

Laboratory production of zirconium carbide compacts for use in inert matrix fuels

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Abstract

Zirconium carbide is being actively considered for use as an inert matrix material in composite nuclear fuel for gas-cooled fast reactors. ZrC can be produced either by the endothermic carbothermal reduction of zirconium dioxide or by the direct exothermic reaction of pure zirconium and graphite powder mixtures. The exothermic reaction is classified as combustion synthesis or self heating synthesis. Experiments were conducted to demonstrate the combustion synthesis reaction of zirconium and graphite powders and measure the ignition and adiabatic temperatures. The heat released during this short reaction time was sufficient only to partially sinter the compacts to less than 40% theoretical density. Subsequently, compacts of ZrC were similarly produced by combustion synthesis followed by a short, high temperature hold at 2440 °C to relieve residual stresses in the compacts following the rapid reaction sintering. External pressures of up to 5.2 MPa were used as an additional driving force for sintering. The effects of reactant particle size and degree of uniaxial pressing on the product density and porosity were also studied. Higher densities in the fabricated compacts were noted for higher uniaxial pressures irrespective of powder size. Also, smaller powder sizes produced compacts up to 92% TD, while larger particle sizes produced compacts up to 84% TD for the same pressure. The compacts were characterized based on composition, microstructure, and density/porosity. Results of the different experiments are presented.

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1. Introduction

Inert matrix fuels [1,2] are under consideration for gas-cooled fast reactor (GFR) applications. One such proposed fuel form consists of mixed carbide or nitride fuel microspheres dispersed in an inert matrix [2–6]. GFR fuels are expected to operate at nominal temperatures of 1400 °C similar to fuels for high temperature reactors (HTR) [1,2,6]. However owing to the differences in design, the maximum transient temperatures may exceed 1600 °C [6]. Hence the fuel bearing matrix is expected to have certain desirable high temperature characteristics such as high thermal conductivity, high melting point, and resistance to corrosion by fission products in addition to good strength and good neutronic properties [1–10]. Zirconium

carbide (ZrC) is being considered as one of the candidate materials for the production of the inert matrix due to its favorable high temperature characteristics mentioned above [1–10].

To establish the fact that ZrC was being produced by combustion synthesis followed by reaction sintering, it was found necessary to divide the experiment into two phases. In the first phase, it was sought to demonstrate combustion synthesis and resulting pressureless, reaction sintering of zirconium and graphite powders. The adiabatic temperature (T_{ad}) [9–12] and the ignition temperatures (T_{ig}) [11–14] were recorded during combustion synthesis. These samples were characterized for porosity/density, chemical composition, and microstructure.

In the second phase, induction heating was employed to initiate combustion synthesis and subsequent sintering of the powders. The mixture was placed in a graphite die-punch assembly and heated to 2440 °C. To accommodate

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advanced fuels involving minor actinide recycle [2–6], it was sought to develop fabrication methods that limit the time that the compacts are exposed to high temperatures. Hence in these experiments, the samples were held at the maximum temperature for only 15 min to allow the reaction to complete and relieve any residual stresses in the compacts following the very high temperature combustion reaction and subsequent rapid cooling. The size of the reactant particles and applied pressure were varied to observe the changes in product characteristics such as density and porosity. The samples were characterized for porosity/density, chemical composition, and microstructure.

The two experiments were conceived as a bridge between combustion synthesis, reaction sintering, and hot pressing to understand and establish an overall ZrC compact production methodology. The results of both experimental phases are presented. The ultimate goal would be to then extend this methodology to the formation of composite fuels containing dispersed fuel microspheres.

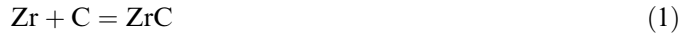
2. Thermodynamical background

ZrC powder can be produced in the laboratory by several methods such as carbothermal reduction of zirconium dioxide (ZrO_2) by graphite powder, the reaction of zirconium hydride with carbon, solution based processing, and by the direct reaction of zirconium (Zr) and graphite [12,16–19,23–25].

