Preparation and Characterization of Carbide and Nitride Simulated Fuel for Generation IV Reactors

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Abstract: Non-oxide ceramics such as carbides and nitrides are potential fuel candidates to be used in Generation IV nuclear reactors. A fissile phase such as UN or PuN is dispersed with an inert phase such as ZrN and TiN to provide structure and retain fission products. In this study cerium was used as a surrogate element instead of U or Pu. Cerium nitride was fabricated by the carbothermic reduction of cerium oxide, This method was investigated and optimized. The internal gelation method (IGM) has been optimized to fabricate sintered CeO₂ microspheres. Optimisation of sol formulations was studied using cerium ammonium nitrate, HMTA and urea in the fabrication of cerium oxide microsphere. CeO₂ spheres doped with carbon powder have also been produced using this method and the reactive sintering parameters of CeN microsphere production have been optimized. Samples were placed in a crucible and heated to in a hydrogen-nitrogen atmosphere to control stoichiometry. Results showed cerium carbide with no oxide phase was detected using X ray diffraction (XRD). Results indicated that internal gelation successfully formed spheres of cerium oxide and carbon. The precipitation of Ce⁴⁺ was corresponded to the pH of the solution and the formed gels. The pH-value determines the point of precipitation of Ce⁴⁺, and dictated the gelation time. Gelation time was observed through the colour change of the spheres from a translucent yellow to opaque white.

Keywords: Non-Oxide Ceramic, Cerium Nitride Fabrication, CeO₂ Spheres

1. Introduction

Currently fuel used in reactor cores is typically enriched uranium dioxide which preceded uranium metal in Magnox reactors due to its ability to achieve higher burn up. The desire to increase this fuel burn up, including higher temperature, intense irradiation and increased heavy metal density in the core, new materials must be found that possess the required Thermophysical properties. Nitride and carbide fuels have received much attention due to their potential application in Generation IV as they combine both the advantages of metallic and oxide fuel [1-3]. Uranium carbide (UC) and uranium nitride (UN) have high heavy metal density, high thermal conductivity and minimal impact on neutron spectrum [2]. The unloaded fuel from the core of the open fuel cycle disposed directly contains some fissionable isotopes of uranium and plutonium. These isotopes can be recovered using an extraction reprocessing process (PUREX) to be returned back into the fuel cycle. As the majority of the existing spent fuel exist as an oxide fuel, carbothermic reduction of the oxide powders is the most attractive route for large scale production of non-oxide fuels. Methods of carbothermic reduction and nitridation of oxides are based on mixing the oxide powder with a carbon source at (1600-2100°C) under inert atmosphere, followed by further heat treatment under the same temperature range under hydrogen-nitrogen atmosphere (10% H₂) to complete the reaction and remove the excess carbon. The basic mechanism of this carbothermic reduction and nitridation method is given by equation (1):

\[ \text{MO}_2 + 3\text{C} \rightarrow \text{MC} + 2\text{CO} \rightarrow \text{MN} + \text{CH}_4 \]  

Thermophysical properties of ZrN and (Pu₀.₂₅, Zr₀.₇₅)N solid solutions have been reported by Basini et al [4]. They produced samples of ZrN and (Pu, Zr) N by pressing pellets from powders with geometrical densities of (70% and 89%TD) respectively. They report the scarcity of thermal conductivity data with few available not reproducible results.
and thermal conductivity for zirconium nitride between 15-20 W m⁻¹ K⁻¹ at 427-2027°C. Conductivity values were then corrected to fully dense materials using a modified Maxwell-Eucken correlation (equation 2) [5].

\[ K_{TD} = K / ((1 – p)/(1+\beta p)) \]  

(2)

where, \( K_{TD} \) is the thermal conductivity of fully dense material, \( p \) is the porosity fraction of the material and \( \beta \) is a coefficient (0.5 ≤ \( \beta \) ≤ 3).

The calculated thermal conductivities were found to be between (35-40 W m⁻¹ K⁻¹) over the same temperature range. Thermal properties including the specific heat, thermal diffusivity and thermal conductivity of ZrN have also reported by Ciriello et al [5]. The analysis was performed with commercial ZrN powder reduced carbothermically into sintered pellets achieving a density of (82.4% TD) as measured by the immersion method and 80.6% TD as measured by the geometrical method, indicating that the open porosity is (~10.2vol%). The authors noticed that the development of an oxide layer on the surface of the pellets as indicated by XRD was undetectable. After correction of density, the thermal conductivity was found to be (15.3-30 Wm⁻¹K⁻¹) at (247-1197°C), which is in good agreement with that given by Hedge et al. [6].

