Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 561–565
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

# Microwave sintering of simulated inert matrix fuel for generation IV nuclear reactors

R.R. Thridandapani [*], D.C. Folz, D.E. Clark

*Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*

Received 17 July 2010; received in revised form 6 August 2010; accepted 24 September 2010
Available online 28 October 2010

## Abstract

Alternative processing methods are being considered for rapid sintering of inert matrix fuel (IMF) at low temperatures to minimize the loss of volatile actinides. Previous studies on microwave-hybrid sintering of the matrix material, 8 mol.% yttria–zirconia (8YZ), showed rapid densification at lower temperatures when compared with a conventional process. The current study examines the applicability of dysprosia ($Dy_2O_3$) as a surrogate for americia ($Am_2O_3$) in investigating the microwave-hybrid sintering of a simulated IMF, 20 wt.% $Dy_2O_3$ dispersed in 8 mol.% yttria–zirconia (8YZ-20D). The results show that 8YZ-20D is sintered to 93% of its theoretical density (TD) at 1300 °C with a soak time of 100 min in a multimode microwave-hybrid furnace. A similar heating schedule in a conventional furnace resulted in 87% TD. The enhancement in densification of 8YZ-20D due to microwave-hybrid sintering did not alter any of the resulting microstructures. Based on these experiments, it was found that low-temperature microwave-hybrid sintering was suitable for fabricating IMF pellets.

*Keywords:* Microwave sintering; Inert matrix fuel; Nuclear fuels; 8 mol.% Yttria–zirconia

## 1. Introduction

### 1.1. Inert matrix fuel

Nuclear stockpiles are an accumulation of long-lived radioactive nuclides from spent nuclear fuel (SNF) and dismantled nuclear weapons [1–3]. Safe disposal methods must be developed to isolate these radioactive materials from the public and to reliably control the inventory so that it cannot be used to produce nuclear weapons [2]. Interest in reducing the stockpiles of SNF by several nations lead to the formation of the Global Nuclear Energy Partnership (GNEP), an organization consisting of different nations (25 partner and 31 observer countries) that share a common goal i.e., recycling of viable energy producing actinides, thereby reducing the risk of nuclear proliferation [4].

One of the methods proposed for recycling the radioactive material present in the SNF is using the inert matrix fuel (IMF) concept [5]. The primary mechanism by which IMFs will satisfy target goals is minimizing the potential for breeding fissile materials inside the reactor by replacing the conventional uranium ($^{238}U$) matrix with the one that is inert to neutrons [5,6]. These fuels consist of a neutron-transparent matrix with the fuel material being dispersed or dissolved in the matrix [7]. It is expected that IMFs will help in extracting energy from the actinides by means of transmutation in the proposed Generation IV reactors. Transmutation results in production of energy through conversion of highly radioactive actinides to their lighter counterparts, thereby enabling safe disposal of SNF in the proposed geological repositories.

Some of the requirements for selecting a suitable inert matrix material are outlined below [6]:

- Low neutron absorption cross-section (<2.7 barns)
- High melting point (>2000 °C)
- High thermal conductivity
- High density (90–95% of theoretical density (TD))

Fully stabilized zirconia ($ZrO_2$) has been identified as a candidate material for the inert matrix due to its structural similarity with uranium dioxide ($UO_2$), high melting point and low neutron absorption cross-section [8]. A recent study on

---

[*] Corresponding author. Tel.: +1 540 231 2356; fax: +1 540 231 8919.
*E-mail address:* traghu@vt.edu (R.R. Thridandapani).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.09.039

$ZrO_2$–10 at.% $Y_2O_3$ (yttria) by Degueldre and Paratte [9] showed that fully stabilized $ZrO_2$ retained its structural stability under different radiation levels (between 60 keV and 1.5 MeV) of Xe ions with $\sim 1.8 \times 10^{16}$ cm$^{-2}$ dosage.

