METAL-ELEMENT COMPOUNDS OF TITANIUM, ZIRCONIUM, AND HAFNIUM AS PYROTECHNIC FUELS

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ABSTRACT

Conventional high-energy pyrotechnic fuels are typically metals, metalloids, or alloys. The use of inorganic compounds including ceramic materials in this role has been far less common. Following the development of boron carbide-based pyrotechnics in our laboratories, we have started to explore the pyrotechnic properties of other inorganic compounds, particularly those of titanium, zirconium, and hafnium. The transition metals of group 4 are well known as potent pyrotechnic fuels. However, metal powders are susceptible to aging and pyrotechnic compositions containing them can be sensitive to unintended ignition by electrostatic discharge. The use of the corresponding metal-element compounds may ameliorate these problems. Commercially available group 4 compounds containing hydrogen, boron, carbon, nitrogen, silicon, and phosphorus were obtained for an initial survey. The as-received materials were characterized by XRD, XRF, and SEM. Binary compositions containing these fuels and KNO₃ or Bi₂O₃ were prepared and tested. The experimental results were compared with the output from FactSage thermochemical software. Diverse observed and predicted behavior suggests that these compounds may be useful for a variety of pyrotechnic applications.

1. INTRODUCTION

The recent use of boron carbide in smoke, delay, and illuminant compositions clearly demonstrates the potential of ceramic materials as advanced pyrotechnic fuels [1-3]. As a natural extension of this work, we have since started to explore the pyrotechnic properties of metal-element compounds containing group 4 metals. The group 4 metals—titanium, zirconium, and hafnium—are potent pyrotechnic fuels. However, the metals themselves are often pyrophoric as fine powders [4,5] and pyrotechnic compositions containing them can be extremely sensitive to unintended ignition from electrostatic discharge [6]. Non-oxide group 4 ceramics (borides, carbides, nitrides, silicides) and related covalent network solids (hydrides, phosphides) allow access to the group 4 elements indirectly. Many of these materials are available commercially as fine powders. The purpose of this initial investigation was to survey their characteristics and reactivity with two common pyrotechnic oxidizers, KNO₃ and Bi₂O₃.

2. EXPERIMENTAL SECTION

2.1. Materials

Potassium nitrate (MIL-P-156B, hammer milled, approximately 15 μm) was obtained from Hummel Croton and contained 0.2 wt% fumed silica, Cabot CAB-O-SIL M-5, as an anticaking agent. Bismuth oxide (Bi₂O₃, approximately 10 μm) was obtained from Alfa Aesar. Group 4 metal-element compounds were obtained from Atlantic Equipment Engineers (AEE), Alfa Aesar, and American Elements. These were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM).

2.2. Material Analyses

XRD was carried out in a Rigaku Ultima III diffractometer with CuKα radiation (1.54 Å). A step size of 0.02 degrees and a scan rate of 0.25 deg/min were used. The patterns were analyzed with JADE 7 software (Materials Data Inc., Livermore CA).
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<td>Conventional high-energy pyrotechnic fuels are typically metals, metalloids, or alloys. The use of inorganic compounds including ceramic materials in this role has been far less common. Following the development of boron carbide-based pyrotechnics in our laboratories, we have started to explore the pyrotechnic properties of other inorganic compounds, particularly those of titanium, zirconium, and hafnium. The transition metals of group 4 are well known as potent pyrotechnic fuels. However, metal powders are susceptible to aging and pyrotechnic compositions containing them can be sensitive to unintended ignition by electrostatic discharge. The use of the corresponding metal-element compounds may ameliorate these problems. Commercially available group 4 compounds containing hydrogen, boron, carbon, nitrogen, silicon, and phosphorus were obtained for an initial survey. The as-received materials were characterized by XRD, XRF, and SEM. Binary compositions containing these fuels and KNO3 or Bi2O3 were prepared and tested. The experimental results were compared with the output from FactSage thermochemical software. Diverse observed and predicted behavior suggests that these compounds may be useful for a variety of pyrotechnic applications.</td>
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Semi-quantitative chemical composition analysis was carried out in a Rigaku ZSX Primus II wavelength dispersive XRF spectrometer. The spectrometer contained a 4 kW Rh anode and the detector system used a scintillation counter for detecting heavy elements and a flow proportional counter for detecting light elements. The samples were tested in a vacuum and the data were analyzed using SQX software that can correct for matrix effects, overlapping lines, and secondary excitation effects by photoelectrons. Increased accuracy was achieved using built-in matching library and perfect scan analysis programs.

SEM was performed with a Zeiss Supra 40VP variable pressure field emission scanning electron microscope. Superb resolution and image quality at low operating voltages allows examination of non-conducting samples without any conductive coating.

2.3. Experimental Methods

Binary mixtures of the fuels and KNO₃ or Bi₂O₃ were prepared by combining the components in small conductive containers and mixing with a Scientific Industries Vortex Genie vibrating shaker. Each composition was mixed for 3 min. Two grams of each mixture was placed in an unconsolidated pile on a steel cylinder. The point of a nichrome wire was placed in the center of each pile. For each test, a digital video recording was used to capture the resulting qualitative behavior as the nichrome wire was electrically heated.

