NONOXIDE CERAMIC INTERACTIONS WITH URANIUM OR CARBON

C. E. Holcombe

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Y-12 Development Division

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ABSTRACT

The interaction of possible nonoxide containment materials (including boron nitride, titanium nitride, hafnium carbide, and two cerium sulfides) with uranium or carbon has been examined by thermal analysis techniques. Additionally, nonoxide-ceramic interaction with beryllia, tungsten, or yttria was investigated. Hafnium carbide is the least reactive nonoxide ceramic tested.
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SUMMARY

The relative reactivities of several nonoxide ceramics with uranium or carbon have been investigated by differential-thermal/thermal-gravimetric-analysis techniques. The data show that boron nitride reacts immediately on melting the uranium, and titanium nitride reacts with uranium above 1685 K. However, hafnium carbide and two cerium sulfides (CeS\textsubscript{x}, where \( x = 1 \) or 1.5; that is, CeS or Ce\textsubscript{2}S\textsubscript{3}) have no significant interactions with uranium to the limit of the tests (1873 K), but interact with beryllia below 1873 K. It is indicated that hafnium carbide is stable with tungsten or yttria to 2273 K; the two cerium sulfides appear to be stable with these materials, but begin to volatilize above 2100 K. Thus, for melting uranium above 1873 K, both hafnium carbide and the two cerium sulfides seem to be optimum candidates for containing molten uranium and for coatings onto graphite, with the upper-use limit of the two cerium sulfides limited to \( \sim 2100 \) K.
INTRODUCTION

This study was undertaken as an extension of previous work at the Oak Ridge Y-12 Plant(a)(b), indicating that certain nonoxide ceramics had a potential for uranium containment. Because of the usefulness of thermal-analysis data for ranking oxide crucible materials as to their stability with uranium and carbon, this study was undertaken with several binary compounds (BN, TiN, HfC, CeS, and Ce2S3). Interactions with beryllia, tungsten (which are the crucibles used for thermal analyses), or yttria (because of possible multilayer application with the carbon substrate, nonoxide interlayer, then yttria) were also determined.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.
(b) Condon, J. B. and Holcombe, C. E.; Crucible Materials to Contain Molten Uranium, Y-2084; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; September 8, 1977.
NONOXIDE CERAMIC INTERACTIONS

EXPERIMENTAL WORK

Materials

The materials selected for this study were considered either to be thermodynamically stable with uranium or to have the possibility of reacting to form a protective barrier to further reaction (as BN). The problems with using standard free-energy data to predict reactions involving uranium, carbon, and the furnace atmosphere and pressure, leading to complex oxides, suboxides, intermetallic compounds, and solid solutions, have been mentioned before. (b)

Characterization of the starting materials used in this study is given in Table 1 and is based on spark-source mass spectrographic (MS) analyses for elemental purity, Coulter Counter or Micromerograph for particle-size distribution, and standard X-ray diffraction (XRD) analyses (Debye-Scherrer camera, CuKα radiation). The uranium was > 99.96% pure, by MS; and the graphite, > 99.52% pure (MS) with a 6.9 µm mean particle diameter, by Micromerograph.

Differential Thermal Analyses

Differential thermal analyses (DTA) were conducted [using a Mettler Thermoanalyzer (Model TA1)], with a high-temperature (1873 K) furnace, using a flowing (4.5 l/hr) argon atmosphere, a heating rate of 6 k/min, and a Pt/Pt-10% Rh thermocouple. All materials were tested alone in beryllia crucibles (blanks) to determine any reaction between the materials and crucible. When a material was shown to interact with beryllia, a new beryllia crucible was used for subsequent uranium/nonoxide-ceramic tests. Uranium interactions with nonoxide ceramics had insignificant weight losses. Thus, in this case, the DTA rather than thermal gravimetric analyses (TGA), which were simultaneously measured with DTA, provided the best interaction data. The temperatures of interaction were determined for both the initial baseline shift of the DTA curve (T₁, or reaction initiation temperature), and by the intersection of tangent lines (Tₑ, or extrapolated reaction temperature). The initiation temperature, then, represents a more conservative upper limit to avoid interaction.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Elemental Purity(1)</th>
<th>Mean Particle Diameter(2)</th>
<th>Initial X-Ray Diffraction Phase Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>97.02(3)</td>
<td>8.0 b</td>
<td>BN</td>
</tr>
<tr>
<td>TiN</td>
<td>99.79</td>
<td>15.1 a</td>
<td>TiN</td>
</tr>
<tr>
<td>HfC</td>
<td>98.25(3)</td>
<td>9.8 a</td>
<td>HfC</td>
</tr>
<tr>
<td>CeS</td>
<td>99.98</td>
<td>11.2 b</td>
<td>CeS</td>
</tr>
<tr>
<td>Ce₂S₃</td>
<td>99.97</td>
<td>3.8 b</td>
<td>Ce₂S₃ or Ce₂O₂S</td>
</tr>
</tbody>
</table>