The carbothermal reduction and solution based processing methods are endothermic processes which require an external high temperature heat source. The reported temperature ranges for the carbothermic conversion is 1900–2100 °C [17,18] and that of solution based processing is 900–1500 °C [18]. The presence of inherent oxygen and other dissolved impurities in the product alters its purity and stoichiometry. It often takes long periods of heating and processing to complete the reaction and produce products of desired purity. In cases where sintering of the end product and formation of compacts is required, additional heating (at least two-thirds the melting point of ZrC) has to be provided for long periods of time. The purity of the end products, processing time and the processing temperatures involved in these methods make them less attractive specifically for production of materials for use in nuclear reactors where a compromise on the purity of the material can change the entire set of desired properties such as thermal conductivity under operating and transient conditions.

The production of ZrC by reacting zirconium hydride with graphite [17,19] is also not uncommon. This reaction is exothermic and falls under the category of combustion synthesis reaction. Since zirconium hydride is highly pyrophoric at room temperature, extreme care has to be taken while handling the reactants.

The other method involves the production of ZrC by the direct reaction of zirconium and graphite powders. The reaction is represented as follows [12]:



The reaction is highly exothermic and is also classified as self heating high temperature synthesis (SHS) or combustion synthesis [11–14]. The product purity is almost guaranteed with this method and handling under an inert atmosphere in a glovebox and vacuum chamber is required due to the pyrophoric nature of zirconium powders. Fine powders of zirconium and graphite thoroughly mixed and pressed to form green bodies of desired shapes are heated to a particular temperature known as the ignition temperature (T_{ig}) within a short period of time. Beyond this point, a combustion wave starts and propagates through the compact converting the reactant mixture into ZrC. External heating is required to ignite the compact unless the auto-ignition temperatures of the mixture is close to standard room temperature under an inert atmosphere. The heating can be achieved by several methods from simple direct resistance heating [11] to induction heating.

Once the ignition starts, minimal external heating may be required depending on the amount of heat released. The entire process occurs in a short period of time (few milliseconds). During the conversion reaction, the sample reaches a temperature known as the adiabatic temperature (T_{ad}). The adiabatic temperature is the maximum temperature attained by the compact during the reaction [11]. T_{ad} can be calculated using the formula given by

$$\Delta H = \int_{298}^{T_{ad}} C_p dt, \quad (2)$$

where ΔH is the change in enthalpy of the reaction and C_p is the sum of the heat capacities of the reactants [11,12].

Many refractory materials have been successfully fabricated by this method [11–15]. Pure reactants used in this method ensure the purity of the end product. The heat released during the reaction can also be used to simultaneously sinter the compact by applying a small pressure during the course of the reaction. This process is referred to as reaction sintering.

Under normal circumstances, the reaction, T_{ig} , T_{ad} , and sustenance of the wave depend on various thermodynamic and thermophysical parameters such as: the external heat rate (before reaching T_{ig}), initial size of the reactant particles, the degree of compaction (pressure applied before or during the reaction), and mixing time of the reactants. At slow heat rates the process competes with solid state diffusion. If the heat rate is very high, the entire reaction becomes an explosion reaction where a physical explosion occurs destroying the green body.

It has been observed that the chances of a stable combustion synthesis reaction are dependent upon the size of the reactant particles. The smaller the size of the particles, the greater is the probability of the reaction and greater is the probability of wave sustenance, which can be explained in part by higher surface to volume ratios and higher packing density leading to increased contact between reactant particles [11]. A thoroughly compacted green body

provides adequate contact between the grains of the reactants thus enhancing the chances of a rapid reaction [11]. At the same time, the thermal conductivity of the reactants in a high density green body ensures that heat is conducted away from the reaction zone, which might inhibit the sustenance of the reaction. Hence an optimum level of green body density has to be achieved during compaction as these two opposing mechanisms tend to compete with each other. As the size of the reactant particles decreases, the mixing time increases. Thorough mixing is required to ensure homogenous distribution of the reactants [11]. The production time and the ensured purity of the products make this method attractive in comparison to the carbo-thermal reduction method discussed earlier.