### 1.2. IMF fabrication issues

Processing of a ceramic nuclear fuel usually involves sintering of powder compacts for long period of times (~10 h) at high temperatures (1600 °C) [10]. As a majority of the actinide materials (mainly Americium (Am) and Plutonium (Pm)) exhibit high vapor pressures [11–13] at these temperatures, it is expected that there will be a loss in material during IMF processing. Alternative processing methods are being considered for rapid sintering of IMF in order to retain volatile actinides.

Microwave processing is one such method that has been shown to accelerate the overall sintering process (compared with conventional methods) [14–20]. The radiotoxic nature of actinides prevents their direct use for the early stage sintering experiments. Instead, surrogate materials are used to mimic the chemical and physical behavior of an actinide [21]. It is only after successful microwave sintering of simulated IMFs that this technology will be considered for processing the actual fuel materials. For this study, dysprosia ($Dy_2O_3$) was selected as a surrogate for americia ($Am_2O_3$) due to the similarity in valence state, coordination number and ionic radii [21].

In prior work, these authors investigated microwave-hybrid sintering of a candidate inert matrix material, 8 mol.% yttria–zirconia (8YZ) and found that this material could either be processed at lower temperatures (1200 °C, with a soak time of 100 min) or in shorter periods of time (20 min, at 1300 °C) [18]. The objective of the study reported in this paper was to examine the microwave-hybrid sintering behavior of simulated IMF. The experimental procedure adopted and the subsequent results obtained during this study are discussed in the following sections.

## 2. Experimental procedure

### 2.1. Green pellet fabrication

Commercially available 8YZ (TZ-8Y, Tosoh Corporation, USA) and $Dy_2O_3$ (11319, Alfa Aesar) powders were selected for this study.

Simulated IMFs were made by dispersing 20 wt.% $Dy_2O_3$ with 8YZ on a roller mill for a period of 12 h. Approximately 2.63 g of the powder was poured into a polyurethane rubber mold (12.5 mm dia. × 50 mm ht.) and the compaction behavior of these powders was studied using an isostatic pressing technique.

### 2.2. Sintering and characterization

Sintering studies were performed inside a multimode microwave and a conventional furnace. The details of the multimode microwave and the conventional furnace have been discussed previously [18]. All of the sintering runs were performed with a heating rate of ~20 °C/min with a constant soak time of 20 min. For each sintering temperature six samples (obtained through two sets of sintering runs) were used for calculating the variation in average density values.

Bulk density of the sintered samples was measured using the Archimedes liquid displacement method (ASTM C 20) [22]. The sample preparation for Scanning Electron Microscopy (SEM) imaging (LEO-Zeiss 1550) of sintered samples included the following three stages: sectioning, grinding and polishing. Longitudinal sectioning was performed using a diamond blade saw (Buehler Isomet 1000) and the sectioned samples were mounted in an epoxy resin. Coarse polishing was done through a standard progression of silicon carbide papers (180, 320, 400, 600 and 1000) and fine polishing was done through 15, 6 and 1 micron diamond suspensions in oil. Grain structure on polished samples was revealed using thermal etching at 150 °C below the actually sintering temperature [23]. A thin layer (~10 nm) of Ag–Pd was coated onto the samples surface to improve the conductivity for SEM imaging. The mean intercept length method adopted for this study is in accordance with ASTM E-112. Four sets of micrographs collected across different regions of the samples were used for estimating the grain size using mean intercept method.

## 3. Results and discussion

### 3.1. Powder characterization and their compaction behavior

Scanning electron imaging of the starting powders is shown in Fig. 1. It can be observed (Fig. 1a) that the 8YZ powders consisted of 50 μm agglomerates. A high magnification image shown in Fig. 1a inset reveals the actual size of the particles to be between 0.1 and 0.2 μm. The agglomerates seen in Fig. 1a were a result of a spray drying process used for manufacturing 8YZ powders. As seen from Fig. 1b, the average particle size for $Dy_2O_3$ powders was ~3 μm.

