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Microwave sintering of 8 mol% yttria–zirconia (8YZ): An inert matrix material for nuclear fuel applications

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ABSTRACT

This study focused on reducing overall processing time and temperature for fully stabilized zirconia, an inert matrix material candidate, to minimize the loss of actinides (that will be incorporated into the matrix material), while maintaining at least 90% theoretical density (TD). The effects of different processing routes on bulk density and microstructure were evaluated. The results obtained by adopting microwave sintering for 8 mol% Y_2O_3–ZrO_2 were compared to conventional sintering. A 20 min soak time at 1300 °C resulted in pellets with 90% TD for microwave-processed samples, compared to 77% TD for pellets processed conventionally. A similar density was obtained at lower temperature (1200 °C) by increasing the soak time to 100 min in microwave processing. This time and temperature resulted in 60% TD conventionally processed pellets. Compressive strength values obtained for a 1300 °C (20 min soak time) microwave-processed sample were higher (1600 MPa) as compared to a conventionally processed sample (1300 MPa).

1. Introduction

Conventional processing of ceramic nuclear fuel involves high-temperature processing of materials, generally above 1600 °C [1]. Due to these processing conditions, it is anticipated that the volatile nature of the actinide-bearing nuclear fuels will result in significant loss of material. The current research aims to process fuel pellets at the lowest possible temperatures in the shortest possible times while maintaining a minimum density of 90% TD, so as to minimize the loss of volatile actinides. This is achieved by adopting a different processing route, i.e., microwave processing. Before giving an overview of microwave processing, a brief background of nuclear fuels is presented. This is followed by experimental procedure, results and discussion.

1.1. Background

Transuranic nuclides (Pu, Np, Am and Cm) are a by-product of nuclear fission reactions [2]. Disposing these long-lived radio nuclides (e.g. ^{239}Pu with a half-life of 24000 years and americium (^{243}Am) with a half-life of 7360 years) raises questions on the long-term integrity of storage facilities [2–4]. Safe disposal methods have to be sought to isolate these long-lived radioactive materials from the public and to reliably control the inventory so that it cannot be used to produce nuclear weapons.

An alternative to storage is to produce energy by transmuting these highly radioactive nuclides (long-lived) into lighter elements (short-lived) by incorporating them in an inert matrix [5,6]. Inert matrix fuels (IMF) are relatively new fuel designs [7] which provide an option to avoid the fertile reaction by replacing the fertile material with one that is 'relatively' transparent (neutron absorption cross-section <2.7 barns [8]) to neutrons. It is expected that during conventional sintering of IMFs containing Am, the potential for Am evaporation is high. This phenomenon is due to the high vapor pressures exhibited by Am (g) and its oxides (Am_2O_3, AmO (g), AmO_2 (g)) [9,10] under normal sintering conditions. One possible approach to prevent the loss of Am is to adopt microwave processing, which can decrease the overall processing time and temperature.

1.2. Microwave processing

The ability of certain materials to convert the electromagnetic energy into heat makes microwave processing possible [11]. For non-magnetic dielectric materials the electric field in a microwave will polarize the charges. These charges tend to follow the oscillating electric field within the material. The incapability of these charges to follow the continuously altering electric field will lead to the loss of electromagnetic energy within the material. This loss in electromagnetic energy within a material would result in a rise in temperature $\left(\frac{\Delta T}{\Delta t}\right)$ which is given by

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$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_0 \varepsilon''_{\text{eff}} E^2_{\text{rms}}}{\rho C_p} \left(\frac{^\circ\text{C}}{\text{sec}}\right), \quad (1)$$

where $\varepsilon''_{\text{eff}}$ is a unit less quantity that accounts for dielectric losses due to ionic and dipolar reorientation, f is the frequency of the microwave $\left(\frac{1}{\text{sec}}\right)$, ε_0 is the permittivity of free space $\left(8.85 \times 10^{-12} \left(\frac{F}{m}\right)\right)$, E^2_{rms} is the root mean square of the electric field within the material $\left(\frac{V}{m}\right)$, ρ is the bulk density of dielectric material $\left(\frac{\text{kg}}{\text{m}^3}\right)$ and C_p is the specific heat of the material at constant pressure $\left(\frac{\text{J}}{\text{kg}\cdot^\circ\text{C}}\right)$ [12].