As the reaction proceeds, heat is lost by conduction and radiation from the compact thus inhibiting the reaction sintering process and hence affecting the final density/porosity of the compact [11,12]. This in turn will have a major effect on the properties of the material such as thermal conductivity, structural strength, the quality of the compact and, for later study, the effective retention or bonding of any dispersed non-reacting components (such as separately produced and mixed fuel microspheres) [12].

3. Experimental

Cylindrical compacts containing ZrC were produced at the Nuclear Materials Laboratory, University of South Carolina by the direct combustion synthesis (CS) reaction of mixed zirconium and graphite powders as a part of ongoing research on dispersed nuclear fuel for use in GFRs.

3.1. Experimental phase I

In the first phase of the experiment, 99.99% pure powders of zirconium (44 μm) and graphite (44 μm) obtained from Alfa Aesar, in a molar ratio of (1:1) were thoroughly mixed in a ball mill for 3 h. Mixing and cold pressing were performed in a positive pressure glove box under high purity argon atmosphere to avoid any contamination. The mixture was cold pressed in a stainless steel die-punch assembly to form cylindrical green bodies of 2.54 cm height and 1.27 cm diameter by employing a hydraulic press. In the four similar runs conducted, a maximum 280 MPa was applied to the compact for duration of 15 min. Breaking of the compact during extraction was observed during initial green body preparation. To overcome this problem and to obtain a stable green body, 0.5 wt% oleic acid binder was added to the powders and mixed as before.

The extracted green body was placed horizontally on a graphite slab with a 1.3 cm groove cut in the center. A 0.158 cm diameter, 9 cm long, pure tungsten electrode was placed close to the top of the compact perpendicular to the axis of the compact. Care was taken to ensure that a gap of at least 3 mm existed between the tungsten filament and the circular top surface of green body to avoid any reaction or inter-diffusion. The entire assembly was placed in a

vacuum chamber evacuated to 4 mTorr and back filled with helium gas at 1 atm. A small welding power source capable of delivering a maximum current of 250 A was connected to the tungsten rod through insulated vacuum feedthroughs. The experimental setup is shown in Fig. 1.

The tungsten rod was heated to 1200 $^{\circ}\text{C}$ at a rate of 400 $^{\circ}\text{C}/\text{min}$. Two Ircon-Modline-3 optical infrared pyrometers were employed to measure the process temperatures. The first pyrometer which had a range of 700–2200 $^{\circ}\text{C}$ was employed to measure the temperature of the tungsten filament and hence the ignition temperature (T_{ig}). The second pyrometer which had a range of 1500–3500 $^{\circ}\text{C}$ was employed to measure the adiabatic temperature (T_{ad}) at a particular point on the green body. The data from the pyrometers was recorded by a digital strip chart recorder. Four similar runs were performed with constant cold pressing pressure, mixing time, pressing time, binder content and reacting particle size to observe statistical variations in the ignition and adiabatic temperatures.

The bulk density of the samples was measured using an XS-105 Metler Toledo balance and density measurement kit by first measuring the weight of the sample in air and then in distilled water. Open surface porosities of the samples were measured by a Quantachrome Poremaster-33 mercury porosimeter. The samples were subject to mercury intrusion and extrusion measurements at both low and high pressures up to 0.35 and 228 MPa respectively. The total intruded pore volumes were obtained from the porosimeter to calculate the open surface porosity of the samples. The resultant data of the experiment are shown in Table 1. Samples produced were further analyzed for

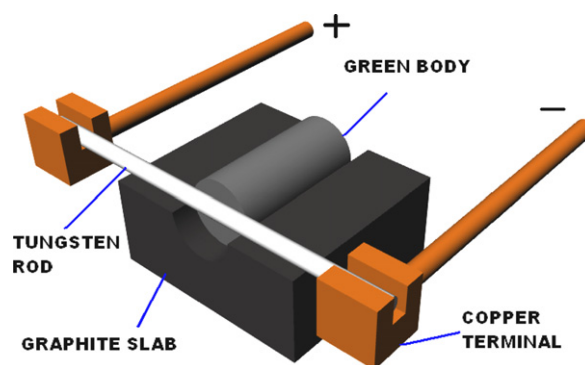


Fig. 1. Experimental setup of tungsten rod heating experiment for measurement of ignition and adiabatic temperatures.