(1) By spark-source mass spectrographic analyses.
(2) By: a - Coulter Counter, or b - Micromerograph.
(3) Major impurities (> 0.1%, approximate values) for materials < 99% pure are as follows: for BN: Si - 2.65% and S - 0.1%; for HfC: Ti - 0.45%, Fe - 0.4%, Ni - 0.6%, and Zr - 0.2%.
Thermal Gravimetric Analyses

Thermal gravimetric analyses (TGA) of nonoxide ceramics with graphite or yttria were conducted in tungsten crucibles under vacuum (< 1.33 x 10⁻³ Pa) to 2273 K, using the Mettler Thermoanalyzer (Model TA1) with an ultra-high-temperature (2773 K) furnace at a heating rate of 10 K/min and a W/W-26% Re thermocouple. An analysis containing a blank with each material in the tungsten crucible was performed to determine any effect on the mixtures of graphite or yttria with nonoxide ceramic. The materials were mixed with graphite or yttria in a molar ratio of 1:1 except when a particular product was anticipated (Ce₂C₃, YB₂, and YN). The temperatures of interaction were determined by three techniques: (1) rapid change in slope of the sensitive-weight-loss curve, Tₛ; (2) intersection of the tangent lines, Tₒ, and (3) point where a 3% weight loss after 1273 K occurred, T₃%.

RESULTS AND DISCUSSION

Table 2 summarizes the nonoxide-ceramic interactions with uranium or beryllia. The boron nitride sample reacted immediately when the uranium melted, yielding two uranium compounds (UN and UB₂), as well as reacting with beryllia at about 1600 K. The titanium nitride sample reacted immediately when the uranium melted, yielding two uranium compounds (UN and UB₂), as well as reacting with beryllia above 1685 K. It is interesting that the previous work at 1673 K showed very little reaction at this temperature, which was about 12 K below the point of significant interaction. The three materials (HfC, CrS, and Ce₂S₃) exhibit the same interaction behavior with beryllia and with uranium, indicating that the observed points result from the beryllia container; also, the XRD analyses show that no uranium compounds have formed. Thus, hafnium carbide and the two cerium sulfides have no significant interactions with uranium below 1873 K, the limiting temperature of this apparatus. The material from blank runs with beryllia for the hafnium and cerium compounds appeared to have sintered, yet no additional phases were detected by XRD. The interaction of these materials with beryllia may be only a small solubility of beryllia, causing only subtle changes by XRD.
Table 3
INTERACTIONS STUDIED BY THERMAL GRAVIMETRIC ANALYSIS

<table>
<thead>
<tr>
<th>Materials Tested</th>
<th>With Carbon</th>
<th>With Yttria</th>
<th>With Tungsten (Blank)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-Ray Diffraction Analysis of Products</td>
<td>X-Ray Diffraction Analysis of Products</td>
<td>X-Ray Diffraction Analysis of Products</td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td></td>
<td>T(1)</td>
<td>T(2)</td>
<td>T(3)</td>
</tr>
<tr>
<td></td>
<td>T(1)</td>
<td>T(2)</td>
<td>T(3)</td>
</tr>
<tr>
<td></td>
<td>T(1)</td>
<td>T(2)</td>
<td>T(3)</td>
</tr>
<tr>
<td>BN</td>
<td>1:1</td>
<td>1455 (6)</td>
<td>2110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>TiN</td>
<td>1:2</td>
<td>1460 (6)</td>
<td>1755</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>HfC</td>
<td>1:2.5</td>
<td>1635 (6)</td>
<td>2125</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>GeS</td>
<td>1:6</td>
<td>1450 (6)</td>
<td>2145</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>Ce2S</td>
<td>1:2</td>
<td>1635 (6)</td>
<td>2125</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Ce2S</td>
<td>1:2</td>
<td>1635 (6)</td>
<td>2125</td>
</tr>
<tr>
<td>HfC</td>
<td>1:2</td>
<td>1635 (6)</td>
<td>2125</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
<td></td>
</tr>
</tbody>
</table>