2.4. Computational Methods

Thermodynamic calculations were performed with FactSage 6.4 (Thermfact/CRCT and GTT-Technologies). The particular calculations presented in this paper made use of the FactPS and FToxid databases. The analyses were conducted in adiabatic mode (ΔH = 0). The results consist of predicted adiabatic reaction temperatures and the thermodynamic products at those temperatures.

3. RESULTS

The results of the experimental ignition tests must be evaluated in the context of the material properties (Table 1). XRD was used to determine phase purity or to detect the presence of other phases. With only two exceptions, the compounds were phase pure or nearly so, containing small amounts of crystalline impurities. Titanium phosphide, sold as TiP, contained a substantial amount of Ti₅P₃. Zirconium silicide (ZrSi₂) contained a large amount of Si, along with ZrSiO₄ and ZrO₂.

Elemental compositions were determined semi-quantitatively by XRF. Common elemental impurities included Fe and Cr. In some cases, these may have been introduced through milling by the manufacturer. The zirconium compounds contained small amounts of Ti and/or Hf. The hafnium compounds all contained small amounts of Zr. Importantly, these impurities were not necessarily present as elemental materials and were most likely contained within compounds that were not detected by XRD or were not crystalline.

SEM was used to assess approximate particle size and qualitative sample characteristics. Many of the materials appeared to have been milled, as evidenced by sharp jagged edges and numerous fines. Some (ZrC, HfB₂, HfC) were clearly present as they had crystallized and did not appear to have been milled to any significant degree. Others (TiB₂, TiC) appeared to have been milled for a short time. Several examples are presented in Figures 1a-d.

Balanced stoichiometries for simple binary combustion reactions may be calculated if certain products are assumed. Tables 2a-d show the results for such assumed reactions. In these tables, the group 4 metals are assumed to form the corresponding dioxides. Other elements are assumed to form simple oxides. Nitrogen from the nitrides and KNO₃ is assumed to form N₂, while the bismuth in Bi₂O₃ is assumed to form elemental Bi.
For each binary system, FactSage was used to determine the stoichiometry with the highest predicted adiabatic temperature ($T_{ad}$). This was accomplished by scanning each combination in 1 wt% intervals. Tables 3a-d show the peak $T_{ad}$ values, the corresponding stoichiometries, and the major predicted products (at the adiabatic temperatures). Some compounds (Ti$_5$Si$_3$, TiP, HfSi$_2$) were not in the FactSage databases, so systems containing them could not be modeled.

Tables 4a-d show the results of experimental ignition tests. In these experiments, the stoichiometries obtained from FactSage (Tables 3a-d) were used where available. For combinations containing Ti$_5$Si$_3$, TiP, and HfSi$_2$, the stoichiometries from Tables 2a-d were used.

### Table 1. Material Properties

<table>
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<tr>
<th>Compound</th>
<th>Vendor</th>
<th>XRD Analysis</th>
<th>XRF Impurities (0.1-2 wt%)</th>
<th>SEM Particle Size (μm)</th>
<th>SEM Apparent Characteristics</th>
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<tr>
<td>TiH$_2$</td>
<td>Alfa Aesar</td>
<td>phase pure (TiH$_{1.95}$)</td>
<td>-</td>
<td>fines $&lt; 2$ intermediate 2-8</td>
<td>milled</td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>AEE</td>
<td>phase pure</td>
<td>-</td>
<td>mostly 1-7</td>
<td>minimally processed</td>
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<tr>
<td>TiC</td>
<td>Alfa Aesar</td>
<td>phase pure (TiC$_{0.9}$)</td>
<td>Fe, Cr, V</td>
<td>fines $&lt; 1$ intermediate 2-8</td>
<td>minimally processed</td>
</tr>
<tr>
<td>TiN</td>
<td>AEE</td>
<td>phase pure</td>
<td>Fe</td>
<td>fines $&lt; 1$ intermediate 2-8</td>
<td>milled</td>
</tr>
<tr>
<td>TiSi$_2$</td>
<td>AEE</td>
<td>trace TiSi, trace SiO$_2$</td>
<td>Fe, Cr, Al</td>
<td>fines $&lt; 2$ int. 5-20, coarse 50-100</td>
<td>milled</td>
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<tr>
<td>Ti$_5$Si$_3$</td>
<td>Alfa Aesar</td>
<td>phase pure</td>
<td>Fe, Cr</td>
<td>fines $&lt; 2$ int. 5-10, coarse 20-40</td>
<td>milled</td>
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<tr>
<td>TiP</td>
<td>American Elements</td>
<td>TiP, Ti$_2$P$_3$</td>
<td>Si, Al, Fe</td>
<td>fines $&lt; 2$ intermediate 5-15</td>
<td>milled</td>
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<tr>
<td>ZrB$_2$</td>
<td>AEE</td>
<td>phase pure</td>
<td>Ti, Fe, Ca</td>
<td>fines $&lt; 2$ intermediate 5-20</td>
<td>milled</td>
</tr>
<tr>
<td>ZrC</td>
<td>AEE</td>
<td>phase pure</td>
<td>Fe, Ti, Cr</td>
<td>fines $&lt; 3$ intermediate 10-30</td>
<td>as crystallized</td>
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<tr>
<td>ZrN</td>
<td>AEE</td>
<td>trace Zr$_3$O</td>
<td>Hf, Ti, Fe, Er, Cr</td>
<td>fines $&lt; 1$ intermediate 5-25</td>
<td>milled</td>
</tr>
<tr>
<td>ZrSi$_2$</td>
<td>AEE</td>
<td>Si, ZrSi$_2$, ZrSiO$_4$, ZrO$_2$</td>
<td>Ti, Hf, Fe, Al, Cr</td>
<td>fines $&lt; 1$ int. 2-10, coarse 30-60</td>
<td>milled</td>
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<tr>
<td>HfB$_2$</td>
<td>AEE</td>
<td>phase pure</td>
<td>Zr</td>
<td>fines 1-2 intermediate 5-10</td>
<td>as crystallized</td>
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<tr>
<td>HfC</td>
<td>AEE</td>
<td>phase pure</td>
<td>Zr</td>
<td>$&lt; 3$</td>
<td>as crystallized</td>
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<tr>
<td>HfSi$_2$</td>
<td>AEE</td>
<td>trace HfO$_2$</td>
<td>Fe, Zr, Cr</td>
<td>fines $&lt; 1$ intermediate 2-25</td>
<td>milled</td>
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Table 2a. Estimated Combustion Stoichiometry – Titanium Compounds, KNO₃