Table 1
Results of first phase of the experiment

| Trial | Zirconium particle size (μm) | Ignition temperature ($^{\circ}\text{C}$) | Adiabatic temperature ($^{\circ}\text{C}$) | Relative density (%) |
|-------|---|---|--|----------------------|
| 1 | 44 | 1200 | 2495 | 38.1 |
| 2 | 44 | 1200 | 2528 | 38.6 |
| 3 | 44 | 1200 | 2422 | 36.2 |
| 4 | 44 | 1200 | 2428 | 36.7 |

microstructure using a Quanta-700 scanning electron microscope (SEM) and phases present were confirmed by X-ray diffraction (XRD) technique.

3.2. Experimental phase II

In the second phase, 99.99% pure powders of zirconium (44 μm) and graphite (44 μm) were thoroughly mixed in the ball mill for 3 hours and small quantities of mixed powders with frequent and thorough tamping were poured into a cylindrical graphite die. Graphite punches were employed to apply uniaxial pressure to the tamped powder. Enough mixture was poured to produce 2.54 cm long, 1.27 cm diameter compacts with 60% green body density. The assembly was inductively heated to 2440 $^{\circ}\text{C}$ by employing a 125 kW induction power source. The experimental setup is shown in Fig. 2. Three runs with applied pressures of 1.4, 3.5, and 5.2 MPa were performed for this particular powder size. Each run had a maximum temperate hold time of 15 min. The external heat rate was adjusted to 400 $^{\circ}\text{C}/\text{min}$ to match the experiment in the first phase. The same optical pyrometers were employed to measure the temperature of the graphite susceptor and the data was subsequently recorded by a digital chart recorder. Trials were repeated at each of the applied pressure values to observe any statistical variations in the product characteristics.

For subsequent trials, 2–3 μm zirconium powder obtained from Alfa Aesar was used. The size of graphite particles remained unchanged at 44 μm . All other conditions remained the same to evaluate the effects of particle size on the final product characteristics. Trials were repeated at each of the applied pressure values to observe any statistical variations in the product characteristics.

Table 2

Results of second phase of the experiment

| Trial | Zirconium particle size (μm) | Applied pressure (MPa) | Bulk density (g/cm^3) | Total porosity (%) | Open porosity (%) | Average porosity (%) |
|-------|---|------------------------|---|--------------------|-------------------|----------------------|
| 1 | 2–3 | 1.4 | 4.613 | 30.10 | 18.06 | 28.75 |
| 2 | | | 4.791 | 27.40 | 16.44 | |
| 3 | | 3.5 | 5.908 | 10.47 | 6.28 | 10.675 |
| 4 | | | 5.882 | 10.88 | 6.09 | |
| 5 | | 5.2 | 6.119 | 7.28 | 4.20 | 7.68 |
| 6 | | | 6.066 | 8.08 | 4.08 | |
| 7 | 44 | 1.4 | 5.112 | 22.5 | 14.15 | 23.24 |
| 8 | | | 5.017 | 23.98 | 15.56 | |
| 9 | | 3.5 | 5.370 | 18.62 | 13.03 | 17.12 |
| 10 | | | 5.426 | 17.79 | 9.78 | |
| 11 | | 5.2 | 5.562 | 15.73 | 9.44 | 16.09 |
| 12 | | | 5.514 | 16.45 | 10.20 | |

The same instruments and techniques were used to characterize the microstructure, phases present, density, and porosity as described in phase one above. The resultant data from the experiments are shown in Table 2.

