High Temperature Oxidation Behaviour of Low Carbon Steel and Austenitic Stainless Steel

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Abstract

The objective of this study is to evaluate high temperature oxidation behaviour of low carbon steel AISI 1020 and austenitic stainless steel AISI 304 in air and in synthetic ash, having 70wt% sodium sulfate (Na2SO4), 20wt% vanadium oxide (V2O5) and 10wt% sodium chloride (NaCl), at 600°C and 800°C with various times, i.e. 50, 100, 150 and 200 hours. From the results, low carbon steel AISI 1020 showed higher oxidation than austenitic stainless steel AISI 304 for the air and synthetic ash at temperatures of 600°C and 800°C. This can be explained by the fact that the oxide film of austenitic stainless steel AISI 304 is more stable than that of plain carbon steel at high temperature. However, oxidation of austenitic stainless steel AISI 304 in synthetic ash at the temperature of 800°C is higher than in the normal atmosphere. The alumina boat could not be used in the hot synthetic ash over a long period of time since it finally corroded and broke.

Key words: High-temperature oxidation, Low carbon steel AISI 1020, Austenitic stainless steel AISI 304, Synthetic ash

Introduction

Plain carbon steels and austenitic stainless steels are generally used in boiler system in a temperature range of 600°C and 850°C because of their cost and mechanical property. It is well known that parts of boiler system are exposed to high temperature oxidation and hot corrosion that are recognized as the main factors for degradation of boiler parts. In general, most of metals are thermodynamically unstable with respect to ambient gases, i.e. CO and CO2 or burning boiler dirty oil, which have main compositions of V2O5, Na2SO4 and NaCl. For dirty oil, vanadium in the fuel condenses as V2O5 on the tube surface of boiler part to from low melting point, oxygen-fast diffusing, and fused salt film. Finally, it reacts with the surface of boiler part to form different compounds such as oxide, nitride, etc. The certain compounds may protect the underlying metals or may also thicken into a nonprotective scale with various defects such as cavities, microcracks and porosities as shown in Figure 1.

However, many service environments incorporate thermal cycling and contain combustion products, such as water vapor, carbon monoxide and dioxide, and sulfur compounds. All have a detrimental influence on oxidation resistance of the underlying metals.

Figure 1. Film and scale formation during high-temperature metal oxidation.

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Moreover, it is well known that oxide films are ductile at high temperature and are often brittle at lower temperature. Most oxide films have different thermal expansion coefficients than those of the underlying metals from which they are formed. Thus, the oxide films formed at high service temperature may lose adherence to the underlying metals, when cooled to lower temperature and become the nonprotective films. These are major reason for high oxidation rate and weight loss of the underlying metals.\(^{(1-7)}\)

In order to understand high temperature oxidation behaviour of bare metals, plain carbon steel AISI 1020 and austenitic stainless steel AISI 304 are selected to be studied in air and synthetic ash with various times of up to 200 hours. A synthetic ash used in this study is mixed of V\(_2\)O\(_5\), Na\(_2\)SO\(_4\) and NaCl because those compositions are mainly compounds in the real boiler system.

### Materials and Experimental Procedures

Two commercial steels were used for this study, i.e. low carbon steel AISI 1020 and austenitic stainless steel AISI 304. Dimensions of samples were 15x15x3 mm. The measured chemical compositions of commercial AISI 1020 steel and AISI 304 stainless steel were shown in Table 1.

**Table 1.** The measured chemical compositions of commercial AISI 1020 steel and AISI 304 stainless steel (wt%).

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 1020</td>
<td>0.22</td>
<td>0.17</td>
<td>0.03</td>
<td>&lt;0.003</td>
<td>0.02</td>
<td>Balanced</td>
</tr>
<tr>
<td>AISI 304</td>
<td>0.05</td>
<td>0.44</td>
<td>16.74</td>
<td>0.25</td>
<td>7.91</td>
<td>Balanced</td>
</tr>
</tbody>
</table>

Samples were polished by silicon carbide paper up to 1200-grit for removing all coarse scratches and contaminations. The samples were then rinsed by distilled water, acetone and were air dried. Weight measurement and surface roughness of each sample have been performed before starting experiment. The high temperature oxidation behaviour of the certain steels was conducted into two conditions, i.e. bare samples and samples coated by the synthetic ash having compositions of 70wt%Na\(_2\)SO\(_4\), 20wt%V\(_2\)O\(_5\) and 10wt%NaCl. The cyclic high temperature oxidation studies for bare and coated samples were performed in air without inert gas at 600°C and 800°C for 4 cycles, each cycle of 50 hours heating at a given temperature by 24 hours cooling in a tube furnace. The samples were put by putting on the alumina boat into the quartz tube and heated up. All of experimental procedures were summarized in Figure 2.

