CERAMIC OXIDE REACTIONS WITH $V_2O_5$ AND $SO_3$

R. L. Jones and C. E. Williams
Naval Research Laboratory
Washington, DC 20375-5000

Ceramic oxides are not inert in combustion environments, but can react with, inter alia, $SO_3$ and $Na_2SO_4$ to yield low melting mixed sulfate eutectics (mp 700-800°C), and with vanadium compounds to produce vanadates, e.g., $YVO_4$, or other species.

Assuming ceramic degradation to become severe only when molten phases are generated in the surface salt (as found for metallic hot corrosion), the reactivity of ceramic oxides can be quantified by determining the $SO_3$ partial pressure necessary for molten mixed sulfate formation with $Na_2SO_4$. The critical $SO_3$ pressures measured for $Y_2O_3$, $CeO_2$, and $ZrO_2$, for example, were of the order of $<10$ Pa, $100$ Pa, and $1000$ Pa, respectively. Therefore, use of oxides such as $CeO_2$ rather than $Y_2O_3$ for stabilization of $ZrO_2$ may increase the resistance of $ZrO_2$-based ceramics to $SO_3$-$Na_2SO_4$ attack, as limited experience seems to confirm.

Vanadium pentoxide is an acidic oxide that reacts with $Na_2O$, $SO_3$, and the different ceramic oxides in a series of Lux-Flood type of acid-base displacement reactions. To elucidate the various possible vanadium compound-ceramic oxide interactions, a study was made of the reactions of a matrix involving, on the one axis, ceramic oxides of increasing acidity ($Y_2O_3 < CeO_2 < ZrO_2 < GeO_2 < Ta_2O_5$ (most acidic)), and on the other axis, vanadium compounds of increasing acidity ($Na_3VO_4 < NaVO_3 < V_2O_5$ (most acidic)). Resistance to vanadium compound reaction increased, up to $ZrO_2$, as the oxide acidity increased with, e.g., $Y_2O_3$ reacting with $NaVO_3$ and $V_2O_5$, although not $Na_3VO_4$, while $CeO_2$ reacted only with $V_2O_5$, and neither $NaVO_3$ or $Na_3VO_4$. Oxides more acidic than $ZrO_2$ displaced $V_2O_5$ (i.e., acted as a stronger acid than $V_2O_5$), giving such reactions as: $2Ta_2O_5 + 2NaVO_3 = Na_3Ta_4O_{11} + V_2O_5$. Sulfur trioxide interacts via the reaction, $2NaVO_3 + SO_3 = Na_2SO_4 + V_2O_5$, and can, for example, cause vanadation of $CeO_2$, which does not react with pure $NaVO_3$, by producing $V_2O_5$ in the melt.

Examination of $Y_2O_3$- and $CeO_2$-stabilized $ZrO_2$ sintered ceramics which were degraded in 700°C $NaVO_3$ has shown good agreement with the reactions predicted above, except that the $CeO_2$-$ZrO_2$ ceramic appears to be inexplicably degraded by $NaVO_3$. 
POTENTIAL CERAMIC COATING BENEFITS TO NAVY

IMPROVED THERMAL EFFICIENCY
CORROSION RESISTANCE
USE OF LOW QUALITY FUEL
WITHSTAND 700°C OPERATION

Figure 1.

CERAMIC REACTION WITH FUEL CONTAMINANTS

\[
\begin{align*}
\text{SO}_3 & \quad Y_2O_3 + SO_3 \rightleftharpoons Y_2O_2(SO_4) \\
& \quad Y_2O_3 + SO_3 + Na_2SO_4 \rightleftharpoons Y_2(SO_4)_3Na_2SO_4 \\
\text{V}_2\text{O}_5 & \quad Y_2O_3 + V_2O_5 \rightleftharpoons 2 YVO_4 \\
\text{V}_2\text{O}_5 + \text{SO}_3 & \quad 2 NaVO_3 \rightleftharpoons Na_2O + V_2O_5 \\
& \quad 2 NaVO_3 + SO_3 \rightleftharpoons V_2O_5 + Na_2SO_4 \\
& \quad CeO_2 + V_2O_5 \rightleftharpoons 2 CeVO_4
\end{align*}
\]

Figure 2.
CoSO₄-Na₂SO₄ PHASE DIAGRAM

Figure 3.