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Equation</th>
<th>Fuel (wt%)</th>
<th>Oxidizer (wt%)</th>
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<tr>
<td>5 TiH₂ + 6 KNO₃ → 5 TiO₂ + 5 H₂O + 3 K₂O + 3 N₂</td>
<td>29</td>
<td>71</td>
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<tr>
<td>TiB₂ + 2 KNO₃ → TiO₂ + BaO + K₂O + N₂</td>
<td>26</td>
<td>74</td>
<td></td>
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<tr>
<td>5 TiC + 8 KNO₃ → 5 TiO₂ + 5 CO₂ + 4 K₂O + 4 N₂</td>
<td>27</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>10 TiN + 8 KNO₃ → 10 TiO₂ + 9 N₂ + 4 K₂O</td>
<td>43</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>5 TiSi₂ + 12 KNO₃ → 5 TiO₂ + 10 SiO₂ + 6 K₂O + 6 N₂</td>
<td>30</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>5 TiSi₃ + 32 KNO₃ → 25 TiO₂ + 15 SiO₂ + 16 K₂O + 16 N₂</td>
<td>33</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>10 TiP + 18 KNO₃ → 10 TiO₂ + 5 P₂O₅ + 9 K₂O + 9 N₂</td>
<td>30</td>
<td>70</td>
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Table 3a. FactSage Calculations – Titanium Compounds, KNO₃

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Tad (°C)</th>
<th>Fuel / KNO₃ (wt% ratio)</th>
<th>Major Products (phase, wt%)</th>
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<tr>
<td>TiH₂</td>
<td>2495</td>
<td>41 / 59</td>
<td>TiO₂ (s, 59.9), K (g, 19.9), N₂ (g, 8.2), H₂O (g, 5.2), KOH (g, 4.0)</td>
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<tr>
<td>TiB₂</td>
<td>2868</td>
<td>26 / 74</td>
<td>TiO₂ (l, 16.3), TiO₃ (l, 8.7), KBO₂ (g, 56.0), N₂ (g, 10.1), TiO (g, 3.5)</td>
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<tr>
<td>TiC</td>
<td>2185</td>
<td>30 / 70</td>
<td>K₂Ti₃O₇ (s, 40.6), TiO₂ (l, 6.0), K (g, 21.1), CO₂ (g, 18.5), N₂ (g, 9.6), CO (g, 2.3)</td>
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<tr>
<td>TiN</td>
<td>2176</td>
<td>45 / 55</td>
<td>K₂Ti₃O₇ (s, 60.8), TiO₂ (l, 7.3), N₂ (g, 17.7), K (g, 12.7)</td>
</tr>
<tr>
<td>TiSi₂</td>
<td>2733</td>
<td>33 / 67</td>
<td>K₂Si₃O₇ (l, 30.6), TiO₂ (l, 23.9), K (g, 18.2), SiO (g, 10.4), N₂ (g, 9.0), O₂ (g, 2.6)</td>
</tr>
<tr>
<td>TiSi₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiP</td>
<td>-</td>
<td>-</td>
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Table 4a. Experimental Results – Titanium Compounds, KNO₃

