O U R N A L O F

Ceramic Processing Research

Fabrication of high density pellets of ZrO₂ via particle processing

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Fabrication of oxide nuclear fuels has generally been unsuccessful due to the instability of fuel loss of americium oxide during the high temperature sintering process. A low temperature-processing route that enables near net shapes in almost theoretical density is highly desirable. In order to carry out low-temperature processing, it is necessary to design oxide blends with controlled particle sizes. A compact made of the right mix of particles can be pressed at room temperature to near theoretical density. Powders have been blended to form multimodal distributions. It should be possible to use these blends to isostatically press samples with fractional densities of greater than 85% at room temperature.

Key words: Particle, Density, Zirconia, Nuclear fuel.

Introduction

High density pellets of ZrO_2 have been produced by various methods for use as a simulant material for UO_2 . UO_2 is a component in the MOX (metal oxide) fuel for the generation IV nuclear reactors. During the sintering stage for this multi-component fuel, one of its components (americium oxide) is lost due to its high vapor pressure.

It would be advantageous if fuel pellets could be prepared at room temperature to a high enough density that a high temperature sintering stage could be reduced or all together eliminated.

This paper is a continuation of a previous paper on this subject [1] that reported on the fabrication of high density pellets of ZrN made by various particle processing routes.

Experimental

Cylindrical zirconia pellets of approximately 0.5 cm height by 0.5 cm in diameter were made by using a variety of processing techniques. Ball milling followed by uniaxial pressing and then isostatic pressing was one route taken. Another was Spex milling (both wet and dry) followed by ball milling followed by uniaxial pressing and lastly isostatic pressing is an example of another. Lastly, resonant acoustic mixing followed by uniaxial pressing and then isostatic pressing was employed. Various powder blends were used as suggested in [2, 3] such as bimodal, trimodal, quadramodal, and five component blends. Table 1 lists the various processing approaches used in this study and Table 2 lists the various powder blends for resonant mixing. Table 3 shows the density results from resonant mixing while Table 4 shows the composition of the four and five component systems along with their density range shown in Table 5.

Resonant mixing is a process that was developed by Resodyn Corporation that uses low-frequency high-intensity sound energy for mixing. Powder blends are subjected to

Table 1. Processing of ZrO₂ powders.

Method	Processing Time
Spec Mill (wet)	3-10 minutes
Spec Mill (dry)	3-10 minutes
Ball Mill (0.5 mm m	edia) 1 hr. to 60 h
Ball Mill (2 mm me	dia) 1 hr. to 72 h
Resonant Acoustic N	Aixing 30 seconds
Uniaxial Processing	27.6-165.5 MPa
Isostatic Pressing	224.1 MPa

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Bimodal: 85 wt% large particles 15 wt% small particles				
Sample	Particle Size	Wt. Fraction of blend	Total Sample Wt.	
Bimodal				
Ι	45 μm/5 μm	8.5 gm/1.5 gm	10 gm	
II	$45\mu m/100nm$	8.5 gm/1.5 gm	10 gm	
III	5 μm/100 nm	8.5 gm/1.5 gm	10 gm	
IV	45 μm/5 μm	7.7 gm/2.3 gm	10 gm	
V	$45\mu m/100~nm$	7.7 gm/2.3 gm	10 gm	
VI	5 µm/100 nm	7.7 gm/2.3 gm	10 gm	
Trimodal	100 nm	5 μm 45 μm		
VII	5.6 gm	11.25 gm 33.15 gm	50 gm	
VIII	5.5 gm	7.0 gm 37.5 gm	50 gm	

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Table 3. Pellet densities using resonant mixing.

Sample	Wt (g)	% Theoretical Density %rt
I-1	3.269	74.1
I-2	3.234	73.3
I-3	3.212	73
II-1	3.228	72.5
II-2	3.191	71.5
II-2	3.320	72.5
III-1	3.191	68.1
III-2	3.195	67.6
III-3	3.537	68
IV-1	3.341	72.3
IV-2	3.168	72.3
IV-3	3.208	
V-1	3.175	71.2
V-2	3.241	71.6
V-3	3.336	71.5
VI-1	3.196	67.7
VI-2	3.188	66.9
VI-3	3.298	68
VII-1	3.212	72.8
VII-2	3.247	72.5
VII-3	3.2000	72
VIII-1	3.239	73.3
VIII-2	3.217	73
VIII-3	3.199	72.5

Table 4. Composition of traditional powder blends.

