CERAMIC OXIDE REACTIONS WITH V₂O₅ AND SO₃

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Ceramic oxides are not inert in combustion environments, but can react with, inter alia, SO₃ and Na₂SO₄ to yield low melting mixed sulfate eutectics (mp 700-800°C), and with vanadium compounds to produce vanadates, e.g., YVO₄, 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 SO₃ partial pressure necessary for molten mixed sulfate formation with Na₂SO₄. The critical SO₃ pressures measured for Y₂O₃, CeO₂, and ZrO₂, for example, were of the order of < 10 Pa, 100 Pa, and 1000 Pa, respectively. Therefore, use of oxides such as CeO₂ rather than Y₂O₃ for stabilization of ZrO₂ may increase the resistance of ZrO₂-based ceramics to SO₃-Na₂SO₄ attack, as limited experience seems to confirm.

Vanadium pentoxide is an acidic oxide that reacts with Na₂O, SO₃, 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 (Y₂O₃ < CeO₂ < ZrO₂ < GeO₂ < Ta₂O₅ (most acidic)), and on the other axis, vanadium compounds of increasing acidity (Na₃VO₄ < NaVO₃ < V₂O₅ (most acidic)). Resistance to vanadium compound reaction increased, up to ZrO₂, as the oxide acidity increased with, e.g., Y₂O₃ reacting with NaVO₃ and V₂O₅, although not Na₃VO₄, while CeO₂ reacted only with V₂O₅, and neither NaVO₃ or Na₃VO₄. Oxides more acidic than ZrO₂ displaced V₂O₅ (i.e., acted as a stronger acid than V₂O₅), giving such reactions as: 2 Ta₂O₅ + 2 NaVO₃ = Na₃Ta₄O₁₁ + V₂O₅. Sulfur trioxide interacts via the reaction, 2 NaVO₃ + SO₃ = Na₃SO₄ + V₂O₅, and can, for example, cause vanadation of CeO₂, which does not react with pure NaVO₃, by producing V₂O₅ in the melt.

Examination of Y₂O₃- and CeO₂-stabilized ZrO₂ sintered ceramics which were degraded in 700°C NaVO₃ has shown good agreement with the reactions predicted above, except that the CeO₂-ZrO₂ ceramic appears to be inexplicably degraded by NaVO₃.
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

SO₃

Y₂O₃ + SO₃ ⇌ Y₂O₂(SO₄)
Y₂O₃ + SO₃ + Na₂SO₄ ⇌ Y₂(SO₄)₃·Na₂SO₄

V₂O₅

Y₂O₃ + V₂O₅ ⇌ 2 YVO₄

V₂O₅ + SO₃

2 NaVO₃ ⇌ Na₂O + V₂O₅
2 NaVO₃ + SO₃ ⇌ V₂O₅ + Na₂SO₄
CeO₂ + V₂O₅ ⇌ 2 CeVO₄

Figure 2.
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

\[
\begin{align*}
\text{Y}_2\text{O}_3 & \quad <10 \text{ Pa} \\
\text{CeO}_2 & \quad 100 \text{ Pa} \\
\text{ZrO}_2 & \quad 1000 \text{ Pa}
\end{align*}
\]

Figure 5.

SODIUM VANADATE COMPOUNDS

\[
\begin{align*}
\text{Na}_2\text{O} + 6 \text{V}_2\text{O}_5 & \rightleftharpoons \text{Na}_2\text{V}_{12}\text{O}_{31} \quad \text{vanadium bronze I} \\
\text{Na}_2\text{O} + 3 \text{V}_2\text{O}_5 & \rightleftharpoons 2 \text{NaV}_3\text{O}_8 \quad \text{vanadium bronze II} \\
\text{Na}_2\text{O} + \text{V}_2\text{O}_5 & \rightleftharpoons 2 \text{NaVO}_3 \quad \text{sodium metavanadate} \\
2 \text{Na}_2\text{O} + \text{V}_2\text{O}_5 & \rightleftharpoons \text{Na}_4\text{V}_2\text{O}_7 \quad \text{sodium pyrovanadate} \\
3 \text{Na}_2\text{O} + \text{V}_2\text{O}_5 & \rightleftharpoons 2 \text{Na}_3\text{VO}_4 \quad \text{sodium orthovanadate}
\end{align*}
\]

Figure 6.
VANADIUM-CERAMIC OXIDE REACTIONS

<table>
<thead>
<tr>
<th></th>
<th>Na₃VO₄</th>
<th>NaVO₃</th>
<th>V₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃</td>
<td>NR</td>
<td></td>
<td>YVO₄</td>
</tr>
<tr>
<td>CeO₂</td>
<td>NR</td>
<td>NR</td>
<td>CeVO₄</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>NR</td>
<td>NR</td>
<td>ZrV₂O₇ (BUT SLOWLY)</td>
</tr>
<tr>
<td>GeO₂</td>
<td>Na₄Ge₉O₂₀</td>
<td>Na₄Ge₉O₂₀(*)</td>
<td>NR</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>NaTaO₃</td>
<td>Na₂Ta₄O₁₁</td>
<td>α-TaVO₅</td>
</tr>
<tr>
<td>NR = NO REACTION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(*) AS PPT FROM H₂O SOL’N</td>
<td></td>
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</tbody>
</table>

Figure 7.

INFLUENCE OF Na₂SO₄ AND SO₃ IN VANADIUM-CERAMIC REACTIONS

2 NaVO₃ + SO₃ ⇌ V₂O₅ + Na₂SO₄

INCREASING SO₃ PROMOTES VANADATE FORMATION

CeO₂ + NaVO₃ + SO₃ → CeVO₄

ZrO₂ + NaVO₃ + SO₃ → NR

(AT LEAST UP TO 110 Pa OF SO₃ AT 700°C)

Figure 8.
DEGRADATION OF $Y_2O_3$-ZrO$_2$ BY NaVO$_3$ AT 700°C

Figure 9.
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

Figure 11.
CONCLUSIONS

CERAMIC CORROSION ELUCIDATED

GUIDELINES LAID FOR DEVELOPMENT OF CORROSION-RESISTANT CERAMICS

EFFECTS OF CERAMIC PROCESSING STILL TO BE IDENTIFIED

Figure 12.