<table>
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<tr>
<th>(a) Mixture (b) wt% Ratio</th>
<th>Ignition</th>
<th>Self-Sustained Combustion</th>
<th>Amount Consumed</th>
<th>(a) Type (b) Duration (s)</th>
<th>Flame</th>
<th>(a) Sparks (b) Smoke (c) Slag</th>
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<td>(a) TiH₂ / KNO₃ (b) 41 / 59</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flash (b) 0.3</td>
<td>large, white with violet tinge</td>
<td>(a) some, white-yellow (b) obscured by flash (c) none</td>
</tr>
<tr>
<td>(a) TiB₂ / KNO₃ (b) 26 / 74</td>
<td>yes</td>
<td>yes</td>
<td>part</td>
<td>(a) sparkler (b) 6</td>
<td>small, white with green tinge</td>
<td>(a) lots, yellow (b) white (c) some</td>
</tr>
<tr>
<td>(a) TiC / KNO₃ (b) 30 / 70</td>
<td>yes</td>
<td>no</td>
<td>part</td>
<td>(a) sparkler (b) 2</td>
<td>small, white with violet tinge</td>
<td>(a) lots, yellow (b) some, white (c) some</td>
</tr>
<tr>
<td>(a) TiN / KNO₃ (b) 45 / 55</td>
<td>no</td>
<td>no</td>
<td>part heated</td>
<td>(a) N/A (b) N/A</td>
<td>N/A</td>
<td>(a) N/A (b) fumes on heating (c) some, where heated</td>
</tr>
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<td>(a) TiSi₂ / KNO₃ (b) 33 / 67</td>
<td>yes</td>
<td>yes</td>
<td>part</td>
<td>(a) incandescent slag pile (b) 5</td>
<td>none</td>
<td>(a) none (b) some, white (c) lots</td>
</tr>
<tr>
<td>(a) TiSi₃ / KNO₃ (b) 33 / 67</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) sparkler (b) 2</td>
<td>small, white</td>
<td>(a) lots, white-yellow (b) white (c) some</td>
</tr>
<tr>
<td>(a) TiP / KNO₃ (b) 30 / 70</td>
<td>yes</td>
<td>no</td>
<td>part</td>
<td>(a) intermittent flash/spark (b) N/A</td>
<td>small, white</td>
<td>(a) some, white (b) white (c) some</td>
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### Table 2b. Estimated Combustion Stoichiometry – Zirconium and Hafnium Compounds, KNO₃

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<th>Equation</th>
<th>Fuel (wt%)</th>
<th>Oxidizer (wt%)</th>
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<tr>
<td>ZrB₂ + 2 KNO₃ → ZrO₂ + B₂O₃ + K₂O + N₂</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>5 ZrC + 8 KNO₃ → 5 ZrO₂ + 5 CO₂ + 4 K₂O + 4 N₂</td>
<td>39</td>
<td>61</td>
</tr>
<tr>
<td>10 ZrN + 8 KNO₃ → 10 ZrO₂ + 9 N₂ + 4 K₂O</td>
<td>57</td>
<td>43</td>
</tr>
<tr>
<td>5 ZrSi₂ + 12 KNO₃ → 5 ZrO₂ + 10 SiO₂ + 6 K₂O + 6 N₂</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>HfB₂ + 2 KNO₃ → HfO₂ + B₂O₃ + K₂O + N₂</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>5 HfC + 8 KNO₃ → 5 HfO₂ + 5 CO₂ + 4 K₂O + 4 N₂</td>
<td>54</td>
<td>46</td>
</tr>
<tr>
<td>5 HfSi₂ + 12 KNO₃ → 5 HfO₂ + 10 SiO₂ + 6 K₂O + 6 N₂</td>
<td>49</td>
<td>51</td>
</tr>
</tbody>
</table>

### Table 3b. FactSage Calculations – Zirconium and Hafnium Compounds, KNO₃

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Tₐ (°C)</th>
<th>Fuel / KNO₃ (wt% ratio)</th>
<th>Major Products (phase, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB₂</td>
<td>3099</td>
<td>36 / 64</td>
<td>ZrO₂ (l, 38.9), KBO₂ (g, 43.8), N₂ (g, 8.8), K (g, 3.8)</td>
</tr>
<tr>
<td>ZrC</td>
<td>2678</td>
<td>49 / 51</td>
<td>ZrO₂ (s, 51.8), ZrO₂ (l, 6.7), K (g, 19.6), CO (g, 11.3), N₂ (g, 7.0), CO₂ (g, 3.2)</td>
</tr>
<tr>
<td>ZrN</td>
<td>2678</td>
<td>61 / 39</td>
<td>ZrO₂ (s, 57.1), ZrO₂ (l, 14.1), K (g, 15.1), N₂ (g, 13.5)</td>
</tr>
<tr>
<td>ZrSi₂</td>
<td>2754</td>
<td>41 / 59</td>
<td>ZrO₂ (l, 34.3), K₂SiO₃ (l, 23.8), K (g, 16.7), SiO (g, 11.2), N₂ (g, 7.9), O₂ (g, 3.0)</td>
</tr>
<tr>
<td>HfB₂</td>
<td>3074</td>
<td>50 / 50</td>
<td>HfO₂ (l, 52.6), KBO₂ (g, 34.6), N₂ (g, 6.8), K (g, 2.8)</td>
</tr>
<tr>
<td>HfC</td>
<td>2557</td>
<td>65 / 35</td>
<td>HfO₂ (s, 71.8), K (g, 13.5), CO (g, 9.2), N₂ (g, 4.8)</td>
</tr>
<tr>
<td>HfSi₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 4b. Experimental Results – Zirconium and Hafnium Compounds, KNO₃

