as powders because of their big area-to-mass ratio, which results in clearer signals in thermogravimetric measurements. The changes in mass and heat of reaction were measured by means of differential thermal analysis and thermal gravimetry (DTA/TG). The runs were performed mainly in synthetic air, but also nitrogen was used. After the DTA/TG runs the samples were analyzed with a scanning electron microscope (SEM).

Chromium oxide seems to be inert in the used conditions, but pure chromium reacted with potassium chloride forming chromium oxide as product. In some runs, a yellow intermediate, probably potassium chromate (K₂CrO₄) was detected. The reaction needs both oxygen and potassium chloride to proceed, but already a tiny amount of potassium chloride is enough to maintain the oxidation of chromium.

Keywords: High temperature corrosion, pure chromium, biomass combustion.
INTRODUCTION

Recovery of energy from biomass and various waste–derived fuels by combustion has become important due to reduction of detrimental CO₂ emissions. Biomass does, however, release significant amounts of chlorine and alkali metals, as e.g. HCl(g), KCl(g), KOH(g) and NaCl(g), into the gas phase during combustion. These compounds may cause deposits, which interfere with operation and eventually may lead to corrosion and/or blockage of the gas path. Due to severe corrosion caused by these compounds, steam temperatures in biomass combustion are kept at significantly lower levels and, consequently, the power production efficiency is lower than in boilers fired with conventional fuels such as coal. In addition, chlorine bound to the chlorides mentioned above may produce unacceptably high emissions of HCl and dioxins. HCl can, as well as released alkali species, form aerosols and condense during cooling in the flue gas.

To prevent and diminish the problems mentioned above, better and more detailed knowledge of the reactions of potassium chloride during combustion is needed. It has been suggested that the reaction between solid potassium chloride and chromium oxide is the one responsible for starting the complex series of corrosion reactions (Eq. 1) (Pettersson, 2005). If the conditions are dry enough, the reaction occurs with oxygen (Eq. 2) (Li, 2004). Chromium oxide forms a protective layer on the surface of stainless steels used for furnace tubes in power plants, but the reaction with potassium chloride may result in breaking of this layer followed by rapid oxidation of the steel. Reactions of solid potassium chloride with chromium usually start to have significance at temperatures between 400 and 600 °C, even though the melting point of potassium chloride is 772 °C.

\[
2\text{KCl}(s) + \text{Cr}_2\text{O}_3(s) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{CrO}_4(s) + 2\text{HCl}(g) \quad (1)
\]

\[
4\text{KCl}(s) + \text{Cr}_2\text{O}_3(s) + 5/2\text{O}_2(g) \rightarrow 2\text{K}_2\text{CrO}_4(s) + \text{Cl}_2(g) \quad (2)
\]

It has been suggested that once the protective oxide layer is destroyed, the corrosion reaction proceeds with the reaction between metallic chromium and potassium chloride (Spiegel, 1999). However, the detailed reaction mechanism is still ambiguous; one proposition includes the so called “chlorine cycle”, where the chloride reacts with chromium without being consumed (Eqs. 3–6) (Shinata, 1987). Eq. 6 is the net reaction of the three previous reactions. Another proposition for the reaction mechanism contains the idea of chloride ions rather than molecular chlorine (Pettersson, 2005).
To get more detailed information about the reactions and their dependencies on conditions, such as temperature; the amount of potassium chloride and the composition of the gas atmosphere, studies with pure substances are needed. In this study experimental work with model substances has been carried out to shed more light on the reaction mechanisms relevant to corrosion problems during combustion of biomass and waste–derived fuels. Later also authentic superheater tube materials and their reactions with potassium chloride will be studied.

**EXPERIMENTAL**

Pure Cr, Cr$_2$O$_3$ and KCl were used in the reaction mixtures for powder samples as well as for Cr-granule samples. KCl was ground with a ball mill prior to the mixing, however the powders were not sieved to any particular particle size. The runs were performed using differential thermal analysis and thermal gravimetry (DTA/TG). The sample was heated at a controlled heating rate to the wanted temperature and the changes in mass and heat of reaction were observed as a function temperature and/or time. During most of the runs synthetic air was used, but also pure nitrogen as well as nitrogen mixed with carbon monoxide was used. After the DTA-TG runs the samples were studied and analyzed with a scanning electron microscope equipped with an energy dispersive x-ray analyzer (SEM/EDXA).