SULFATION OF 50 m/o ZrO₂-Na₂SO₄ AT 700 C

Figure 4.
SO$_3$ PARTIAL PRESSURE FOR MOLTEN MIXED SULFATE FORMATION AT 700°C

- Y$_2$O$_3$ < 10 Pa
- CeO$_2$ 100 Pa
- ZrO$_2$ 1000 Pa

**Figure 5.**

SODIUM VANADATE COMPOUNDS

- **Na$_2$O + 6 V$_2$O$_5$ ⇌ Na$_2$V$_{12}$O$_{31}$** vanadium bronze I
- **Na$_2$O + 3 V$_2$O$_5$ ⇌ 2 NaV$_3$O$_8$** vanadium bronze II
- **Na$_2$O + V$_2$O$_5$ ⇌ 2 NaVO$_3$** sodium metavanadate
- **2 Na$_2$O + V$_2$O$_5$ ⇌ Na$_4$V$_2$O$_7$** sodium pyrovanadate
- **3 Na$_2$O + V$_2$O$_5$ ⇌ 2 Na$_3$VO$_4$** sodium orthovanadate

**Figure 6.**
## VANADIUM-CERAMIC OXIDE REACTIONS

<table>
<thead>
<tr>
<th></th>
<th>$\text{Na}_3\text{VO}_4$</th>
<th>$\text{NaVO}_3$</th>
<th>$\text{V}_2\text{O}_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}_2\text{O}_3$</td>
<td>NR</td>
<td>YVO$_4$</td>
<td>YVO$_4$</td>
</tr>
<tr>
<td>$\text{CeO}_2$</td>
<td>NR</td>
<td>NR</td>
<td>CeVO$_4$</td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>NR</td>
<td>NR</td>
<td>ZrV$_2$O$_7$ (BUT SLOWLY)</td>
</tr>
<tr>
<td>$\text{GeO}_2$</td>
<td>Na$_4$Ge$<em>9$O$</em>{20}$</td>
<td>Na$_4$Ge$<em>9$O$</em>{20}$ (*')</td>
<td>NR</td>
</tr>
<tr>
<td>$\text{Ta}_2\text{O}_5$</td>
<td>NaTaO$_3$</td>
<td>Na$_2$Ta$<em>4$O$</em>{11}$</td>
<td>$\alpha$-TaVO$_5$</td>
</tr>
</tbody>
</table>

NR = NO REACTION

(*) AS PPT FROM H$_2$O SOL’N

Figure 7.

## INFLUENCE OF Na$_2$SO$_4$ AND SO$_3$ IN VANADIUM-CERAMIC REACTIONS

$$2 \text{NaVO}_3 + \text{SO}_3 \rightleftharpoons \text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$$

INCREASING SO$_3$ PROMOTES VANADATE FORMATION

$\text{CeO}_2 + \text{NaVO}_3 + \text{SO}_3 \rightarrow \text{CeVO}_4$

$\text{ZrO}_2 + \text{NaVO}_3 + \text{SO}_3 \rightarrow \text{NR}$

(AT LEAST UP TO 110 Pa OF SO$_3$ AT 700°C)

Figure 8.
DEGRADATION OF $Y_2O_3^2$-ZrO$_2$ BY NaVO$_3$ AT 700°C
DEGRADATION OF CeO$_2$-ZrO$_2$ BY NaVO$_3$ AT 700°C
ATTACK OF CeO$_2$-ZrO$_2$ BY NaVO$_3$ UNDER 40 Pa OF SO$_3$ AT 700°C
CONCLUSIONS

CERAMIC CORROSION ELUCIDATED

GUIDELINES LAID FOR DEVELOPMENT OF CORROSION-RESISTANT CERAMICS

EFFECTS OF CERAMIC PROCESSING STILL TO BE IDENTIFIED

Figure 12.