One of the primary goals of inert matrices is that they need to support the actinide phase by maintaining good mechanical integrity throughout irradiation [7]. Two common ways of loading the actinide phase with the inert matrix are through dispersion and solid solution. Dispersion of actinide phase within the inert matrices is preferred [7,24] to solid solutions as it would limit irradiation damage (caused by the release of fission products) to the inclusions as opposed to the damage experienced by the entire matrix (in solid solutions). For this reason, $Dy_2O_3$ was dispersed in 8YZ. It was observed that the result of dispersing $Dy_2O_3$ in 8YZ showed no difference between the pour density[1] and the tap density[2]; they both showed the same value of 1.52 g/cc, implying that the milling process (Section 2.1) may eliminate the tapping stage.

---

[1] Pour density is the bulk density of the powder "as poured" or as passively filled into a measuring cylinder.

[2] Tap density is the bulk density of the powder after "tapping down", usually vibrated under specified conditions (ASTM B523 is adopted for this study).

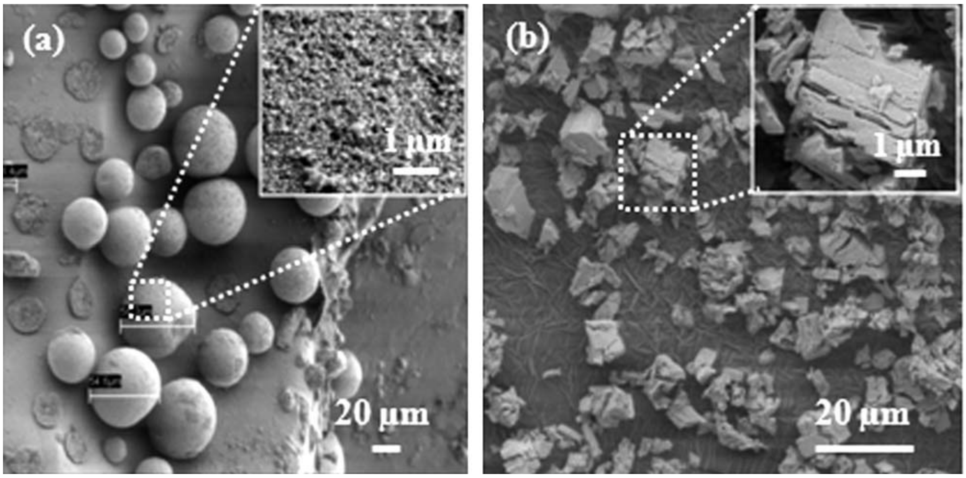

Fig. 1. Scanning electron imaging of (a) 8YZ [18] and (b) $Dy_2O_3$ powders.

The compaction behavior of 8YZ-20D powder was studied with respect to pressure (Fig. 2). As a reference, the data corresponding to the compaction behavior of 8YZ [18] was added to Fig. 2. From this figure, it can be observed that the density of powder compacts increased with the increase in applied pressure. This increase is most likely due to simultaneous particle rearrangement due to the fracture of agglomerates. Due to the limitation with the operating pressures of the instrument, a green density of 49% TD[3] (150 MPa) was selected for performing sintering experiments. While addition of $Dy_2O_3$ particles to 8YZ matrix showed a slight increase (46 [18] vs. 49% TD) in the average values of green density over the 8YZ, this difference was minimal if the scatter in data was considered. The $Dy_2O_3$ powders used for this study were not spray dried and the result was a wide distribution of $Dy_2O_3$ agglomerates. It was anticipated that higher green densities (>49% TD) could have been obtained by adopting a more controlled particle size for $Dy_2O_3$.