<table>
<thead>
<tr>
<th>(a) Mixture (b) wt% Ratio</th>
<th>Ignition</th>
<th>Self-Sustained Combustion</th>
<th>Amount Consumed</th>
<th>(a) Type (b) Duration (s)</th>
<th>Flame</th>
<th>(a) Sparks (b) Smoke (c) Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ZrB₂ / KNO₃ (b) 36 / 64</td>
<td>yes</td>
<td>yes</td>
<td>part</td>
<td>(a) pulsating flash/flame (b) 4</td>
<td>moderate, green</td>
<td>(a) none (b) white (c) moderate</td>
</tr>
<tr>
<td>(a) ZrC / KNO₃ (b) 49 / 51</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 1.7</td>
<td>moderate, white with violet tinge</td>
<td>(a) minimal, yellow (b) white (c) crusty white slag</td>
</tr>
<tr>
<td>(a) ZrN / KNO₃ (b) 61 / 39</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 1.3</td>
<td>moderate, yellow</td>
<td>(a) some, yellow (b) white (c) crusty white slag</td>
</tr>
<tr>
<td>(a) ZrSi₂ / KNO₃ (b) 41 / 59</td>
<td>no</td>
<td>no</td>
<td>part heated</td>
<td>(a) N/A (b) N/A</td>
<td>N/A</td>
<td>(a) N/A (b) fumes on heating (c) some, where heated</td>
</tr>
<tr>
<td>(a) HfB₂ / KNO₃ (b) 50 / 50</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 1.6</td>
<td>large, green</td>
<td>(a) on ignition, white (b) white (c) almost none</td>
</tr>
<tr>
<td>(a) HfC / KNO₃ (b) 65 / 35</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) photoflash (b) &lt; 0.1</td>
<td>large, white with violet tinge</td>
<td>(a) some, yellow (b) obscured by flash (c) none</td>
</tr>
<tr>
<td>(a) HfSi₂ / KNO₃ (b) 49 / 51</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) sparkler (b) 5</td>
<td>small, white</td>
<td>(a) lots, white (b) white (c) lots</td>
</tr>
</tbody>
</table>
### Table 2c. Estimated Combustion Stoichiometry – Titanium Compounds, Bi₂O₃

<table>
<thead>
<tr>
<th>Equation</th>
<th>Fuel (wt%)</th>
<th>Oxidizer (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiH₂ + Bi₂O₃ → TiO₂ + H₂O + 2 Bi</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>3 TiB₂ + 5 Bi₂O₃ → 3 TiO₂ + 3 Bi₂O₃ + 10 Bi</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>3 TiC + 4 Bi₂O₃ → 3 TiO₂ + 3 CO₂ + 8 Bi</td>
<td>9</td>
<td>91</td>
</tr>
<tr>
<td>6 TiN + 4 Bi₂O₃ → 6 TiO₂ + 3 N₂ + 8 Bi</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>TiSi₂ + 2 Bi₂O₃ → TiO₂ + 2 SiO₂ + 4 Bi</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>3 TiSis + 16 Bi₂O₃ → 15 TiO₂ + 9 SiO₂ + 32 Bi</td>
<td>12</td>
<td>88</td>
</tr>
<tr>
<td>2 TiP + 3 Bi₂O₃ → 2 TiO₂ + P₂O₅ + 6 Bi</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

### Table 3c. FactSage Calculations – Titanium Compounds, Bi₂O₃

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Ta (°C)</th>
<th>Fuel / Bi₂O₃ (wt% ratio)</th>
<th>Major Products (phase, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiH₂</td>
<td>1531</td>
<td>14 / 86</td>
<td>TiO₂₃ (s, 19.0), Ti₃O₅ (s, 2.8), Bi₂ (g, 44.7), Bi (g, 32.5)</td>
</tr>
<tr>
<td>TiB₂</td>
<td>1618</td>
<td>9 / 91</td>
<td>Ti₃O₅ (s, 9.4), Bi₂O₃ (l, 8.4), Bi₂ (g, 48.3), Bi (g, 33.4)</td>
</tr>
<tr>
<td>TiC</td>
<td>1402</td>
<td>9 / 91</td>
<td>TiO₂ (s, 12.0), Bi (l, 60.7), Bi₂ (g, 14.1), Bi (g, 6.8), CO₂ (g, 5.9)</td>
</tr>
<tr>
<td>TiN</td>
<td>1375</td>
<td>17 / 83</td>
<td>Ti₂O₇ (s, 19.5), Ti₃O₁₉ (s, 2.2), Bi (l, 60.1), Bi₂ (g, 9.8), Bi (g, 4.6), N₂ (g, 3.8)</td>
</tr>
<tr>
<td>TiSis</td>
<td>1994</td>
<td>10 / 90</td>
<td>SiO₂ (l, 11.5), TiO₂ (l, 7.7), Bi (g, 64.3), Bi₂ (g, 15.8)</td>
</tr>
<tr>
<td>TiP</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 4c. Experimental Results – Titanium Compounds, Bi₂O₃