4. Results and discussions

In the first phase of the experiment where the green body containing 44 μm , zirconium and graphite powders was heated using the tungsten rod, the combustion wave was observed to set in when the temperature of the tungsten filament reached 1200 $^{\circ}\text{C}$. This particular ignition temperature was observed in all the four statistical runs. However, the observed adiabatic temperatures varied from 2422 to 2528 $^{\circ}\text{C}$ as shown in Table 1, followed by a steady decrease in the temperature due to conduction. It is noted here that the median temperature achieved during combustion synthesis was greater or equal to two-thirds the melting point of ZrC (sufficient to expect some degree of sintering). The sample was observed to glow indicating very high temperatures after the passage of the wave. A plot of the pyrometer readings showed a sharp peak at the point of focus on the green body surface indicating the passage of the combustion wave through the point within a fraction of a minute.

Simple visual inspection of the samples indicated partial sintering of the green body. This observation is significant in view of the fact that the compact was not fully supported nor any pressure was applied. The partial sintering could be explained in part due to the temperatures attained during the reaction and duration of the reaction itself. SEM revealed a highly porous microstructure as shown in Fig. 3. A maximum of 38.6% theoretical density was observed in the partially sintered compacts. XRD analysis of compacts revealed that the reaction was complete and the mixture had been converted into pure, stoichiometric ZrC as shown in Fig. 4.

The results of this phase clearly showed that combustion synthesis was occurring converting the compacts into ZrC.

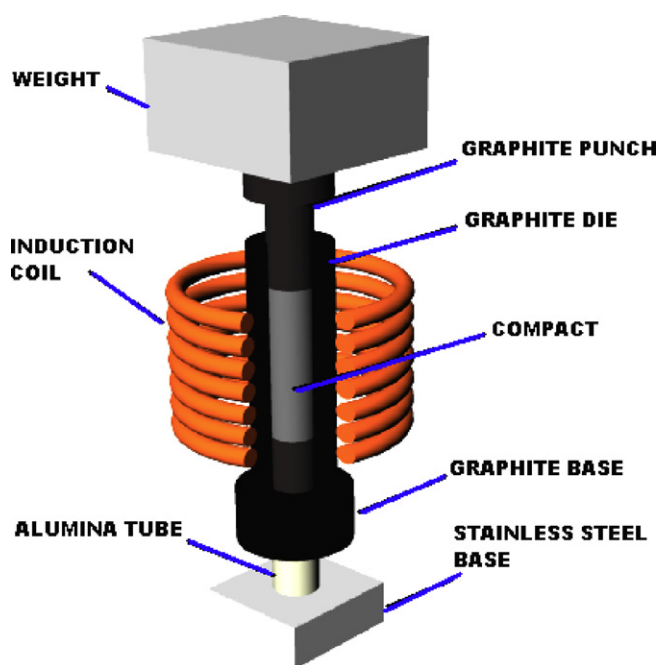


Fig. 2. Experimental setup of the induction heating experiment.

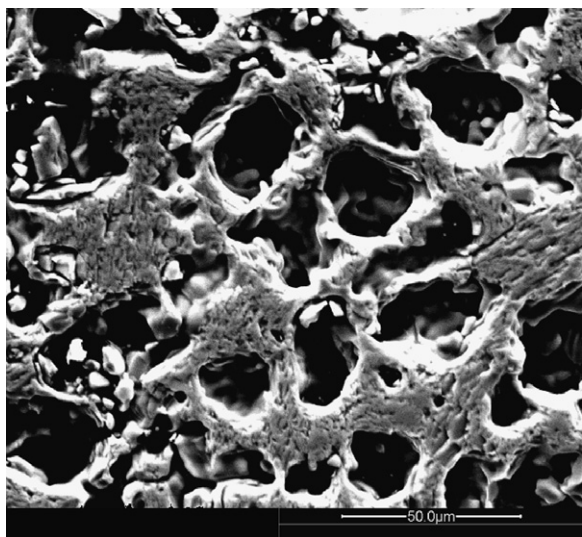


Fig. 3. Scanning electron micrograph showing highly porous microstructure as a result of pressureless sintering. Maximum density achieved in such samples was 38.6%.