Microwave hybrid heating (MHH) is a technique developed to process materials that are low microwave absorbers ($\varepsilon''_{\text{eff}} < 0.08$) at room temperature and show good microwave absorption ($\varepsilon''_{\text{eff}} > 1$) at higher temperatures. In MHH, the initial heating is provided by means of a susceptor. A susceptor is a microwave-absorbing material which supplies heat to the sample (through conduction/convection) until a critical temperature (T_c) is reached. At that point, the sample starts to absorb microwaves and heats independent to the susceptor. In MHH, the sample experiences a combination of both conventional (radiant) heating and microwave heating. This technique may also be used for processing high microwave-absorbing materials, as this technique would provide uniformity in heat distribution within a furnace/oven.

Numerous reports have been cited in the literature on the advantages of MHH over conventional heating [13–19]. For instance, Janney et al. [13] reported a 100–150 °C reduction in sintering temperatures. Goldstein et al. [15] achieved fully sintered samples (5 mol% Y_2O_3–ZrO_2) using MHH at temperatures as low as 1200 °C with a 15–20 min dwell time. Dé [17] reported enhanced results in density, homogeneity in microstructure, and uniformity in mechanical properties for a microwave hybrid sintered Al_2O_3 as compared to a conventionally sintered Al_2O_3.

2. Experimental procedure

2.1. Materials

Commercially available 8 mol% Y_2O_3–stabilized ZrO_2 (8YZ[1]) powders produced through a hydrolysis process in the form of spray dried granules were used for this study. The detailed compositional analysis is shown in Table 1.

2.2. Pellet fabrication

Green pellets (or unfired pellets) were fabricated using uniaxial pressing followed by isostatic pressing. Four grams of as-received powder were poured into a uniaxial mold of 12.5 mm diameter and 70 mm height and subjected to a pressure of 37 MPa. Uniaxially pressed pellets were transferred to isostatic bags and were further subjected to different pressures up to a maximum of 200 MPa.

2.3. Sintering

A commercially available microwave oven[2] (2.45 GHz fixed frequency unit with a maximum power rating of 2100 W) was used for the study. Home model microwave ovens usually have a cavity which supports a large number of resonant modes in a given frequency range. These cavities are also termed as *multimode microwave cavities*. The insulation system for this cavity was built using a refractory material made from aluminosilicate fibers[3] capable of withstanding temperatures up to 1700 °C. A susceptor was made by mixing 2 wt% partially stabilized ZrO_2 with 98 wt% Al_2O_3 cement. A desired heating rate of 20 °C/min was maintained by manually switching the power on and off. Temperature measurements for all the sintering runs were monitored using a two-color pyrometer.[4] The field of view of the pyrometer (20 mm) was larger than the sample size (~13.2 mm); therefore, three samples were sintered simultaneously so as to fill in the field of view and avoid any discrepancies with the temperature reading.

The conventional sintering runs were performed in a high-temperature furnace.[5] Temperature measurements for all conventional sintering runs were monitored using an R-type thermocouple. A feedback controller maintained a constant heating rate of ~20 °C/min for all the sintering runs.

Table 1
Compositional analysis for 8YZ.

Composition	Mol%
ZrO_2	91.9813
Y_2O_3	7.8385
Al_2O_3	0.0063
SiO_2	0.0065
Fe_2O_3	0.0032
Na_2O	0.1639

2.4. Characterization and testing

The particle size distribution was determined through sieve analysis, particle size analyzer[6] and scanning electron microscope.[7] Scanning electron microscopy (SEM) was also used for imaging the fracture surface of sintered and green samples. Green densities of the samples were calculated from geometric measurements. Bulk densities for the sintered samples were measured using the liquid displacement method according to ASTM C 373. Theoretical density was determined through X-ray diffraction analysis.