	NOAH 4 μm- 90 μm	TOSOH- 45 µm soft aggolermates	ZTECH 45 µm soft aggolermates	Alddrich 5 µm	Aldrich 100 µm
Group I	73 wt%	10 wt%		14 wt%	3 wt%
Group II	73 wt%		10 wt%	14 wt%	3 wt%
Group III	73 wt%	10 wt%	3 wt%	14 wt%	
Group IV	73 wt%	3 wt%	10 wt%	14 wt%	
Group V	60.5 wt%	9.7 wt%	7 wt%	18.5 wt%	4.3 wt%

Table 5. Density range for four and five component blends.

Group	Average (%rt)	High (%r _t)
Ι	75	77
II	69	70
III	72	73
IV	70	70
V	72	73

g forces as high as 100 g during mixing. Zirconia blends were mixed at frequencies of from 61.15 to 61.28 Hz and all samples were exposed to 100 g forces during mechanical mixing. All powder blends were mixed for 30 seconds.

Following the mixing step, approximately 3 gram samples were uniaxially pressed (pressure ranged from 27.6 MPa to 137.9 MPa) into right circular cylinders. Samples were

then isostatically pressed at 224.1 MPa and held at this pressure for 30 seconds. Table 4 summarizes the results obtained using this type of mixing approach.

Traditional ball milling and Spex milling followed by uniaxial and isopressing were also used to fabricate green unsintered pellets of zirconia. The ball milling time was varied from one hour to as long as 72 hours while the spex milling time was varied from 3 minutes to 15 minutes. Uniaxial pressures of from 27.6 MPa to 165.5 MPa were used and samples were isopressed at 224.1 MPa. Both bimodal and trimodal blends were processed as described above and quadramodal blends were also used. Densities obtained for these powder blends ranged from 58% to 72% of theoretical.

Lastly five different powder blends were produced using NOAH, Aldrich, TOSOH and ZTECH zirconia powders. Both the TOSOH and ZTECH powders were soft aggolermates which when subjected to ball milling broke down into much smaller particles (from submicrometer size to a few micrometers). Table 4 shows the powder blends used for the traditional processing of multicomponent samples. All powder blends were ball milled using 2 mm zirconia media for 50 hours. Right circular cylinder samples of 0.5 cm in diameter and 0.5 cm in height were uniaxially pressed at 55.2 MPa followed by isostatic pressing at 224.1 MPa. Table 5 shows the density range for the various groups processed. The highest density samples were from Group I in the four component samples.

Results

Traditional dry ball milling and dry Spec milling of bimodal powder blends followed by uniaxial and then isostatic pressing resulted in densities in the range of from 60 to 72% of theoretical. Adding more components resulted in more efficient packing resulting in the most densely packed pellets of 77% of theoretical for one of the four component systems.

Mixing powders using low frequency acoustic energy resulted in pellet densities as shown in Table 3 that ranged from 67% to 74% of theoretical. The highest density obtained was 74% of theoretical and this was obtained using a bimodal blend using size fractions suggested in [4] of 85 wt% of 45 μ m and 15 wt% of 5 mm powders. The lowest densities were for those blends that contained the 100 nm powder. This may be due to the presence of large agglomerates in the 100 nm powder. Resonant mixing will not break up agglomerates.

Conclusions

Traditional ball milling and Spec milling of powder blends followed by uniaxial and isostatic pressing resulted in the highest overall pellet density. However, resonant accoustic mixing demonstrated the ability to quickly mix powder blends that resulted in compact densities not much lower than the traditional processing route. Fabrication of high density pellets of ZrO₂ via particle processing

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References

- 1. T.T. Meek, K. Gwathney, C.K. Narula and L.R. Walker, submitted to Ceramic Transactions. (Refereed)
- 2. K. Ridgway and K.J. Tarbuck, *Chemical and Process Engineering*, 1968m 49 [2] 103-105.
- 3. C.C. Furnas, *Industrial and Engineering Chemistry*, 23 (1931) 1052-1058.
- 4. R.K. McGeary, *Journal of the American Ceramic Society*, 44 (1961) 513-522.