Some Water Vapor Effects during the Oxidation of Alloys that are \( \alpha\text{-Al}_2\text{O}_3 \) Formers

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Oxidation studies were performed at 1100 °C in dry air and air containing fixed partial pressures of water vapor on a number of alloys and coatings that form \( \alpha\text{-Al}_2\text{O}_3 \) scales under oxidizing conditions. The alloys investigated included RENÉ N5, PWA 1484, diffusion aluminide coatings (with and without Pt modification) on RENÉ N5, and a Ni-8 wt pct Cr-6 wt pct Al model alloy. The water vapor affected the oxidation of the alloys in three important ways: (1) The scales spalled more profusely during cyclic oxidation in wet air than in dry air, particularly for those alloys with alumina scales, which are only moderately adherent under dry conditions. The results were consistent with the mechanism previously proposed (Reference 1), whereby the water molecules decrease the fracture toughness of the alumina/alloy interface. (2) Thicker oxides are formed during oxidation in wet air than dry air. This effect comes primarily from accelerated transient oxidation during exposure in wet air. (3) Spinel was found to form on top of the alumina scales during long-term exposure. This phenomenon occurred in all atmospheres but was much more pronounced for exposures in wet atmospheres. Mechanisms for the preceding observations are proposed.

I. INTRODUCTION

WATER vapor has been found to affect the oxidation of metals and alloys in a variety of ways.\(^{1,15-17}\) Most of these effects are detrimental in that the oxidation rates are increased. The effect of water vapor on the oxidation of alloys that develop oxidation resistance via the formation of continuous \( \alpha\text{-Al}_2\text{O}_3 \) scales is important because numerous high-temperature alloys and coatings rely on such a selective oxidation process for oxidation resistance. For these types of alloys, water vapor has been shown to cause the \( \alpha\text{-Al}_2\text{O}_3 \) scales to crack and spall.\(^{1,15-17}\) It has been proposed that water vapor lowers the toughness of the \( \alpha\text{-Al}_2\text{O}_3 \)/alloy interface. For alloy systems with extremely adherent \( \alpha\text{-Al}_2\text{O}_3 \) scales, water vapor did not cause substantial cracking and spalling of the oxide. It appears that when the interfacial toughness is very high, even with water vapor interaction, the interfacial toughness is still sufficient to inhibit spalling.

The major effect of water vapor on the oxidation resistance of the alumina formers appears to be increased cracking and spalling of the oxide scales. However, Buscail et al.\(^{14}\) have reported that water vapor causes the transient stage, during which the continuity of the \( \alpha\text{-Al}_2\text{O}_3 \) is being established, to be extended. There are also some results available that show other phases (i.e., Ni (Al,Cr)\(_2\)O\(_4\), Cr\(_2\)O\(_3\)) may form on \( \alpha\text{-Al}_2\text{O}_3 \) scales as the substrate alloys become depleted of aluminum. In some cases, this phase is spinel (i.e., Ni (Al,Cr)\(_2\)O\(_4\)) and is observed at the \( \alpha\text{-Al}_2\text{O}_3 \)/gas interface,\(^{18,19}\) whereas in the other cases, this phase is Cr\(_2\)O\(_3\) and is located at the \( \alpha\text{-Al}_2\text{O}_3 \)/alloy interface.\(^{20}\) This article is concerned with examining in more detail the cracking and spalling of \( \alpha\text{-Al}_2\text{O}_3 \) scales in water vapor, as well as investigating the effects of water vapor on the selective oxidation of aluminum and spinel development on \( \alpha\text{-Al}_2\text{O}_3 \) scales.