<table>
<thead>
<tr>
<th>(a) Mixture (b) wt% Ratio</th>
<th>Ignition</th>
<th>Self-Sustained Combustion</th>
<th>Amount Consumed</th>
<th>(a) Type (b) Duration (s)</th>
<th>Flame</th>
<th>(a) Sparks (b) Smoke (c) Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) TiH₂ / Bi₂O₃ (b) 14 / 86</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) burst (b) 0.2</td>
<td>large, yellow-orange</td>
<td>(a) white, branching (b) lots, yellow (c) none</td>
</tr>
<tr>
<td>(a) TiB₂ / Bi₂O₃ (b) 9 / 91</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) burst (b) 0.2</td>
<td>large, yellow-orange</td>
<td>(a) none (b) lots, yellow (c) almost none</td>
</tr>
<tr>
<td>(a) TiC / Bi₂O₃ (b) 9 / 91</td>
<td>difficult</td>
<td>no</td>
<td>part heated</td>
<td>(a) N/A (b) N/A</td>
<td>small, orange, where heated</td>
<td>(a) none (b) some, yellow (c) some, where heated</td>
</tr>
<tr>
<td>(a) TiN / Bi₂O₃ (b) 17 / 83</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) slow-burning (b) 6</td>
<td>small, orange</td>
<td>(a) none (b) minimal, yellow (c) lots</td>
</tr>
<tr>
<td>(a) TiSis / Bi₂O₃ (b) 10 / 90</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) incandescent slag pile (b) 5</td>
<td>very small, orange</td>
<td>(a) none (b) minimal, yellow (c) lots</td>
</tr>
<tr>
<td>(a) TiSis / Bi₂O₃ (b) 12 / 88</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 0.6</td>
<td>moderate, orange</td>
<td>(a) some, white (b) lots, yellow (c) metallic beads</td>
</tr>
<tr>
<td>(a) TiP / Bi₂O₃ (b) 10 / 90</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) burst (b) 0.2</td>
<td>large, yellow-orange</td>
<td>(a) none (b) lots, yellow (c) none</td>
</tr>
</tbody>
</table>
Table 2d. Estimated Combustion Stoichiometry – Zirconium and Hafnium Compounds, Bi₂O₃

<table>
<thead>
<tr>
<th>Equation</th>
<th>Fuel (wt%)</th>
<th>Oxidizer (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ZrB₂ + 5 Bi₂O₃ → 3 ZrO₂ + 3 B₂O₃ + 10 Bi</td>
<td>13</td>
<td>87</td>
</tr>
<tr>
<td>3 ZrC + 4 BiO₃ → 3 ZrO₂ + 3 CO₂ + 8 Bi</td>
<td>14</td>
<td>86</td>
</tr>
<tr>
<td>6 ZrN + 4 Bi₂O₃ → 6 ZrO₂ + 3 N₂ + 8 Bi</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>ZrSi₂ + 2 BiO₃ → ZrO₂ + 2 SiO₂ + 4 Bi</td>
<td>14</td>
<td>86</td>
</tr>
<tr>
<td>3 HfB₂ + 5 Bi₂O₃ → 3 HfO₂ + 3 B₂O₃ + 10 Bi</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>3 HfC + 4 BiO₃ → 3 HfO₂ + 3 CO₂ + 8 Bi</td>
<td>23</td>
<td>77</td>
</tr>
<tr>
<td>HfSi₂ + 2 Bi₂O₃ → HfO₂ + 2 SiO₂ + 4 Bi</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 3d. FactSage Calculations – Zirconium and Hafnium Compounds, Bi₂O₃

<table>
<thead>
<tr>
<th>Reactant Fuel</th>
<th>Tₐd (°C)</th>
<th>Fuel / Bi₂O₃ (wt% ratio)</th>
<th>Major Products (phase, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB₂</td>
<td>1711</td>
<td>13 / 87</td>
<td>ZrO₂ (s, 14.0), B₂O₃ (l, 6.5), Bi (g, 41.4), Bi₂ (g, 36.6)</td>
</tr>
<tr>
<td>ZrC</td>
<td>1554</td>
<td>21 / 79</td>
<td>ZrO₂ (s, 24.4), Bi₂ (g, 43.1), Bi (g, 27.8), CO (g, 3.1)</td>
</tr>
<tr>
<td>ZrN</td>
<td>1494</td>
<td>26 / 74</td>
<td>ZrO₂ (s, 29.4), Bi (l, 9.8), Bi₂ (g, 37.4), Bi (g, 19.1), N₂ (g, 3.3)</td>
</tr>
<tr>
<td>ZrSi₂</td>
<td>2266</td>
<td>14 / 86</td>
<td>ZrO₂ (s, 11.7), SiO₂ (l, 10.4), Bi (g, 71.4), Bi₂ (g, 5.5)</td>
</tr>
<tr>
<td>HfB₂</td>
<td>1712</td>
<td>20 / 80</td>
<td>HfO₂ (s, 21.0), B₂O₃ (l, 6.2), Bi (g, 37.0), Bi₂ (g, 31.8), BiO (g, 3.1)</td>
</tr>
<tr>
<td>HfC</td>
<td>1562</td>
<td>33 / 67</td>
<td>HfO₂ (s, 36.1), Bi₂ (g, 36.1), Bi (g, 24.0), CO (g, 2.5)</td>
</tr>
<tr>
<td>HfSi₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4d. Experimental Results – Zirconium and Hafnium Compounds, Bi₂O₃