The Japanese Atomic Energy Agency has also proposed ZrN and TiN as diluents for GFR fuel. Both materials showed higher thermal conductivity and melting temperature values than that given by the actinide mononitrides and are free from phase transformation and offer a stable structure. Arai et al [7] noted that, although both diluent materials have the same crystal structure, ZrN is likely due to formation of solid solution with PuN, while the solubility of PuN in TiN is negligible. Arai and Nakajima [7] and Minato et al [8] prepared plutonium nitride pellets containing ZrN and TiN as inert matrices using PuO₂ powder. The carbothermically reduced PuN was prepared by mixing PuO₂ and graphite with a 2:2 molar ratio. The powders were then compacted into discs at 100MPa and heated in N₂ at (1550°C) for (10 h), followed by heating at (1450°C) for (20 h) in hydrogen / nitrogen atmosphere.

Streit et al [9, 10] studied the suitability of carbothermic reduction in fabrication of zirconium nitride matrix using the sol-gel method and the dry powder route. The sol-gel route was used to fabricate microspheres of ZrN, Ce₂₀₋₂Zr₀₇₅N, Nd₀₂₋₂Zr₀₈₅N, U₀₂₋₂Zr₀₈₅N and Pu₀₂₋₂Zr₀₈₅N. The dry powder route was used for carbothermic reduction and nitridation which was split into two mechanisms. First carbothermic reduction of cerium oxide CeO₂ to cerium carbide (CeC₂) powder, second nitridation of CeC₂ to CeN were performed.

Microstructures of the spheres showed a uniform distribution of pores (~5-10 μm diameter) due to gas release from the reaction reaction and a second phase which is proposed as unreacted oxide and carbon black. Densities of the spheres were between (91-103%) and unreacted oxide phases or carbon is stated as possible cause of greater than (100% TD). However, no quantitative analysis of these phases or carbon and oxygen content is noted. Nakagawa et al [11] reported the formation of uranium and cerium nitrides from their respective carbides using NH₃ or N₂H₃ gas mixtures. They noted that in the first step, the reduction of ceria needs a cerium oxide to carbon ratio of (1:4.8 wt.%) to complete the reaction. However, XRD of cerium carbide reacting with ammonia showed the presence of graphite.

The powders of PuN and ZrN were mixed in ratio of (40Pu:60Zr wt%), and powders of PuN and TiN were mixed in a ratio of (50Pu:50Tiwt%). The mixed powders were compacted into discs and heated in hydrogen/nitrogen atmosphere for 5 h. This step was repeated three times, then the discs were ground and compacted into green pellets at 300 MPa and sintered in argon atmosphere at (1730°C) for (5 h), followed by heating in a hydrogen / nitrogen atmosphere at (1400°C) to control stoichiometry. Nitrogen, carbon and oxygen quantities were determined by combustion gas chromatography, inert gas fusion coulometer and high frequency heating coulometer, respectively.

The aim of this work is to fabricate fuel forms using cerium nitride as an actinide surrogate by the carbothermic reduction of cerium oxide. Microspheres of CeN will also be produced via the Internal Gelation Method (IGM) and carbothermic reduction. Optimisation of sol formulations using cerium ammonium nitrate, HMTA and urea in the fabrication of cerium oxide microsphere have been studied. Cerium oxide microspheres doped with carbon black will be investigated and reactive sintering was studied.

2. Experimental

2.1. Ceramic Fabrication

Production of cerium nitride (CeN) from cerium oxide (CeO₂) via a carbothermic reduction and nitridation route was investigated. The process of carbothermic reduction and nitridation splits into two mechanisms given by the following equations, first optimisation of cerium carbide (CeC₂) powder preparation, second nitridation of CeC₂ to CeN:

\[ \text{CeO}_2 + 4\text{C} \rightarrow \text{CeC}_2 + 2\text{CO} \]  

(3)

\[ \text{CeC}_2\text{CeN} + \text{CH}_4 \xrightarrow{\text{N}_{2}/\text{H}_2} \text{CeN} \]  

(4)

The heat treatment parameters that influence the carbothermic reduction of CeO₂ were investigated. The process route, evolved over several iterations as improvements noted by reaction product characterisation, were implemented. All iterations used the same composition of starting powders.