### 3.2. Densification behavior of simulated IMF with temperature

Conventional and microwave-hybrid sintering runs were performed on 8YZ-20D composite pellets. The results are shown in Fig. 3. It can be observed that, at lower temperatures (1100 and 1300 °C), the microwave-hybrid sintered 8YZ-20D pellets showed higher density values, as compared to conventionally sintered samples. At 1500 °C, there was a slight difference in the densities obtained between conventionally sintered and microwave-hybrid sintered samples, but this difference was minimal considering the scatter in data.

Fracture surfaces of the samples sintered at 1300 °C is showed in Fig. 4. Except for the regions along the interface (with $Dy_2O_3$) the microwave-hybrid sintered pellet (Fig. 4a) showed better sintering of 8YZ matrix than conventionally sintered pellet (Fig. 4b). These observations confirm the lower bulk density values observed at 1300 °C in the case of the conventionally sintered sample (73% TD), as opposed to the microwave-hybrid sintered sample (83% TD).

### 3.3. Isothermal densification behavior of simulated IMF

The density of the nuclear fuel pellets used in reactors ranges between 90% and 95% TD [25]. Performing isothermal sintering runs at 1300 °C temperatures gave an estimate of the minimum time required to reach these target densities. The results of these isothermal sintering runs are shown in Fig. 5a.

It can be observed that, for all the soak times, the microwave-hybrid sintered samples exhibited a higher density than the conventionally sintered samples. It took approximately 100 min to reach the 93% TD during microwave-hybrid sintering; whereas, conventional sintering resulted in a density of 87% TD. These results suggest that, by adopting microwave processing (rather than conventional processing), the fabrication temperatures and timings could be reduced. The results of a comparative study on the isothermal sintering (microwave-hybrid) of 8YZ and 8YZ-20D composite is also seen in Fig. 5a. It can be observed that the matrix material sintered to 90% TD

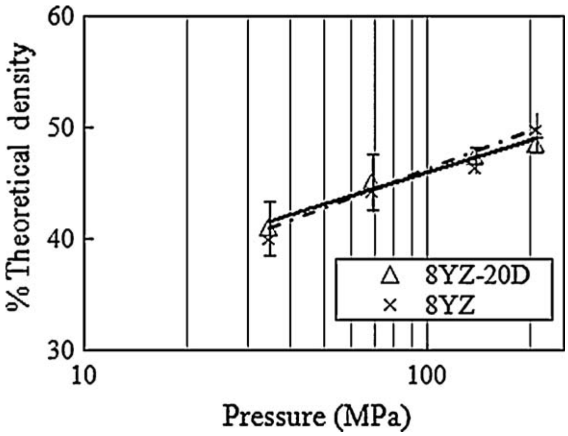

Fig. 2. Compaction behavior of 8YZ-20D and 8YZ powders.

---

[3] TD (theoretical density for 8YZ-20D) = 6.31 g/cc (calculated using rule of mixtures from the values obtained using X-ray diffraction).

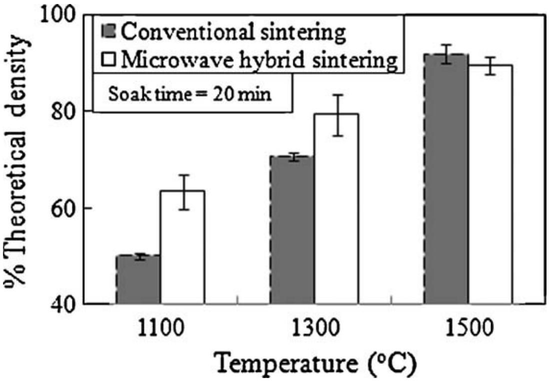

Fig. 3. Sintering behavior of simulated inert matrix fuel (8YZ-20D) in a conventional and a microwave-hybrid furnace.

within 20 min and the addition of $Dy_2O_3$ has increased these sintering times to 60 min.

