Moisture Induced Damage in Oxide Scales

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Introduction

Water vapor is present in most environments used in high temperature applications. The water vapor content can vary from a few vol.% for example in coal combustion environments, to as much as 100 vol.% in steam turbines. The effect of water vapor on oxide scale growth has been the focus of high temperature materials research for over a decade, revealing for example increased growth rates or more pronounced inward growing oxides in the presence of water vapor. However, the effects of water vapor and liquid water on oxide scale integrity and mechanical properties have, up to now, not been investigated in detail, even though a few reports exist that show increased alumina scale spallation on contact with liquid water [1, 2]. Also, moisture induced failure of thermal barrier coatings has been reported [3, 4]. Since high-technology materials used in high temperature applications rely on protective oxide scales, a loss of the protective oxide limits the materials life time and has to be avoided.

The aim of this study is therefore to investigate the effect of water vapor on the mechanical integrity of typical metal oxides found in high temperature environments.

Theoretical Approach

The mechanical stability of oxide scales is strongly influenced by the physical defect structure present in the scale. Consequently, the critical strain εc to cause oxide scale failure (i.e. delamination or spallation) in a mechanical loading condition will decrease with increasing defect size c. The characteristics of the critical strain can be modeled for each failure mode using the advanced Oxide Scale Failure Model [5] based on the classical theory from Griffith [6]:

\[ \varepsilon_c = \frac{\eta_1}{(1 + \nu) \sqrt{\pi c}} \]

interfacial cracking / beginning of delamination

\[ \varepsilon_c = \frac{\eta_1}{(1 + \nu) \sqrt{\pi c}} \]

through cracking

\[ c - \text{defect size}, \quad \varepsilon_c - \text{form normalizing}, \quad E - \text{scale Young's modulus}, \quad f - \text{defect geometry factor}, \quad \nu - \text{poisson ratio}, \quad K_c - \text{scale fracture toughness} \]

Experimental

Mechanical 4-Point Bending

High purity Nickel (99.99%) and Titanium (99.6%) were used as substrate materials in an attempt to form oxide scales with a minimum amount of impurities. High temperature oxidation was performed at 800°C in dry synthetic air and humid synthetic air with 10 Vol.% H2O for durations of up to 100 hours. 4-point bending with in-situ acoustic emission measurement was carried out at room temperature to examine the mechanical properties of the oxide scales formed by high temperature oxidation.

Nickel Oxide

Figure 2: SEM micrographs of high purity Ni after 50h oxidation at 800°C in dry (left) and humid (right) atmosphere, respectively.

Figure 4: Physical defect kinetics (top left) and oxide scale growth kinetics (bottom left) and “classical” scale failure diagram (right) for nickel oxide.

Figure 6: Advanced oxide scale failure diagram for nickel oxide.

Figure 7: Advanced oxide scale failure diagram for titanium oxide.

Table: Theoretical value of critical strain εc vs. d

<table>
<thead>
<tr>
<th>Material</th>
<th>Theory</th>
<th>Experiment</th>
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</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.25</td>
<td>0.15</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.30</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Summary

Nickel oxide
- Scale growth kinetics is parabolic (only little difference in kp humid / dry)
- Physical defect growth kinetics linear at 800°C, similar for dry / humid
- Clear tendencies in εc vs. c in contrast to η vs. d
- No significant effect of water vapor on critical strain

Titanium oxide
- Scale growth kinetics is parabolic (κc slightly higher in humid)
- Physical defect growth kinetics decelerating with time, faster for humid
- Clear difference between humid / dry in εc vs. c in contrast to κc vs. d
- Water vapor increases κc and εc

References