**Figure 2.** Experimental procedures for high temperature oxidation behaviour of low carbon steel and austenitic stainless steel.

**Table 2.** Samples and conditions of high temperature oxidation test.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Materials</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600°C</td>
</tr>
<tr>
<td>A</td>
<td>1020</td>
<td>X</td>
</tr>
<tr>
<td>B</td>
<td>1020</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>304</td>
<td>X</td>
</tr>
<tr>
<td>D</td>
<td>304</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>1020</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>1020</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>304</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>304</td>
<td>-</td>
</tr>
</tbody>
</table>

The conditions for bare and coated samples were summarized in Table 2. The deterioration of each sample was determined by weight measurement in each cycle after high temperature exposure. After high temperature exposure, microstructural examination was performed by an optical microscope. Compounds produced during high temperature exposure were qualitatively investigated by XRD.
Results and Discussion

Weight Loss of AISI 1020 Carbon Steel and AISI 304 Stainless Steel at High Temperature

After exposure to high temperature in each cycle (one cycle is composed of heating for 50 hours and cooling in the tube furnace for 24 hours), the sample was scrubbed by plastic blush in order to remove all of oxides before weighing the sample by four decimal positions. Then, the sample was heated, cooled and weighed again until the cycle of experiment reaches 4 times. Finally, the diagrams of weight loss of AISI 1020 and AISI 304 that is exposed to 600°C and 800°C in the air and synthetic ash are shown in Figures 3 and 4, respectively.

Figure 3. Weight loss and time diagram for bared and coated AISI 1020 and AISI 304 steels at 600°C.

At 600°C and without synthetic ash, weight loss of AISI 1020 and AISI 304 is less than 0.10 grams even though those steels are exposed of up to 200 hours. This means that at the certain temperature, oxidation resistance of AISI 1020 and AISI 304 is the same. For experiment with synthetic ash, weight loss of AISI 1020 gradually increases of up to 0.25 grams at 150 hours and it is drastically rose of up to 0.50 grams at 200 hours; while weight loss of AISI 304 seems to be sharply increase of up to 0.40 grams at the first 100 hours but it is decreased to be less than 0.10 grams at 150 and 200 hours. This might be explained that oxide of stainless steel is normally more stable than that of low carbon steel. This is confirmed by considering Figure 5. It is seen that the oxide of stainless steel has good adherence at high temperature and longer exposure time than the oxide of low carbon steel as shown in Figure 5 (b) and (d). Therefore, the oxide of stainless steel protects the substrate metal from the corrosive environment, i.e. ambient gases in the furnace and some compounds from the synthetic ash. From Figure 5, these are the examples of AISI 1020 and AISI 304 after exposed to 600°C for 50 and 150 hours. It is seen that the oxide of AISI 1020 breaks off from the surface of metal substrate. From the discontinuity of the oxide, the metal reacts with the corrosive gases and losses its metal again.

Figure 4. Weight loss and time diagram for bared and coated AISI 1020 and AISI 304 steels at 800°C.

Figure 5. Cross section of bared AISI 1020 and AISI 304 samples after exposure at 600°C for 50 and 150 hours.

At the beginning of high temperature exposure time of up to 100 hours, AISI 1020 is less
attacked than AISI 304 in experiments with synthetic ash. And, after exposure of more than 100 hours AISI 304 strongly resists to oxidation and the weight loss is not changed. This is due to the fact that the oxide evolution of austenitic stainless steel is dependent on time. After it generated completely; the corrosion resistance of stainless steel is better.\(^{1,2}\) This is only true at a temperature of 600°C. At 800°C, it found that AISI 1020 and AISI 304 are strongly affected by the synthetic ash. However, the weight loss of AISI 1020 is higher than AISI 304. This could say that the bare AISI 1020 and AISI 304 must not be used at 800°C associated with the dirty oil product.

