MODEL ALLOY OXIDATION IN OXYFUEL CHARACTERISTIC ENVIRONMENT

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Abstract

In the oxyfuel process, pure oxygen is burned in boilers with recycled gas producing a gas rich in CO\textsubscript{2}, making it easier to capture the CO\textsubscript{2} in the end of the process. The present work investigates the high temperature corrosion characteristics of a model Fe-Cr-Co alloy in typical oxyfuel process environment. Samples were oxidized at 600°C during 1000 hours in single atmosphere condition, where the samples is exposed to the same gas in all faces, and in a dual atmosphere condition, where the sample is exposed to water vapor in one side and to oxyfuel gas in the other. Samples where characterized by SEM and EDX. Results showed that corrosion is higher in a dual atmosphere condition than in single condition.

Key-words: Oxy-fuel process; Corrosion; High-Temperatures; CO\textsubscript{2}
Introduction

Several alternatives are being developed and used in order to reduce the CO\textsubscript{2} emission by substituting the burning of fossil fuels by biofuel and other renewable energy sources. However, the increase in the use of renewable sources is accompanied by an even larger increase in the use of energy, especially in developing countries like China and India. For this reason, fossil fuel is expected to be the major global source of energy at least until 2030 \cite{1,2,3}. Oxyfuel is a new process, under development, to be used in new coal-fired power plants together with carbon capture and storage technology (CCS), producing energy with zero CO\textsubscript{2} emission. In this process, flue gas at the end of the process bears only water vapor and CO\textsubscript{2}, which is compressed to be sold or stored \cite{4,5}.

Tubes used in boilers are exposed to water vapor in the inner side and to flue gas in the outer side. The two sides of the tube are, therefore, exposed to different hydrogen partial pressure, what can lead to hydrogen diffusion from the water vapor side to the flue gas side \cite{6,7}.

Several studies on the corrosion behavior of steels in dual atmosphere condition have been reported. In some works, the dual condition has accelerated the corrosion rate \cite{6,7,8,9,10,11,12}, either by the growth of Fe-rich nodules on the surface of the steel or by the formation of thick iron oxides layers. One hypothesis for the corrosion rate increase is that hydrogen diffuses in steel as a proton and when reaches the gas side it reacts with oxygen forming H\textsubscript{2}O \cite{7}, that usually increases the corrosion rate of steels \cite{13}. In other works \cite{14,15}, the hydrogen effect was negligible and this was attributed to the formation of a protective Cr\textsubscript{2}O\textsubscript{3} layer that severely decreased the hydrogen diffusion from one side to the other \cite{15}.

In the present work a model Fe-Cr-Co alloy was investigated under atmospheres related to the oxyfuel process. The samples were exposed to single and dual atmosphere conditions at 600°C for 1000h. In exposed to water vapor in one side and gases with CO\textsubscript{2}, SO\textsubscript{2} and different H\textsubscript{2}O content in the other side, creating a hydrogen gradient in the sample. The aim of this work is to characterize the oxide layer formed on the alloy surface before the corrosion tests in order to describe the corrosion mechanism.
Materials and Methods

The model alloy with 14.1 wt% Cr, 3.04 wt% Co and 0.01 wt% C was produced in the National Institute of Standards and Technology (NIST) using a vacuum electric furnace. Before the corrosion experiments, the model alloys were heat treated at 760°C for 1 hour, cooled in calm air and then cut with water to produce samples for the single and dual experiments.

Samples were exposed to two different gases (Table 1) which simulated atmospheres related to the oxyfuel process at 600°C for 1000h in single and dual atmosphere conditions.

Table 1. Gases compositions in vol%.

<table>
<thead>
<tr>
<th>Gases</th>
<th>CO₂</th>
<th>SO₂</th>
<th>Ar</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas A</td>
<td>70</td>
<td>1</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>Gas B</td>
<td>70</td>
<td>1</td>
<td></td>
<td>29</td>
</tr>
</tbody>
</table>

In a single atmosphere condition, samples where glued to a sample holder and put in a cylindrical furnace in such a way that the same gas flowed with a constant velocity through all their faces. In a dual atmosphere condition, a special sample holder was built, in which the samples were exposed to water vapor on one side and gas on the other. Scheme of the dual atmosphere furnace is shown in Figure 1.

![Scheme of the dual atmosphere furnace](image)

Figure 1. Scheme of the dual atmosphere furnace
After the corrosion tests, the cross section of the samples was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

Results and Discussion

Figure 2 shows SEM images of the cross section of the alloy exposed to gas A in single and dual conditions. A thin (~ 1 µm) protective and compact Cr₂O₃ scale with dispersed small Fe-rich nodules was formed when the alloy was exposed to single atmosphere condition (Fig. 2A). On the other hand, a thick (~ 100 µm) and porous scale composed by two layers was observed when the alloy was exposed to gas A in dual condition (Fig. 2B). The external layer is composed by hematite and magnetite, and the internal layer by Fe/Cr spinel and sulfides, as shown in figure 3.