(1) Interaction temperatures are rounded to the nearest 5 K.
(2) Reaction initiation temperature, as determined by a rapid change in the slope of the sensitive-weight-loss curve.
(3) Extrapolated reaction temperature, as determined by the intersection of the tangent lines—one to the base curve and one to the point on the curve where a 10% weight loss (based on the initial weight) after 1273 K occurred. Where inflection points occurred in the weight-loss curve, a line was used that was parallel to the region before the inflection point instead of the tangent.
(4) Reaction temperature at which a 3% weight loss occurred (based on the initial weight) after 1273 K.
(5) Ma - major; I - intermediate; Mi - minor.
(6) Less than 10% weight loss.
(7) Less than 3% weight loss.
(8) Probably a cerium/yttrium solid solution with the formula R292s, where R = Ce or Y.
(9) Discontinued at 2243 K.
Table 3 summarizes the nonoxide-ceramic interactions with graphite, yttria, or tungsten. The boron nitride sample was stable with carbon or tungsten, with significant weight losses resulting from volatilization above 1900 K. Boron nitride, however, reacts with yttria to yield yttrium boride by 2130 K. The titanium nitride sample was stable with yttria and tungsten, but reacted with carbon by 1755 K, yielding titanium carbide. The hafnium carbide sample did not react with yttria or tungsten to 2273 K—the maximum temperature tested.

There was little or no significant interaction of the cerium sulfides with carbon or tungsten. Volatilization appears to become significant above 2100 K, accounting for the weight losses above that temperature. The cerium sulfides react with yttria, forming an oxysulfide (\(R_2O_2S\), where \(R = Ce\) or \(Y\)) above ~ 1500 K. The actual interaction temperatures are not certain since little weight losses would be expected in forming this compound.

CONCLUSIONS

These data indicate that boron nitride could only be used if the resulting yttrium boride and uranium nitride form an adherent, protective film. This result may be the case, since it causes extensive wetting (as illustrated previously\(^{(b)}\)), yet leads to relatively low pickups of boron and nitrogen. It appears that titanium nitride could be used with little interaction with uranium below 1685 K (since both uranium and carbon reactions would be minimal). If the carbon reaction initiates, the resulting titanium carbide could be adherent to graphite crucibles and the evolved nitrogen gas could form a protective uranium nitride barrier at the uranium/titanium nitride interface.

Hafnium carbide appears to be the most stable material for higher-temperature (> 1873 K) uranium containment as it can be used with uranium, yttria, tungsten, or carbon. The two cerium sulfide samples are also stable with uranium, tungsten, or carbon, and probably can be used until volatilization becomes a problem (~ 2100 K). Previously,\(^{(b)}\) a uranium sample was melted in cerium monosulfide at 2175 K with relatively little contamination of the uranium. There is also some evidence that cerium monosulfide is wetting while cerium sesquisulfide may be nonwetting, but these observations should be further substantiated.
ACKNOWLEDGEMENTS

The author extends appreciation to L. M. Steckel and W. M. Swartout of the Y-12 Plant Laboratory for obtaining the thermal analysis data.
APPENDIX

THERMAL-ANALYSIS CURVES

Values of the intersecting tangent lines ($T_e$) are shown in boxes. For all DTA responses (Figures A-1 through A-5), distinct thermal effects are designated in the graphs (either □ or ■); for TGA responses (Figures A-6 through A-10), initial weights of materials tested are also included.

![Figure A-1. DIFFERENTIAL-THERMAL-ANALYSIS CURVES FOR BORON NITRIDE.](image1)

![Figure A-2. DIFFERENTIAL-THERMAL-ANALYSIS CURVES FOR TITANIUM NITRIDE.](image2)
Figure A-3. DIFFERENTIAL-THERMAL-ANALYSIS CURVES FOR HAFNIUM CARBIDE.

Figure A-4. DIFFERENTIAL-THERMAL-ANALYSIS CURVES FOR CERIUM MONOSULFIDE.

Figure A-5. DIFFERENTIAL-THERMAL-ANALYSIS CURVES FOR CERIUM SESQUISULFIDE.
Figure A-10. THERMAL-GRAVIMETRIC ANALYSIS CURVES FOR CERIUM SESQUISULFIDE.
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Townsend, A. B.
White, J. D.
Williams, R. D.
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