**XRD Analysis**

XRD patterns of the surface of AISI 1020 carbon steel after exposed to 800°C for 50 hours are shown in Figure 6. The oxide phases found are Magnetite (Fe_3O_4), Wüstite (FeO) and Hematite (Fe_2O_3). It can be explained by following reactions:

\[
2\text{Fe} + \text{O}_2 = 2\text{FeO} \tag{1}
\]

\[
6\text{FeO} + \text{O}_2 = 2\text{Fe}_3\text{O}_4 \tag{2}
\]

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2 = 6\text{Fe}_2\text{O}_3 \tag{3}
\]

![Figure 6. XRD profiles for AISI 1020 after exposed to 800°C for 50 hours.](image)

As illustration the iron-oxygen phase diagram is shown in Figure 7. There are three oxide phases: Wüstite (FeO), Magnetite (Fe_3O_4) and Hematite (Fe_2O_3), since the iron reacts with oxygen. It can be seen that the Wüstite phase is not stable below 570°C and it is transformed to iron and Magnetite. In order to confirm the generation of oxide phases during exposure to high temperature, one sample of AISI 1020 was tested at 800°C for 8 hours in Thermal Galvanic Analyze (TGA). The result from TGA is shown in Figure 8. It is seen that the sample continuously increases in weight during the reaction, especially above 500°C. This means that there are many oxide phases, i.e. Magnetite, Wüstite and Hematite, generates above the certain temperature.

![Figure 7. The iron-oxygen phase diagram.](image)

However, the oxide phases, generated at high temperature exposure, are dependent on the corrosive environment. This can be seen by considering the XRD profiles of AISI 1020 and AISI 304, exposed to 800°C and coated with the synthetic ash, as shown in Figures 9 and 10.

In order to confirm those mentions, the qualitative analysis of compounds produced on the surface of all samples was performed by XRD analysis. For example, for AISI 1020 after expose
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to 800°C for 50 hours in the synthetic ash, the compounds are mainly composed of FeS, Fe$_7$S$_8$ and MgFe$_2$O$_4$. While for AISI 304 the main compounds are Fe$_2$O$_4$, Na$_2$Ni(SO$_4$)$_2$·4H$_2$O, NiCO$_3$, NiS, (Fe,Ni)$_3$S$_4$, Ni$_3$S$_4$ and FeS·Cr$_2$S$_3$.

Moreover, it is found that the test time significantly affects on the generation of another compounds as shown in Figure 11. Increasing test time of up to 200 hours, the new compounds are generated, i.e. Fe$_2$O$_3$, V$_2$O$_3$, NiSO$_4$·H$_2$O, Fe$^+$2Cr$_3$S$_4$/FeS·Cr$_2$S$_3$, and FeCl$_2$. It is noticeable that some parts of the iron always react with the synthetic ash to form intermetallic compounds as shown in Figures 9, 10 and 11.

Table 3 shows the synthetic ash weight before and after experiment. It is seen that the weight is lost more than 50wt% and it is drastically affected by temperature. From these results, it may be a reason for high corrosion attack in AISI 1020 and AISI 304. Because important elements, i.e. sodium, sulfur, chloride and vanadium that are known as the catalyst for corrosion, are decreased and the elements react with the metal.

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>Weight in grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>600</td>
<td>70.8910</td>
</tr>
<tr>
<td>800</td>
<td>70.3910</td>
</tr>
</tbody>
</table>

Figure 8. Thermogravitric analysis of AISI 1020 at 800°C for 8 hours.

Figure 9. XRD profiles for AISI 1020 after heated and coated with the synthetic ash at 800°C for 50 hours.

Figure 10. XRD profiles for AISI 304 after heated and coated with the synthetic ash at 800°C for 50 hours.
The high temperature oxidation behaviour of low carbon steel and austenitic stainless steel was studied. The following conclusions can be drawn:

1. Air and synthetic ash attack AISI 1020 and AISI 304 steels during high temperature exposure. And, the degree of attack is strongly dependent on time and temperature.

2. High oxidation degradation in AISI 1020 is higher than that in AISI 304. This is due to the fact that the oxide of AISI 304 adheres on the surface better than the oxide of AISI 1020.

3. Some parts of the synthetic ash react with the metal surface; subsequently the compounds, i.e. Fe₂O₃, V₂O₃, NiSO₄·7H₂O, Fe⁺²Cr₃S₄/FeS·Cr₂S₃, and FeCl₂, were generated on the surface.

References