The data corresponding to the loss in weight of the sample before and after sintering was also evaluated (Fig. 5b). It was observed that the percentage loss in weight for all the sintering runs was always less than 1%. These results indicated that $Dy_2O_3$ (which was selected as a simulant to $Am_2O_3$) did not exhibit a significant weight loss.

The loss in materials due to evaporation is a time/temperature dependent process [11]. Since microwave sintering resulted in faster densification at lower temperatures, it was expected that the weight loss associated with a microwave process would be lower. The simulant used for this study ($Dy_2O_3$) did not show appreciable weight loss (Fig. 5b) during sintering. This result is due to the fact that the oxide form of Dysprosium is more stable than its metallic form [26]. Any material exhibiting vapor pressure's higher than 0.4 torr (vapor pressure of Americium at melting temperatures) [27] can be used as an alternative surrogate for investigating the material loss during sintering (e.g. manganese, 0.75 torr at melting temperatures).

### 3.4. Microstructural observation

Fig. 6 shows representative micrographs of a 93% dense 8YZ-20D sample processed at different sintering conditions in microwave-hybrid and conventional furnaces. Microstructural observations show that the host matrix experienced a near complete densification. The average grain size for 8YZ matrix was 1.65 μm for a microwave-hybrid sintered sample and 1.3 μm for a conventionally sintered sample. It is important to note that even with the reduction in processing temperatures, the microwave-hybrid sintered 8YZ-20D exhibited similar structure when compared with a conventionally sintered 8YZ-20D.

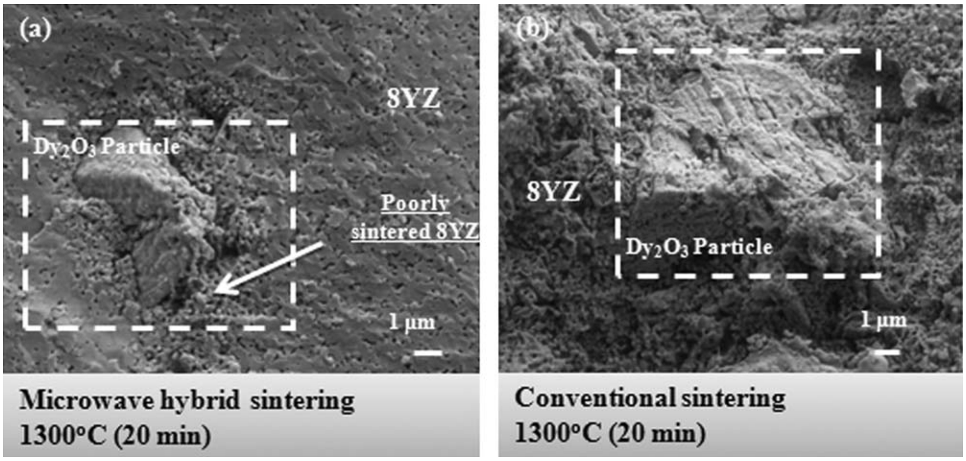

Fig. 4. Fracture surface image of 8YZ–$Dy_2O_3$ pellet: (a) microwave-hybrid sintered pellet and (b) conventionally sintered pellet.

