The extent of surface destabilization of ZrO$_2$ - 8 wt % Y$_2$O$_3$ ceramic disks was determined after exposure to molten salt mixtures of sodium sulfate containing up to 15 mole% sodium metavanadate (NaVO$_3$) at 1173 K. The ceramic surface was observed to transform from the cubic/tetragonal to monoclinic phase, concurrent with chemical changes in the molten salt layer in contact with the ceramic. Significant attack rates were observed in both pure sulfate and metavanadate-sulfate melts. The rate of attack was found to be quite sensitive to the mole fraction of vanadate in the molten salt solution and the partial pressure of sulfur trioxide ($1 \times 10^6$ to $1 \times 10^{-3}$ atm) in equilibrium with the salt melt. The observed parabolic rate of attack is interpreted to be caused by a reaction controlled by diffusion in the salt that penetrates into the porous layer formed by the destabilization. The parabolic rate constant in mixed sodium metavanadate - sodium sulfate melts was found to be proportional to the SO$_3$ partial pressure and the square of the metavanadate concentration. In-situ Raman spectroscopic measurements allowed simultaneous observations of the ceramic phases and salt chemistry during the attack process.

This work supported by the U.S. Dept. of Energy, Office of Basic Energy Sciences.
Table I
Exposure Environment Composition
( percent )

<table>
<thead>
<tr>
<th>Initial Gas Composition</th>
<th>Equilibrium Composition at 1173 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_2$</td>
</tr>
<tr>
<td></td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>99.985</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Table II
Parabolic Rate Constants
( $P_{SO_3} = 2.4 \times 10^{-3}$ )

<table>
<thead>
<tr>
<th>NaVO3 Concentration (mole percent)</th>
<th>Parabolic Rate Constant (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$1 \times 10^{-11}$</td>
</tr>
<tr>
<td>0.2%</td>
<td>$1 \times 10^{-11}$</td>
</tr>
<tr>
<td>1.0%</td>
<td>$1.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>2.0%</td>
<td>$5.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>3.9%</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
RAMAN EFFECT

\[ \omega_1 - \omega_5 = \omega_{\text{VIB}} \]

Figure 1.

RAMAN BACKSCATTERING CONFIGURATION

488 NM

LENS

AIR

OXIDE

METAL

Figure 2.

RAMAN ADVANTAGES

1. NON-PERTURBING
2. IN SITU
3. QUANTITATIVE CHEMICAL COMPOUND IDENTIFICATION
4. SENSITIVE TO LATTICE SYMMETRY
5. LATERAL RESOLUTION - 1 \( \mu \)m
6. DEPTH RESOLUTION - (100 \( \AA \) - 100 \( \mu \)m)
7. GAS ENVIRONMENT CHARACTERIZATION
8. SAMPLE/GAS TEMPERATURE
9. TEMPORAL RESOLUTION (ms - hs)

Figure 3.

97
Experimental Procedure

- Stabilized zirconia ceramics immersed in sulfate-vanadate melts contained in platinum crucibles.
- Temperature, sulfur dioxide and sulfur trioxide content varied.
- Post-exposure analysis by electron microscopy, electron microprobe and Raman spectroscopy.

Figure 4.

Figure 5.
ZrO$_2$ – 8 wt% Y$_2$O$_3$

Exposure: 900°C

Pure Na$_2$V$_2$O$_6$

10 min.

1 hr.

Figure 6.
Figure 7.

Figure 8.
ZrO$_2$ - 8wt% Y$_2$O$_3$
NaVO$_3$ 24hr 700°C

Figure 9.
ZrO$_2$ - 8 wt% Y$_2$O$_3$

Exposure: 900°C 24 hr.

2 mol% Na$_2$V$_2$O$_6$ in Na$_2$SO$_4$

Exposed in air

Exposed to 93% SO$_2$ 5% SO$_3$ 2% O$_2$

Figure 12.
Figure 13.

Figure 14.
Figure 15.

1173 K 1% $\text{SO}_2$ in $\text{O}_2$

24 hr

164 hr

452 hr

105
Figure 16.

ZrO$_2$ - 8 wt% Y$_2$O$_3$
2% NaVO$_3$ in Na$_2$SO$_4$
900°C

Intensity vs. Frequency Shift (cm$^{-1}$)

7 hr
16 hr
198 hr
500 hr

Figure 17.

Monoclinic Layer Thickness (µm)

$P_{SO_3}$

Vanadate Conc.
- △ 0.1%
- × 2%
- □ 1%

Figure 18.

1% SO$_2$ in O$_2$

Parabolic Rate Constant (cm$^2$/sec)

Percent NaVO$_3$ in Na$_2$SO$_4$
YTTRIUM LEACHING REACTIONS

- in sulfate melts
  \[ \text{Y}_2\text{O}_3 + 3 \text{SO}_3 \rightleftharpoons 2 \text{Y}^{3+} + 3 \text{SO}_4^{2-} \]

- in sulfate-vanadate melts
  \[ \text{Y}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightleftharpoons 2 \text{Y}^{3+} + 2 \text{VO}_4^{-3} \]

Figure 19.

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3 \]

\[ \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{O} + \text{SO}_3 \]

\[ a_{\text{Na}_2\text{O}} = \frac{K_2}{p_{\text{SO}_3}} a_{\text{Na}_2\text{SO}_4} \]

\[ 2 \text{NaVO}_3 \rightleftharpoons \text{Na}_2\text{O} + \text{V}_2\text{O}_5 \]

\[ a_{\text{V}_2\text{O}_5} = \frac{K_3}{p_{\text{SO}_3}} \left( \frac{a_{\text{NaVO}_3}}{a_{\text{Na}_2\text{O}}} \right)^2 = \frac{K_3}{K_2} \frac{p_{\text{SO}_3}}{a_{\text{Na}_2\text{SO}_4}} \]

Figure 20.
1173 K 1% SO$_2$ in O$_2$

ZrO$_2$ - 1.5 wt% MgO
96 hr

ZrO$_2$ - 8 wt% Y$_2$O$_3$
164 hr

Figure 22.
Summary

• Attack of zirconia ceramics is sensitive to sodium metavanadate concentration, and thus to vanadium impurity level in fuel.

• The attack is also sensitive to sulfur dioxide content of the environment.

• The attack follows parabolic kinetics and is proportional to the square root of the sulfur trioxide partial pressure.

Figure 23.