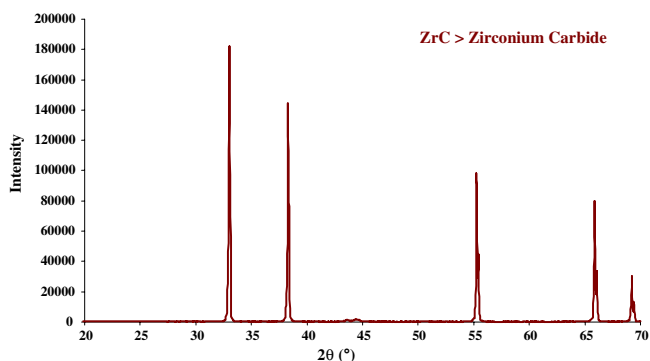


Fig. 4. Results of XRD analysis of sample-3 from Table 1 indicating complete conversion of reactants to ZrC.

However, losses due to conduction in the sample and convection in the flowing gas, lack of external pressure, and duration of time for which the sample was exposed to high temperature prevented a high degree of sintering. This clearly indicated the need for an additional driving force for sintering either longer time at high temperature and/or applied pressure.

In the second phase of the experiment, external heating in the form of induction heating with a graphite susceptor was provided for the purposes of ignition and a short period of extended sintering. The samples obtained were well consolidated owing to the increased driving force provided by the applied external pressure. Diffusion bonding with the graphite punch was observed requiring the ends of the samples to be cut in order to separate the compacts. In samples where 44 μm size zirconium powder was used, the density increased with increasing pressures as expected. A maximum theoretical density of 84% was achieved with the applied pressure of 5.2 MPa. XRD analysis indicated that the reaction was complete in all the runs and the sam-

ples contained ZrC and no free zirconium or graphite. SEM revealed strongest intra-granular bonding in case of 5.2 MPa as compared to cases of 1.4 and 3.5 MPa. Representative micrographs and results of the XRD analysis of sample 12 of Table 2 are shown in Fig. 5 and Fig. 6 respectively. Porosity measurements showed that the number of large voids decreased with increased pressure as expected with the samples produced with 1.4 MPa having the highest number of larger voids thus increasing the total pore volume. The variation in measured open porosity with applied pressure is shown in Table 2.

For samples fabricated from 2–3 μm zirconium powder, XRD similarly revealed that pure, stoichiometric ZrC was produced. The density also increased with increase in pressure as expected. A maximum theoretical density of 92% was achieved with an applied pressure of 5.2 MPa compared to 84% obtained with 44 μm zirconium powder.

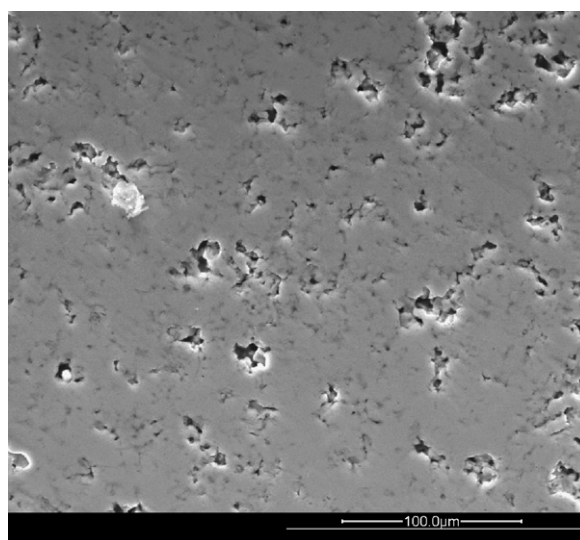


Fig. 5. Scanning electron micrograph of sample-12 of Table 2 fabricated with 44 μm zirconium powder and applied pressure of 5.2 MPa showing a fair amount of intra-granular bonding. Large pores can be easily seen from the micrograph.