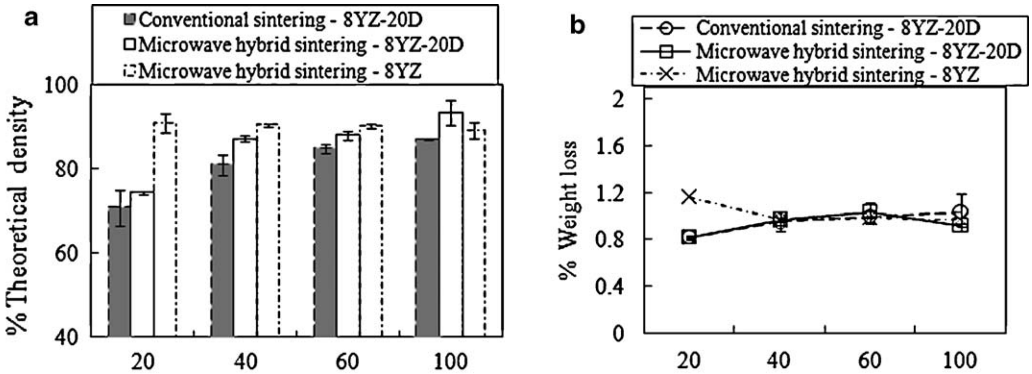

Fig. 5. (a) Isothermal densification at 1300 °C and (b) percentage weight loss behavior of 8YZ-20D in a conventional and a microwave-hybrid furnace.

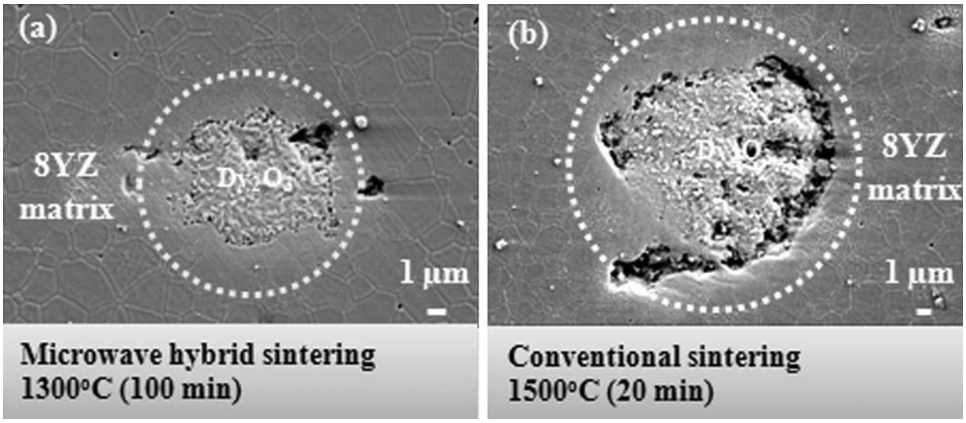

Fig. 6. SEM imaging of 93% dense 8YZ-20D: (a) microwave-hybrid and (b) conventionally sintered pellets.

## 4. Summary

This research demonstrated the possibility of using microwave energy for fabricating IMFs (with a non-radioactive material) at temperatures lower than is possible with conventional processing. The sintering results showed that, at lower temperatures (1100 and 1300 °C), microwave-hybrid sintering produced higher density 8YZ-20D pellets when compared to conventionally sintered samples. A 100 min soak time at 1300 °C resulted in the target density of 93% TD for a microwave-sintered sample, whereas conventionally sintered 8YZ resulted in a density of 87% TD. The reduction in processing temperatures during microwave-hybrid sintering did not alter any of the resulting properties.

## Acknowledgements

The microwave processing research facility team at Virginia Tech gratefully acknowledges the Department of Energy for funding this work under project no. DE-FC07-06-ID14731.