Samples for compression testing were harvested from ~9.5 mm diameter disks (4 mm height) that were cut from the pellets using a diamond wafering saw. These disks were quartered using the same saw. These quarters were then ground into small rectangular parallelepipeds (~2.5 mm × 2.5 mm × 2.7 mm) using a 6 μm diamond-impregnated grinding disk followed by 600 grit SiC paper. Uniaxial compression was performed at ambient temperature using a servo-hydraulic load frame[8] with a displacement rate of 0.002 in./min. A custom-made self-aligning fixture was used for testing. Compression testing was also performed at the same displacement rate and with the same fixture at an intermediate temperature (800 °C) in a gettered ultra-high purity argon atmosphere.

3. Results and discussion

3.1. Powder characterization and its compaction behavior

Powder characterization shown in Fig. 1(a)–(c) was performed using SEM imaging, sieve analysis, and particle size analysis, respectively. The SEM imaging of the as-received powder is shown in Fig. 1(a). It can be observed that the starting powders mainly consisted of agglomerates/granules of ~50 μm in size. The inset in Fig. 1(a) shows that the average particle size within the agglomerates was less than 0.5 μm. The results from SEM observations

[1] TZ-8Y, Tosoh Corporation, USA.
[2] Panasonic model no. NE 2157R.
[3] Rathboard KVS/400.
[4] Omega, model no. OS3750.
[5] CM bloomerg model no. 0100153.
[6] Horiba model no. LA-950.
[7] LEO (Zeiss) 1550.
[8] Instron 1331.

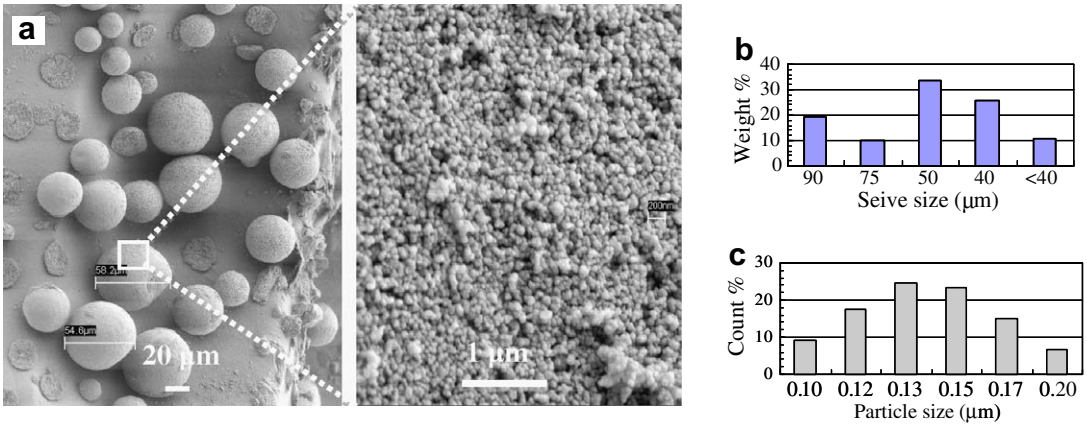

Fig. 1. (a) SEM imaging of 8YZ powder, and particle size distribution through (b) sieve analysis and (c) particle size analysis.

were confirmed through sieve analysis and particle size analysis. Fig. 1(b) is a plot between the weight fractions of particles on each screen vs. the screen size. As can be seen in Fig. 1(b), the average particle size was ~50 μm. As the lower limit of measurement with sieves was ~20 μm, particle size analysis was used to determine the actual particle size. The results from particle size analysis are shown in Fig. 1(c); it is plot between count fractions of particles vs. the particle size diameter. It shows that the particles within the agglomerates were less than 0.3 μm. This result was used to confirm the SEM observations. It was concluded that particles were in the form of ~50 μm agglomerates during the fabrication of green pellets.

The compaction behavior of these powders can be seen in Fig. 2. There was an increase in green density with increasing pressure (isostatic) from 35 to 200 MPa analysis, and particle size analysis, respectively. Gibson et al. [20] observed a similar behavior for 8YZ powders produced through a co-milling technique. Due to the limitation with the operating pressure in the isostatic press, the green pellets selected for this study were ~46% TD (X-ray calculated as 5.96 g/cc).