Cerium oxide (Alfa-Aesar, 99.9%, 5µm) and carbon black (~400nm) were wet ball milled for 12 h with media and ethanol to afford a homogeneous mixture with C/Ge of 4/1 molar ratio. Powders were either pressed into pellets (1g) or compacted into a graphite cylinder and subjected to heat treatments. Samples of CeO₂ and C were heated in graphite furnace at (1500-1800°C) (+20°C min⁻¹) for (5-12 h) under vacuum or static inert atmosphere and cooled under vacuum. Samples were then cooled to 298K for 4 h. Samples of CeC₂
were placed in alumina or zirconia crucibles and heated in a hydrogen / nitrogen atmosphere at (1600-1800°C) for (6-8 h), and then cooled to (298K) for (1-2 h). Surface microstructure was characterised using scanning electron microscopy (SEM) applying secondary electron imaging (SEI). Qualitative chemical analysis was performed using energy dispersive X-ray spectroscopy (EDX). EDX was carried out using an INCA ultra-thin polymer detector at (20 kV). Measurements was performed by XRD at (40 kV) and (40 mA).

2.2. Microsphere Fabrication

Microsphere fabrication of \((\text{NH}_4)_2\text{Ce(NO}_3)_6\) was performed by mixing cerium oxide with hexamethyltetramine (HMTA) and urea at (0-5°C) forming a broth or ‘sol’. Droplets of this sol were then contacted with hot silicone oil (90°C) to form spheres. In this form cerium was in the 4th oxidation state, which precipitates at pH 2.7 [12]. Urea was employed as a complexing agent. As the temperature of the droplet increases when contacted with the hot silicone, decomplexation occurs. Hydrolysis of the cerium ion occurs generating hydrogen ions which protonate to HMTA. Once (\(\geq 95\%\)) of the HMTA molecules were protonated, they decompose into ammonia molecules, increasing the pH of the system, as follows [13]:

1. Urea complexation/decomplexation

\[
2 \text{CO(NH}_2)_2 + \text{Ce}^{4+} \rightarrow \text{Ce} \left( \text{CO(NH}_2)_2 \right)_2^{4+} \quad (5)
\]

2. Hydrolysis of cerium

\[
\text{Ce}^{4+} + \text{H}_2\text{O} \rightarrow \text{Ce(OH)}_2 \cdot 9\text{H}_2\text{O} + 4\text{H}^+ \quad (6)
\]

Formulations of the end product forming good spheres of cerium oxide and carbon were then observed. The pH of the solution and gels plays an important role in the precipitation of \(\text{Ce}^{4+}\). Stock solutions of 3.18 M HMTA and urea and 1.5 M cerium ammonium nitrate were prepared by dissolving each in deionised water. The stock solutions were mixed together at 0-5°C to form the sol, then droplets of the sol contacted with hot silicone oil (90°C) were added. The spheres were then washed in chloroform to remove any silicone oil, and \(\text{NH}_4(\text{OH})\) to remove any unreacted products and to complete the precipitation process.

3. Results and Discussion

3.1. Ceramic Fabrication

Five Iterations of carbothermic reduction parameters are given in Table 1. XRD spectra of reactant products (Figures 1 and 2) reveal that all peaks in iterations 4 and 5 correspond to tetragonal \(\text{CeC}_2\) with no oxide phase. Incomplete reactions in iterations 1 and 2 may be due to the form of the sample. A pellet did not allow complete release of CO compared to a loosely packed powder, which may slow the reaction. EDX analysis (Figure 3) reveals the presence of C, N and O light elements in the sample. Free carbon from unreacted materials is also present in the samples.