## References

[1] D. Westlèn, Reducing radiotoxicity in the long run, Prog. Nucl. Energy 49 (2007) 597.
[2] F.N.V. Hippel, How to simplify the plutonium problem, Nature 394 (1998) 415–416.
[3] R.C. Ewing, Nuclear waste forms for actinides, Proc. Natl. Acad. Sci. 96 (1999) 3432–3439.
[4] Global Nuclear Energy Partnership, http://www.gneppartnership.org/, accessed on 4th April, 2010.
[5] C. Degueldre, J.M. Paratte, Concepts for an inert matrix fuel, an overview, J. Nucl. Mater. 274 (1999) 1–6.
[6] International Atomic Energy Agency, Viability of Inert Matrix Fuel in Reducing Plutonium Amounts in Reactors, IAEA-TECDOC-1516, 2006.
[7] N. Chauvin, R.J.M. Konings, H. Matzke, Optimisation of inert matrix fuel concepts for americium transmutation, J. Nucl. Mater. 274 (1999) 105–111.
[8] H. Kleykamp, Selection of materials as diluents for burning of plutonium fuels in nuclear reactors, J. Nucl. Mater. 275 (1999) 1.
[9] C. Degueldre, J.M. Paratte, Basic properties of a zirconia-based fuel material for light water reactors, Nucl. Technol. 123 (1998).
[10] P. Balakrishna, C.K. Asnani, R.M. Kartha, K. Ramachandra, K.S. Babu, V. Ravichandran, B.N. Murty, C. Ganguly, Uranium dioxide powder preparation, pressing, and sintering for optimum yield, Nucl. Technol. 127 (1999) 375.
[11] T.B. Lindemer, Thermochemical Analysis of Gas-cooled Reactor Fuels Containing Am and Pu Oxides, Oak Ridge National Laboratory, 2002 ORNL/TM-2002/133.
[12] M. Osaka, I. Sato, T. Namekawa, K. Kurosaki, S. Yamanaka, Oxygen potentials of $(U_{0.685}Pu_{0.270}Am_{0.045})O_{2-x}$ solid solution, J. Alloys Compd. 397 (2005) 110–114.
[13] M.K. Meyer, U.S Program for the Development of Inert-matrix Fuel for Transmutation Systems, Argonne National Laboratory-West, Idaho Falls, 2001.
[14] W.H. Sutton, D.E. Clark, Microwave processing of ceramic materials, Ann. Rev. Mater. Sci. 26 (1996) 299–331.
[15] J.P. Cheng, D.K. Agrawal, S. Komarneni, M. Mathis, R. Roy, Microwave processing of WC-Co composities and ferroic titanates, Mater. Res. Innov. 1 (1997) 44–52.
[16] J.D. Katz, Microwave sintering of ceramics, Ann. Rev. Mater. Sci. 22 (1992) 153–170.
[17] W.H. Sutton, Microwave processing of ceramic materials, Ceram. bull. 68 (1989) 376–386.
[18] R.R. Thridandapani, C.E. Folgar, D.C. Folz, D.E. Clark, K. Wheeler, P. Peralta, Microwave sintering of 8 mol.% yttria–zirconia (8YZ): an inert matrix material for nuclear fuel applications, J. Nucl. Mater. 384 (2009) 153–157.
[19] Y.V. Bykov, K.I. Rybakov, V.E. Semenov, High-temperature microwave processing of materials, J. Phys. D 34 (2001) R55–R75.
[20] P.A. Bingham, R.J. Hand, M.C. Stennett, N.C. Hyatt, M.T. Harrison, The use of surrogates in waste immobilization studies: a case study of plutonium, Mater. Res. Soc. Symp. Proc. 1107 (2008) 421.
[21] ASTM, B527—06, Metallic and Inorganic Coatings, vol. 15.01, Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA, 2009.
[22] ASTM, C 20, Refractories, Activated Carbon; Advanced Ceramics, vol. 15.01, Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA, 2009.
[23] U. Taffner, V. Carle, U. Schafer, Preparation and Microstructural Analysis of High-performance Ceramics, ASM Handbook, ASM International, 2004, pp. 1057–1066.
[24] A. Fernández, R.J.M. Konings, J. Somers, Design and fabrication of specific ceramic-metallic fuels and targets, J. Nucl. Mater. 319 (2003) 44–50.
[25] D.R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, Energy Research and Development Administration, Berkeley, 2004.
[26] D.R. Gaskell, Introduction to the Thermodynamics of Materials, Taylor and Francis, 2003.
[27] J.J. Moore, The application of self-propagating-high-temperature synthesis (SHS) to the fabrication of actinide bearing nitride and other ceramic nuclear fuels, in: ANS/ENS International Meeting and Nuclear Technology Expo, Washington, DC, 2007.