3.2. Sintering behavior of 8YZ

3.2.1. Effect of processing technique and temperature on density

Microwave and conventional furnaces were used to study the sintering behavior of 8YZ pellets (shown in Fig. 3). All sintering runs had a constant soak time of 20 min. Fig. 3 is a plot of bulk densities, expressed as a percentage of theoretical density vs. sintering temperature. At low temperatures (i.e., 1100–1300 °C), the densities obtained in microwave-sintered pellets were significantly higher than those achieved in conventionally sintered pellets. At high temperatures (1400 and 1500 °C), the densities obtained for microwave-processed samples were slightly lower when compared to the conventionally processed samples. A significant difference in densities can be seen in 8YZ pellets at a processing temperature of 1300 °C. A value of 91% TD was obtained for the microwave-processed sample as compared to a 77% TD for the conventionally processed sample.

There are differences in density values obtained in this work when compared to the values reported in literature. Janney et al. [13] showed >99% TD for a microwave-sintered 8YZ pellet at 1195 °C. This difference may be attributed to the starting powders and green pellet fabrication. Janney used an isostatic pressure of 210 MPa to fabricate green pellets and prefired the pellets (green) at 1100 °C before subjecting them to microwave sintering. A one-to-one comparison with Janney's results is difficult as the dwell times for the sintering cycle were not the same, i.e., 1 h (Janney's study) vs. 20 min (this study). Samuels and Brandon [18] obtained a similar difference in density values at 1300 °C for a material similar in structure to 8YZ, i.e., 12 mol% Y_2O_3–ZrO_2. They observed ~85% TD for a microwave hybrid sintered sample to ~61% TD for a conventionally sintered sample. A microwave sintering study on 8YZ performed by Nightingale et al. [14] showed a density value of ~89% TD at 1300 °C. Nightingale's value is in close agreement with this work (~91% TD).

Microstructural characterization of pellets processed at 1300 °C was performed via SEM. As a baseline for comparing the microstructural evolution of sintered pellets, SEM imaging was also performed on a green pellet. Fig. 4 contains fractographic images of a green pellet, a conventionally sintered pellet and a microwave-sintered pellet. Individual particles with very little interconnection and grain growth can be clearly seen in Fig. 4b, indicating that

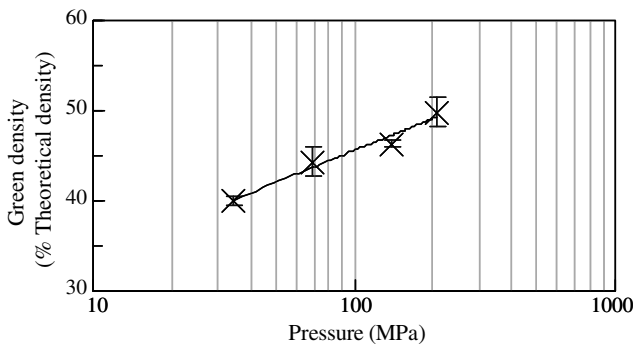

Fig. 2. Effect of isostatic pressure on green density of 8YZ pellets.

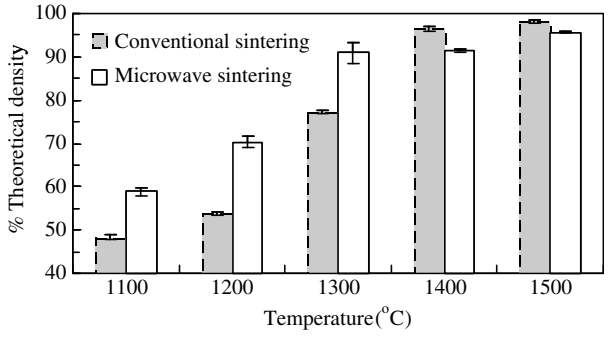

Fig. 3. Effect of processing technique and temperature on densification behavior of 8YZ.