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Form</th>
<th>Temperature/°C</th>
<th>Time/h</th>
<th>Atmosphere</th>
<th>Phase by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>Pellet</td>
<td>1500</td>
<td>12</td>
<td>Vacuum</td>
<td>(\text{CeO}_2, \text{CeC}_2, \text{C})</td>
</tr>
<tr>
<td>C-2</td>
<td>Pellet</td>
<td>1800</td>
<td>5</td>
<td>Argon (100%)</td>
<td>(\text{CeO}_2, \text{CeC}_2, \text{C})</td>
</tr>
<tr>
<td>C-3</td>
<td>Powder</td>
<td>1800</td>
<td>5</td>
<td>Argon (100%)</td>
<td>(\text{CeO}_2, \text{CeC}_2, \text{C})</td>
</tr>
<tr>
<td>C-4</td>
<td>Powder</td>
<td>1800</td>
<td>12</td>
<td>Argon (100%)</td>
<td>(\text{CeC}_2, \text{C})</td>
</tr>
<tr>
<td>C-5</td>
<td>Powder</td>
<td>1800</td>
<td>12</td>
<td>Nitrogen (100%)</td>
<td>(\text{CeC}_2, \text{C})</td>
</tr>
</tbody>
</table>

Table 1. Reaction parameters for carbothermic reduction of \(\text{CeO}_2\).

Figure 1. Comparison between experimental XRD of reacted powder.

Figure 2. XRD of powder obtained from iteration C-4, all peaks correspond to tetragonal \(\text{CeC}_2\).
As no oxide phase was detected by XRD, nitridation was attempted. In these experiments the sample were placed in a crucible and heated to in a hydrogen doped nitrogen atmosphere (10% hydrogen, 90% nitrogen). Reaction parameters are given in Table 2. In the first iteration an alumina crucible was used, but no product was retrieved due to possible reaction between the crucible and sample and so subsequent reactions used zirconia crucibles.

**Table 2. Reaction parameter for nitridation experiments of CeC.**

<table>
<thead>
<tr>
<th>Iteration (N-nitridation)</th>
<th>Crucible</th>
<th>Temperature/°C</th>
<th>Dwell time/h</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-1</td>
<td>Alumina</td>
<td>1800</td>
<td>6</td>
<td>H₂(10%)N₂(90%)</td>
</tr>
<tr>
<td>N-1</td>
<td>Zirconia</td>
<td>1800</td>
<td>6</td>
<td>H₂(10%)N₂(90%)</td>
</tr>
<tr>
<td>N-1</td>
<td>Zirconia</td>
<td>1800</td>
<td>8</td>
<td>H₂(10%)N₂(90%)</td>
</tr>
</tbody>
</table>

**Figure 3.** (a) SEM of experimental powder iteration C-4. (b) EDX spectrum from square area.

**Figure 4.** Experimental XRD of reacted CeC₂ powder, heated to 1800°C in H₂ (10%) N₂ (90%).

**Figure 5.** (a) SEM of powder iteration N-2. (b) EDX spectrum of Experimental. (c) SEM image of iteration N-3. (d) EDX spectrum.
The reacted powder from iteration 2 yielded an orange powder, XRD of the reacted powders, shown in Figure 4, matched a phase patterns for a Ce$_2$O$_2$N$_2$ and Ce$_2$O$_3$ phase. However, EDX analysis no nitrogen was detected as shown in (Figure 5), indicating the presence of Ce$_2$O$_3$ phase. Carbon peaks in iteration 3 may be present due to unreacted carbon powder from the carbothermic reduction, which was not the case in iteration 2 due to the higher sintering temperature.

### 3.2. Microsphere Fabrication

Fabrication of CeO$_2$ rigid spheres was performed by the

![SEM image of CeO$_2$ microsphere produced by IGM, sintered at 1400°C for 4h.](image)

<table>
<thead>
<tr>
<th>Iteration (MS-microsphere)</th>
<th>HMTA/ml</th>
<th>Urea/ml</th>
<th>Ce$_4^+$/ml</th>
<th>NH$_4$(OH) (3M/ml)</th>
<th>pH</th>
<th>Gelation Time/s</th>
<th>Rigidity (scale 1-5)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-01</td>
<td>5.0</td>
<td>5</td>
<td>2</td>
<td>0</td>
<td>2.45</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>MS-02</td>
<td>5.5</td>
<td>5.5</td>
<td>9.4</td>
<td>2.4</td>
<td>1.00</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>MS-03</td>
<td>2.7</td>
<td>2.7</td>
<td>4.6</td>
<td>5.0</td>
<td>2.35</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>MS-04</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0</td>
<td>1.27</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>MS-05</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0.4</td>
<td>2.06</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