Figure 2. SEM images of the cross section of the alloy exposed to gas A at 600°C for 1000h in single (A) and dual conditions (B).

Figure 3. EDX analysis of the alloy exposed to Gas A in a dual condition at 600°C for 1000h.
SEM images of the cross section of the alloy exposed to gas B in single and dual conditions are shown in Fig. 4. As occurred when the alloy was exposed to gas A, a thin Cr₂O₃ scale was formed on the alloy surface exposed to gas B in single atmosphere condition (Fig. 4 A). Instead of a continuous scale, porous oxides nodules were observed in the surface of the alloy after the corrosive tests in dual condition (Fig. 4 B). The nodules thickness was in the range of 10 to 100 μm. The EDX line scan presented in Fig. 5 shows that the nodules are formed by an external layer composed by iron oxides (hematite and magnetite) and an internal layer composed by Fe/Cr spinel.

Figure 4. SEM images of the cross section of the alloy exposed to gas B at 600°C for 1000h in single (A) and dual conditions (B).

Figure 5. EDX analysis of the steel exposed to Gas B in a dual condition at 600°C for 1000h.
The results presented in this work show that the corrosion in dual atmosphere condition was more severe than in single condition. Furthermore, porosity was observed only in the scale formed in dual condition (Figs. 2 and 4) and a scale composed mainly by chromium oxide was formed in single condition while a complex scale was identified in dual condition (Figs 3 and 5). Several studies have investigated the dual effect in steel in different temperatures, compositions, atmospheres and methods and the results are very diverse. In some works, the dual condition has accelerated the corrosion rate \[^6,7,8,9,10,11,12\], either by the growth of Fe-rich nodules on the surface of the steel or by the formation of thick iron oxides layers. One hypothesis for the corrosion rate increase is that hydrogen diffuses in steel as a proton and when reaches the gas side it reacts with oxygen forming H\(_2\)O \[^7\], that usually increases the corrosion rate of steels \[^13\]. In other works \[^14,15\], the hydrogen effect was negligible and this was attributed to the formation of a protective Cr\(_2\)O\(_3\) layer that severely decreased the hydrogen diffusion from one side to the other \[^15\].

It is clear that the chromia layer plays an important role in inhibiting hydrogen diffusion from the gas to the steel and decreasing the hydrogen gradient in the steel \[^15,16\]. In some studies \[^10,12,17,18\], even when a protective scale is formed in a single condition experiment, iron rich nodules are formed in a dual condition. The faster corrosion would be a result of the higher porosity caused by the atmospheres with high hydrogen partial pressure. The porosity would increase the scale diffusion by changing the oxygen diffusion mechanism from a point defect O\(^-2\) diffusion to a molecular O\(_2\) diffusion through pores \[^7\].

The water vapor is well known to increase the oxidation rate in steels \[^19\], because of the molecular transportation of oxygen in the scale caused by it. However, the results presented in this work show that scale thickness did not increase with the increase of water vapor concentration in the gas. An evidence of this observation is the non formation of a continuous layer when the alloy was exposed to gas B in dual conditional (Fig. 4B). This feature could be probably related to the high chromium content and to the microstructure of the alloy, in addition to the effect of the dual atmosphere condition. Further studies will be performed to clarify this feature.
Conclusions

A thin, protective and compact Cr$_2$O$_3$ scale with dispersed small Fe-rich nodules was formed when the alloy was exposed to single atmosphere condition in both gas composition;

A porous scale composed by an external layer of iron oxides and an internal layer of Fe/Cr spinel was observed when the alloy was exposed to gas A in dual condition;

Porous nodules composed by hematite, magnetite and Fe/Cr spinel were observed in the surface of the alloy after the corrosive tests in dual conditions;

The faster corrosion observed in dual condition atmosphere may be related to the effect of the hydrogen diffusing from the water vapor side, resulting in higher porosity due to its reaction with oxygen in the other side of the sample.

References


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OXIDAÇÃO DE LIGA SUBMETIDA A TEMPERATURA ELEVADA EM AMBIENTES CARACTERÍSTICOS DO PROCESSO DE OXI-COMBUSTÃO

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Resumo

O processo de oxi-combustão tem como conceito básico a substituição do ar por oxigênio puro. Essa substituição gera uma atmosfera livre de N\textsubscript{2}, permitindo a reciclagem do gás de combustão e a não emissão de CO\textsubscript{2} durante a produção de energia. O presente trabalho analisa as características de corrosão em altas temperaturas de uma liga experimental produzida pelo NIST, submetida a ambientes característicos do processo de oxi-combustão. As amostras foram oxidadas a 600°C durante 1000 horas tanto em condição simples, onde as amostras foram expostas a um mesmo gás em ambas as faces, quanto em condição dupla onde a amostra foi exposta a vapor d’água de um lado e ao gás corrosivo de outro. As amostras foram caracterizadas por MEV e EDS. Os resultados demonstraram que há uma maior corrosão em condição dupla que em condição simples.

Key-words: Processo de oxi-combustão; Corrosão; Altas temperaturas; CO\textsubscript{2}