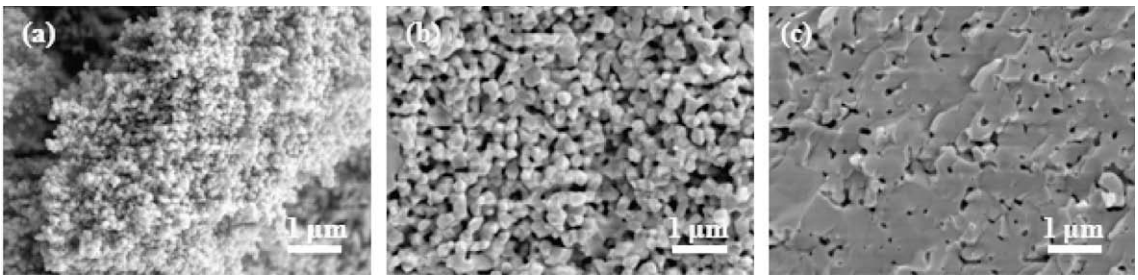

Fig. 4. Fracture surface imaging of (a) a green pellet, (b) a conventionally sintered pellet and (c) a microwave-sintered pellet.

there is less sintering between particles for this sintering profile. Whereas, Fig. 4(c) is an image which shows an enhancement in sintering (i.e., increased particle interconnection, densification and grain growth). From these images, it is clear that the microstructure of the conventionally sintered pellet (Fig. 4(b)) is similar to its green state (Fig. 4(a)) for this specific set of sintering conditions, unlike the microwave-sintered pellet (Fig. 4(c)) which exhibits more traditional sintering characteristics.

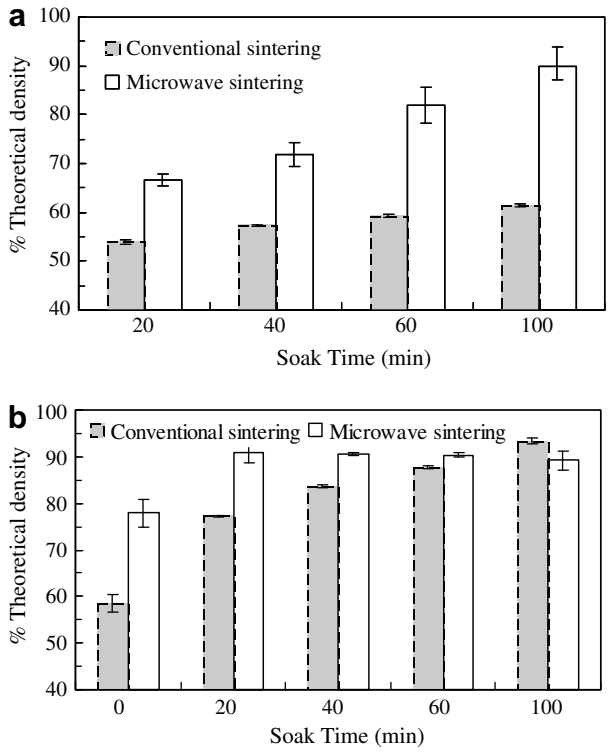

Fig. 5. Effect of processing technique and time on densification behavior of 8YZ at (a) 1200 °C and (b) 1300 °C.

3.2.2. Effect of processing technique and time on density

To further understand the sintering behavior of 8YZ, isothermal sintering experiments were performed at 1200 °C and 1300 °C. Fig. 5(a) and (b) shows the isothermal sintering behavior of 8YZ processed in microwave and conventional furnaces.

At 1200 °C, microwave-processed pellets showed a substantial increase in bulk density from 67% to 90% TD with increase in soak time from 20 to 100 min (Fig. 5(a)). A similar set of experiments performed in a conventional furnace at 1200 °C resulted in a slow increase in density values from 54% to 60% TD (Fig. 5(a)). The rate of increase in bulk density for microwave-processed samples was higher than for conventionally processed samples at 1200 °C. The 8YZ pellets showed very little or no sintering at 1200 °C in a conventional furnace. Isothermal sintering runs performed at 1300 °C (Fig. 5(b)) show that there was no change in density values for microwave-sintered pellets after 20 min as they had achieved their maximum density (~90% TD) for that temperature; whereas, isothermal sintering in a conventional furnace showed a gradual increase in density from 58% to 93% TD with increase in soak time (0–100 min).