* Rigidity scale from 1 – 5, 1 - no spheres formed, 5 - rigid spheres formed

<table>
<thead>
<tr>
<th>Microsphere iteration</th>
<th>HMTA (ml)</th>
<th>Urea (ml)</th>
<th>Ce$_4^+$(ml)</th>
<th>NH$_4$(OH) (3M/ml)</th>
<th>C (g)</th>
<th>pH</th>
<th>Rigidity Scale*</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-06</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0.4</td>
<td>0.16</td>
<td>2.34</td>
<td>4</td>
</tr>
<tr>
<td>MS-07</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0.4</td>
<td>0.16</td>
<td>2.34</td>
<td>4</td>
</tr>
<tr>
<td>MS-08</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0.0</td>
<td>0.16</td>
<td>2.06</td>
<td>4</td>
</tr>
<tr>
<td>MS-09</td>
<td>2.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0.0</td>
<td>0.12</td>
<td>2.06</td>
<td>5</td>
</tr>
</tbody>
</table>

Solutions that were not partially pre-neutralized showed greater rigidity, but it takes longer time to gel formation. This means that the gelation process had not fully completed before contacting with the bottom of the column. However, spheres that were partially pre-neutralized are precipitated faster but insufficiently rigid to remain spheres in contact with the bottom of the column. After several evolutions of the sol mixtures, iteration 5 gave rigid spheres that could be sintered without cracking. Figure 6 shows the SEM of a CeO$_2$ microsphere produced using iteration 5, sintered at 1400°C for 4 h in air. Once a sol formulation gives a uniform rigid spheres, the next step was to disperse carbon black to fabricate CeO$_2$ + C spheres, which undergo carbothermic reduction. Iterations of sol-gel formulations are summarized in Table 3. Some solutions were partially pre-neutralized by adding NH$_4$(OH). The pH-value determines the point of precipitation of Ce$^{4+}$, and so dictates the gelation time. Gelation time was measured optically through the colour change of the spheres from a translucent yellow to opaque white.
Finally, pyrolysis was carried out by heating the spheres at (500°C), (4°C per min) for (4h) in argon atmosphere to remove any organic matter or NH₄OH, causing cracking and splitting during the sintering process. However, cracking of spheres was still observed after this step, indicating incomplete gelation, or incomplete drying with either reactants or water causing the cracking during evaporation. Carbon powder does not disperse well in water and some authors [13] report the use of a dispersing agent to achieve a homogenous mixture. A homogenous sol mixture is essential for gelation to produce complete uniform spheres, which may overcome the cracking problem seen in the pyrolysis step. An even distribution of carbon and CeO₂ particles is also required for the sintering stage to achieve complete carbothermic reduction and to ensure the linear shrinkage of the sphere at the volume changes during the reaction.

4. Conclusion

Cerium carbide could be produced via carbothermic reduction of ceria with no ceria phases as identified using XRD by increasing temperature and time. However, nitridation has not been achieved with reactions giving Ce₂O₃, using oxygen of (<0.0001 ppb). The product was analysed immediately by XRD to avoid any room temperature oxidation. Nitridation experiments was performed in ammonia atmosphere which has greater activity of nitridation process. Quantitative analysis of light elements in the powders, such as C, N and O were evaluated and optimisation of the carbothermic reduction process was carried out stochiometric determination of carbides and nitrdes was performed. In this analysis the sample was placed in a graphite crucible and a high current was passed through the crucible to increase the temperature. Oxide phases react with the crucible and was released as CO and oxidised to CO₂ and oxygen which is determined using a non-dispersive Infra-Red analyser. Carbon content was measured by a similar method by oxidising to CO and then CO₂ which is then detected by a non-dispersive Infra-Red analyser. Nitrogen was extracted as N₂ gas and determined by a thermal conductivity detector. Cerium oxide microspheres and unsintered cerium oxide doped with carbon black spheres could be fabricated using the sol-gel process. However, the carbon black doped spheres showed extensive cracking during pyrolysis to remove organic and un-reacted material. Once CeN has been produced, production of surrogate fuel pellets using CeN as an actinide surrogate can be fabricated. Microstructures of the sintered pellets were characterised using SEM and TEM. Group IV nitride materials also exhibit a broad range of non-stoichiometry.

References