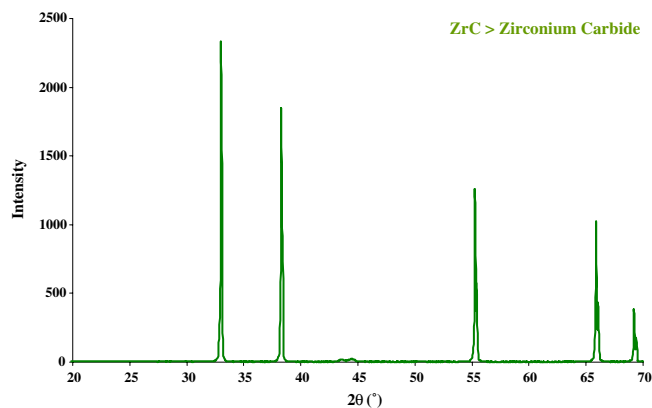


Fig. 6. Results of XRD analysis of sample-11 from Table 2 fabricated from 2–3 μm zirconium powder with an applied pressure of 5.2 MPa.

The significant increase in density for samples with smaller zirconium particles could be attributed in part to the increased contact between the reactants. SEM of these samples indicated a very high degree of consolidation in cases of 5.2 MPa applied pressure compared to cases of 1.4 and 3.5 MPa. SEM also indicated that very few large voids were present in these samples in comparison to the ones containing 44 μm zirconium. The representative scanning electron micrographs and results of the XRD analysis for sample-5 of Table 2 are shown in Fig. 7 and Fig. 8 respectively.

For all samples, non-uniform porosity/density was observed with lower porosity close to the center and top half of the compact compared to higher porosity close to the bottom end of the cylindrical compact. This may be explained in part by variation in the applied stress throughout the length of the compact given the fact that the die-

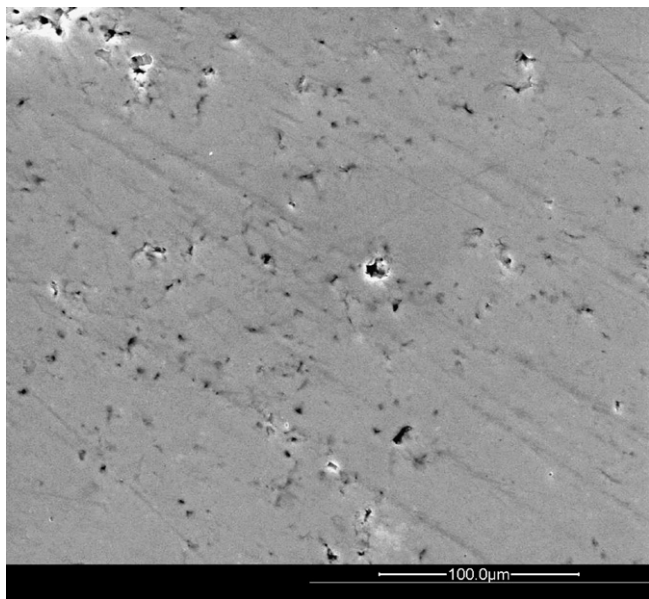


Fig. 7. Scanning electron micrograph of sample-5 from Table 2 fabricated from 2–3 μm zirconium powder with an applied pressure of 5.2 MPa showing strong intra-granular bonding.