II. EXPERIMENTAL

Both isothermal and cyclic oxidation experiments were performed. Cyclic oxidation conditions were achieved by moving the specimens in and out of a furnace once every hour, 45 minutes in the hot zone at 1100 °C and 15 minutes in the cool zone at 100 °C. The experiments were performed in dry air with a dew point of \(-46 \, ^\circ\text{C} \left(P_{\text{H}_2\text{O}} = 6 \times 10^{-5} \, \text{atm}\right)\) and in air saturated with water at 46 °C \(P_{\text{H}_2\text{O}} = 0.1 \, \text{atm}\) and at 88 °C \(P_{\text{H}_2\text{O}} = 0.5 \, \text{atm}\). The air was saturated with water vapor by passing air through two consecutive water baths at the required temperature. The gas flowed through the reaction tube at 0.1 cm/s. The specimens were coupons about 1-cm square and 2-mm thick and were moved from the hot zone to the cool zone or vice versa in 250 seconds. The specimens were removed periodically from the apparatus and weight change measurements were performed along with visual examination of the specimens. Upon conclusion of the tests, the specimens were examined in detail using optical metallography, scanning electron microscopy, and X-ray diffraction techniques.

The experiments were performed on Ni-base superalloys RENÉ\(^{\ast} \) N5 and PWA1484, as well as RENÉ N5 with aluminide and platinum-modified aluminide coatings. The compositions of the superalloys are presented in Table I. In some experiments, superalloys with low sulfur concentrations were used. These alloys had the same concentration of elements as indicated in Table I, but less than 1 ppm sulfur compared to 5 to 8 ppm sulfur in the normally processed superalloys. The aluminate coatings were prepared using CVD with conditions of high temperature and low aluminum activity. The platinum was electrolytically deposited (5 to

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\(^{\ast}\)RENÉ is a trademark of General Electric Co.
7 μm) on the surface of the superalloy prior to the aluminizing process. A typical as-processed platinum aluminide coating is shown in Figure 1. In some of the experiments, to investigate the selective oxidation of aluminum, a Ni-8Cr-6Al alloy was used because this alloy had aluminum and chromium concentrations similar to the superalloys without the complications of additional elements.

III. RESULTS AND DISCUSSION

A. Effects of Water Vapor on Cracking and Spalling of α-Al₂O₃ Scales

In Figure 2, weight change vs time measurements are presented for N5 and low sulfur content N5 specimens exposed at 1100 °C in gases with different amounts of water vapor. It can be seen that the weight losses are less for the low sulfur content N5 compared to N5 specimens. It is also apparent that the amount of degradation of N5 increases as the pressure of H₂O in the gas increases. Surface micrographs of specimens exposed in this test are presented in Figure 3. It can be seen that more spalling of oxide is evident for N5 compared to low sulfur content N5 and the amount of spalled oxide increases as the water vapor pressure in the gas phase is increased, whereas the water vapor pressure had no significant effect on degradation of low sulfur N5. Scanning electron micrographs showing cross-sectional views of the exposed specimens are consistent with the previous results. An external scale containing NiO with virtually no continuous α-Al₂O₃ is evident on the N5 specimen exposed for 802 cycles at 1100 °C in a gas mixture with 0.5 atm of water vapor, (Figure 4(a)), whereas the low sulfur N5 exposed to similar conditions (Figure 4(b)) exhibits a scale of continuous α-Al₂O₃ with an overlayer of transient oxides. The transient oxides in the case of nickel-base superalloys such as N5 are generally NiO, Cr₂O₃, and Ta₂O₅, but the oxides of other elements in the alloy can also be present. With the

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Table I. Nominal Compositions of Alloys in Weight Percent

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<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Al</th>
<th>Cr</th>
<th>Ta</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Y</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>RENÉ N5</td>
<td>base</td>
<td>6.2</td>
<td>7.0</td>
<td>6.5</td>
<td>7.5</td>
<td>1.5</td>
<td>6.0</td>
<td>3.0</td>
<td>0.01</td>
<td>0.15</td>
</tr>
<tr>
<td>PWA1484</td>
<td>base</td>
<td>5.6</td>
<td>5.0</td>
<td>8.7</td>
<td>10.0</td>
<td>2.0</td>
<td>6.0</td>
<td>3.0</td>
<td>—</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni-Cr-Al</td>
<td>base</td>
<td>6.0</td>
<td>8.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
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