As was observed in Fig. 3, temperature had a significant effect on densification for the microwave as well as the conventionally processed samples. The results shown in Fig. 5(a) imply that, at lower temperatures, time (kinetics) has a significant effect on densification for the microwave process than the conventional process. Sintering is a process of bonding particles through heat treatment, resulting in a solid structure. Particle–particle bonding takes place through various types of mass transport mechanisms along the particle–particle interface [21]. These results are indicating that at low temperatures, the mass transport mechanisms responsible for sintering are taking place at a faster rate in a microwave sintering process then in a conventional sintering process.

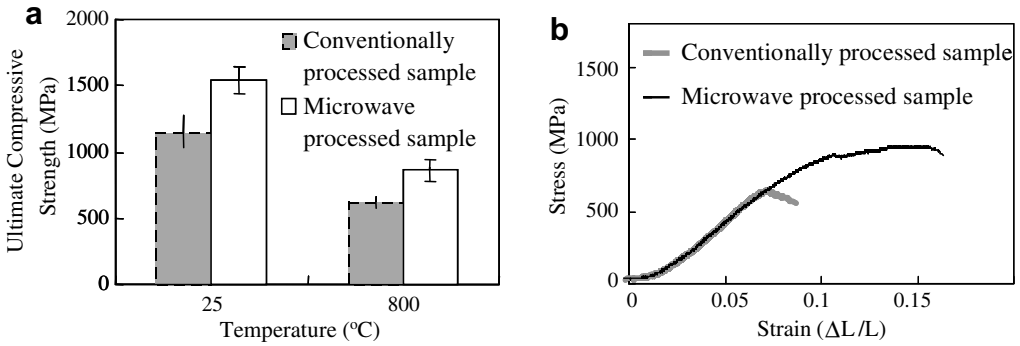

Fig. 6. (a) Comparison of strength for 8YZ at 25 °C and 800 °C; (b) engineering stress–strain plot at 800 °C.

3.3. Compression testing

Compression testing was performed at both ambient (25 °C) and elevated temperatures (800 °C) in order to evaluate the temperature dependence of the mechanical strength of these materials. Samples sintered at 1300 °C with a soak time of 20 min were selected for the comparative study. The results are presented in Fig. 6.

At both 25 °C and 800 °C (Fig. 6(a)) the microwave-processed samples have a higher compressive strength as compared to the conventionally processed samples. Both sample types exhibit a similar reduction in compressive strength when tested at 800 °C. Fig. 6(b) is the engineering stress and strain plots at 800 °C, and it can be observed that the microwave-sintered samples show an increased capacity for damage tolerance when compared to the conventionally sintered samples. It is possible that the structure of the conventionally sintered sample was not stable enough to withstand the micro-cracking to the same degree as the microwave samples at elevated temperatures. The density difference is undoubtedly a contributing factor to the strength and damage tolerance difference of these two sample types (77% TD conventionally sintered sample vs. 91% TD microwave-sintered sample).

4. Summary

The initial objective for this study was to process materials at lowest possible temperatures in shortest periods of time while achieving at least 90% TD. From the results obtained, it can be concluded that low-temperature processing can be accomplished using MHH. By adopting microwave sintering, 90% TD (in 8YZ) can be obtained at lower temperatures (i.e., 1200 °C with a soak time of 100 min) or in shorter periods of time (i.e., 20 min at 1300 °C). It was also observed that, at 1200 °C, time had a significant effect on the densification process of 8YZ in a microwave process than conventional process. The microwave-processed samples showed a higher compressive strength (1600 MPa) than conventionally processed samples (1300 MPa). Even at higher temperatures (800 °C), the microwave-processed samples showed higher compressive strength and an increased capacity to accumulate damage than the samples processed conventionally.

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