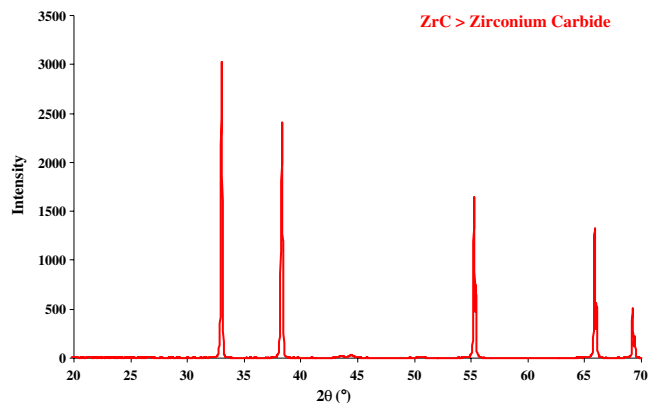


Fig. 8. XRD analysis of sample-5 from Table 2 fabricated from 2–3 μm zirconium powder with an applied pressure of 5.2 MPa.

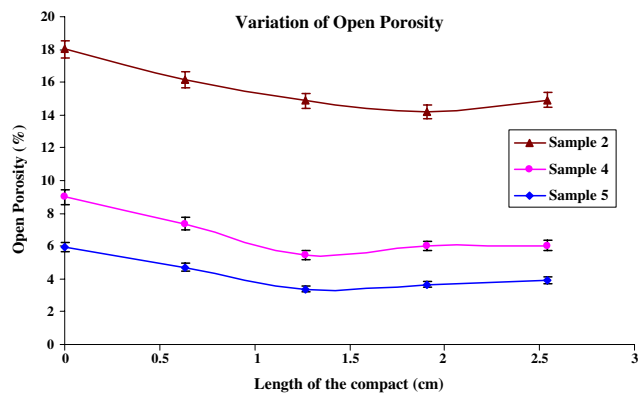


Fig. 9. Variation in open porosity along the axial length of samples 2, 4, and 5 from Table 2. The bottom of the compact is 0 cm (see Fig. 2 for setup).

punch assembly was a single ended system with only the top punch being allowed to move [19,20]. The uneven stress providing a variable driving force for sintering could then result in zones of varying porosity in the compacts [20–22].

The process of filling the die and tamping the powder will produce varying densities in the green body, which would give rise to varying rates of combustion and sintering or consolidation during the reaction leading to non-uniformities in the porosity. Finally, the general rapid heating and cooling and any additional non-uniformity of the combustion wave is also likely to cause an uneven stress distribution in the compact [20–22]. The axial variation in the porosity for three samples is shown in Fig. 9. Error bars are indicated by estimating the uncertainty in the measured data by repeated measurements of a standard sample where a maximum of 7% variation was observed. It is likely that these non-uniformities could be eliminated by further high temperature sintering. However, this would run counter to the objective of producing the compacts in short times at high temperatures to limit minor actinide losses in the future intended composition and composite form.

Superimposing the observations of the two experiments, it can be argued that induction heating initiated combustion synthesis in the second set of experiments. The heat from combustion synthesis facilitated reaction sintering but by itself was not sufficient to produce a high density compact. However, combustion synthesis initiated by external heating and maintaining samples at 2440 °C for an additional 15 min with applied pressures up to 5.2 MPa did produced samples with densities as high as 92% TD.

5. Conclusions

Sintered cylindrical pellets of pure, stoichiometric ZrC were produced in the laboratory by combustion synthesis. When no pressure was applied during combustion synthesis, results indicated that the heat released during the reaction was enough to complete the reaction and achieve theoretical densities only up to 39%. Subsequent heat loss from the compact prevented further reaction sintering.

The ignition and adiabatic temperatures of the reaction were measured.

In the second phase of experiments, two different powder sizes of zirconium were used to produce the compacts. Three different pressures were applied to the compacts through uniaxial pressing during the trials. A maximum theoretical density of 92% was observed in samples with an applied pressure of 5.2 MPa. Samples with larger size zirconium powder were found to have higher porosities than samples with smaller zirconium particle size. The porosity of the compacts decreased with increasing pressure as expected.

It was concluded that the combustion synthesis method with applied external pressure could produce compacts of a quality necessary for further study with the inclusion of dispersed fuel microspheres produced separately that do not take part in the combustion reaction. Further study of non-uniform porosity in the compact would best be addressed through examination in their intended form with the dispersed microspheres present.

Acknowledgements

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