**RESULTS**

The DTA/TG runs were started with a mixture of pure chromium oxide and potassium chloride, but no changes in mass and no endothermic or exothermic peaks were observed under the test conditions. The smooth peak, which can be seen in every DTA/TG-curve at around 200°C, is not a real reaction peak, but just a baseline drift of the equipment. After this the chromium oxide was replaced with metallic chromium powder. In both cases the samples were heated up to 700°C in synthetic air with a heating rate of 2°Cmin$^{-1}$. Potassium chloride started to react with chromium approximately at 550°C and the mass of the sample started to increase, first slower and then rapider, which indicates the formation of chromium oxide (Fig. 1). 

4Cr + 12 KCl → 4CrCl$_3$ + 12K

4CrCl$_3$ + 3O$_2$ → 2Cr$_2$O$_3$ + 6Cl$_2$

6Cl$_2$ + 12K → 12KCl

4Cr + 3O$_2$ → 2Cr$_2$O$_3$
Figure 1. DTA/TG-curves for KCl/\(\text{Cr}_2\text{O}_3\) (a) and KCl/Cr (b) heated up to 700°C in synthetic air. The smooth peak at around 200°C results from baseline drift.

The importance of oxygen for the reaction was tested by replacing the synthetic air with nitrogen gas (\(\text{N}_2\)). In both cases the heating program was the same; 2°C/min\(^{-1}\) up to 700°C (Fig. 2).
The product of the reaction was identified to be chromium oxide, Cr$_2$O$_3$. The identification was done by comparing the elemental spot analyses of the product and pure chromium oxide. The SEM images revealed that the structure of the formed oxide was highly porous, consisting of small oxide particles, which are very loosely attached to each other (Fig. 3). In some samples a yellow color was noted and it was indirectly identified as potassium chromate, K$_2$CrO$_4$ (Fig. 4). The identification was done with both elemental line analysis and elemental mapping: in some areas potassium, chromium and oxygen were found, but no chlorine.
Figure 3. SEM images from an untreated Cr-particle (a), a reacted Cr-particle (b) and formed \( \text{Cr}_2\text{O}_3 \) (c).
Figure 4. An optical microscope image of $\text{K}_2\text{CrO}_4$ (a) and an elemental analysis from a KCl/Cr sample heated to 700°C (b). The clear crystal in (a) is unreacted KCl.
The role of potassium chloride was investigated by using Cr-granules in two runs, the other one without KCl and the other one with KCl. In the sample with KCl the amount of potassium chloride was 0.6 mass-% of the total sample. In both runs the samples were first heated $10^\circ\text{Cmin}^{-1}$ to 400°C, then $2^\circ\text{Cmin}^{-1}$ up to 700°C, where they were held for 240 minutes (Figs. 5 and 6).

Figure 5. Optical microscope images of Cr-granule with one KCl crystal (circled) before the DTA/TG run (a), Cr-granule without KCl (b) and Cr-granule with KCl after the DTA/TG run (c).
CONCLUSIONS

In this work the reaction mechanisms between both pure chromium oxide and potassium chloride as well as between pure chromium and potassium chloride were studied. Pure compounds were used as model substances for the high temperature corrosion reactions, which occur on the surfaces of the superheater tubes in combustion power plants. The runs were performed using differential thermal analysis and thermal gravimetry (DTA/TG). During most of the runs synthetic air was used, but also pure
nitrogen as well as nitrogen mixed with carbon monoxide was used. After the DTA-TG runs the samples were studied and analyzed with a scanning electron microscope equipped with an energy dispersive x-ray analyzer (SEM/EDXA).

Even though the studies on the detailed reaction mechanism of this corrosion reaction have just started, already some conclusions can be drawn from the results presented earlier in this paper.

- Chromium oxide seems to be inert in the used conditions.
- The reaction needs both potassium chloride and oxygen to proceed.
- Although potassium chloride is essential, already a tiny amount is sufficient.
- The reaction proceeds at least via one solid intermediate, potassium chromate.
- The product is highly porous chromium oxide, consisting of small particles.

REFERENCES