<table>
<thead>
<tr>
<th>(a) Mixture (b) wt% Ratio</th>
<th>Ignition</th>
<th>Self-Sustained Combustion</th>
<th>Amount Consumed</th>
<th>(a) Type (b) Duration (s)</th>
<th>Flame</th>
<th>(a) Sparks (b) Smoke (c) Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ZrB₂ / Bi₂O₃ (b) 13 / 87</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 0.6</td>
<td>moderate, orange</td>
<td>(a) some, orange (b) lots, yellow (c) some</td>
</tr>
<tr>
<td>(a) ZrC / Bi₂O₃ (b) 21 / 79</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) spark/slag shower (b) 0.7</td>
<td>minimal, orange</td>
<td>(a) lots, orange (b) moderate, yellow (c) minimal</td>
</tr>
<tr>
<td>(a) ZrN / Bi₂O₃ (b) 26 / 74</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 1.2</td>
<td>moderate, orange</td>
<td>(a) some, white (b) lots, yellow (c) some</td>
</tr>
<tr>
<td>(a) ZrSi₂ / Bi₂O₃ (b) 14 / 86</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) incandescent slag pile (b) 5</td>
<td>minimal, orange</td>
<td>(a) none (b) some, yellow (c) large metallic beads</td>
</tr>
<tr>
<td>(a) HfB₂ / Bi₂O₃ (b) 20 / 80</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 0.5</td>
<td>moderate, orange</td>
<td>(a) none (b) lots, yellow (c) small metallic beads</td>
</tr>
<tr>
<td>(a) HfC / Bi₂O₃ (b) 33 / 67</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) burst (b) ~ 0.15</td>
<td>large, orange</td>
<td>(a) none (b) lots, yellow (c) none</td>
</tr>
<tr>
<td>(a) HfSi₂ / Bi₂O₃ (b) 20 / 80</td>
<td>yes</td>
<td>yes</td>
<td>all</td>
<td>(a) flame (b) 1</td>
<td>moderate, orange</td>
<td>(a) none (b) some, yellow (c) large metallic beads</td>
</tr>
</tbody>
</table>

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4. DISCUSSION

The fuel/oxidizer weight ratios estimated using the assumed reactions in Tables 2a-d are, for the most part, remarkably similar to those predicted with FactSage in Tables 3a-d. Exceptions include TiH$_2$/KNO$_3$ and reactions involving ZrC and HfC. Notably, the weight ratios predicted to give peak $T_{ad}$ values (Tables 3a-d) either match those in Tables 2a-d or are seemingly fuel-rich. The greatest discrepancies are due to the predicted formation of K(g) and CO(g) instead of K$_2$O and CO$_2$. In other cases, the estimated and predicted weight ratios match or are similar despite substantially different predicted products such as potassium silicates and titanates. Potassium in the presence of boron is predicted to form KBO$_2$. Indeed, “KBO$_2$” is one known crystalline phase in the often glassy and non-stoichiometric K$_2$O-B$_2$O$_3$ system [7,8].

Combustion temperatures of the metal-element compound/oxidizer mixtures are expected to be lower than those of the corresponding metal/oxidizer systems for two reasons. First, the metal-element compounds have negative enthalpies of formation. Second, production of additional reaction products in the liquid and gas phases (KBO$_2$, B$_2$O$_3$, SiO$_2$, and others) consumes energy that would otherwise increase temperature. As shown in Tables 5a and 5b, reactions involving the group 4 metals have greater predicted peak $T_{ad}$ values (compare to Tables 3a-d). The combustion temperatures of metal/oxidizer systems, especially those containing very reducing metals and strong oxidizers, are limited by the substantial enthalpies of vaporization of the metal oxide products. The predicted adiabatic reaction temperatures and reaction products in Table 5a illustrate this well.
Diverse reactivity was observed in qualitative ignition tests (Tables 4a-d). The titanium and zirconium disilicides were relatively unreactive, while the hafnium analogue and Ti₅Si₃ were much more reactive. Other compounds appeared to be more reactive with one of the oxidizers but less so with the other (examples include TiB₂, TiC, TiN, TiP, and ZrB₂). Of these, TiC and TiN were the least reactive. ZrC, ZrN, and HfB₂ were vigorously reactive with both KNO₃ and Bi₂O₃. The only two compounds that were violently reactive with both oxidizers were TiH₂ and HfC (Figures 2a-d). The HfC sample was composed of very fine particles and appeared to have a large surface area (Figures 1d and 3). Titanium hydride (TiH₂) and subhydrides (TiHₓ) paired with KClO₄ have been studied.

**Table 5a. FactSage Calculations – Group 4 Metals, KNO₃**

<table>
<thead>
<tr>
<th>Reactant Flu</th>
<th>Tad (°C)</th>
<th>Fuel / KNO₃ (wt% ratio)</th>
<th>Major Products (phase, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>3257</td>
<td>49 / 51</td>
<td>Ti₂O₅ (l, 58.5), K (g, 19.7), TiO (g, 8.8), N₂ (g, 7.0), TiO₂ (g, 5.5)</td>
</tr>
<tr>
<td>Zr</td>
<td>3717</td>
<td>58 / 42</td>
<td>ZrO₂ (l, 58.5), K (g, 16.2), ZrO (g, 9.3), ZrO₂ (g, 9.2), N₂ (g, 5.7)</td>
</tr>
<tr>
<td>Hf</td>
<td>4404</td>
<td>72 / 28</td>
<td>HfO₂ (l, 82.6), K (g, 10.8), N₂ (g, 3.8)</td>
</tr>
</tbody>
</table>

**Table 5b. FactSage Calculations – Group 4 Metals, Bi₂O₃**

<table>
<thead>
<tr>
<th>Reactant Flu</th>
<th>Tad (°C)</th>
<th>Fuel / Bi₂O₃ (wt% ratio)</th>
<th>Major Products (phase, wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2515</td>
<td>15 / 85</td>
<td>Ti₃O₅ (s, 17.2), TiO₂ (l, 5.9), Bi (g, 73.5), Bi₂ (g, 2.5)</td>
</tr>
<tr>
<td>Zr</td>
<td>3004</td>
<td>23 / 77</td>
<td>ZrO₂ (l, 30.0), Bi (g, 68.5)</td>
</tr>
<tr>
<td>Hf</td>
<td>3015</td>
<td>37 / 63</td>
<td>HfO₂ (l, 42.7), Bi (g, 56.0)</td>
</tr>
</tbody>
</table>

**Figures 2a-d.** Images from tests involving TiH₂ and HfC (see Tables 4a-d).
TiH₂/KNO₃ (a) top left; TiH₂/Bi₂O₃ (b) top right; HfC/KNO₃ (c) bottom left; HfC/Bi₂O₃ (d) bottom right.
extensively as spark-insensitive pyrotechnic actuators and igniters intended for nuclear weapons applications [9]. To the best of our knowledge, HfC has not been examined in a pyrotechnic context before.

**Figure 3.** SEM image of HfC at 10,000 X.

The perceived vigor of the reactions is largely influenced by burning rate, temperature, and gas production. Compositions that burn rapidly at a high temperature with sufficient gas production produce a blinding flash, as observed for some of the fuel/KNO₃ mixtures. In contrast, the fuel/Bi₂O₃ mixtures seem to burn at lower temperatures, with even the most rapid reactions producing large orange fireballs of moderate intensity. These observations are in agreement with the corresponding trend in predicted $T_{ad}$ (Tables 3a-d). Although, it should be noted that the predicted adiabatic reaction temperatures represent upper limits. The actual events are expected to occur at lower temperatures due to heat loss to the surroundings and the formation of non-equilibrium products.

Many of the compositions produced sparks, particularly the ones containing KNO₃ (Figure 4). Other notable qualitative characteristics included the violet and green hues of some of the flames, presumably caused by gaseous K and BO₂, respectively (Figures 2a, 2c, and 5). Some of the reactions with Bi₂O₃ produced metallic beads – elemental bismuth. Additionally, many of the reactions with Bi₂O₃ produced yellow smoke. This is attributed to the formation of gaseous Bi, which re-oxidizes in the air forming a yellow bismuth oxide aerosol.

**Figure 4.** HfSi₂/KNO₃ sparking (see Table 4b).

**Figure 5.** ZrB₂/KNO₃ green flame (see Table 4b).

5. SUMMARY AND CONCLUSIONS

Metal-element compounds of titanium, zirconium, and hafnium have been surveyed as pyrotechnic fuels. A variety of observed qualitative effects indicate that these fuels may be useful for multiple pyrotechnic applications. Considering that this survey made use of as-received materials, it may be possible to achieve more vigorous reactivity through the use of finer samples. Experiments with other oxidizers and characterization of mixture sensitivity to various ignition stimuli are areas of ongoing research in our laboratories.
6. ABBREVIATIONS AND ACRONYMS

AEE, Atlantic Equipment Engineers
ARDEC, Armament Research, Development and Engineering Center
RDECOM, Research, Development and Engineering Command
SEM, scanning electron microscopy
XRD, X-ray diffraction
XRF, X-ray fluorescence

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8. REFERENCES