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Preparation of rock-like oxide fuels for the irradiation test in the Japan Research Reactor No. 3

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Abstract

Three types of uranium-based rock-like oxide (ROX) fuel were prepared for an irradiation test in the Japan Research Reactor No. 3 (JRR-3). The first one was a particle dispersed type fuel where $(U,Zr,Y)O_2$ particles of 250 μm in diameter were dispersed in a matrix of spinel or corundum. The second one was a homogeneous mixture type of $(U,Zr,Y)O_2$ and spinel or corundum. The third one was a $(U,Zr,Y)O_2$ single phase fuel. In all case, the sintering of the pellets was carried out at 2020 K for 4 h in a stream of $75\%H_2/25\%N_2$ mixed gas. The characterization tests showed that the pellets fabricated had small void volume fraction (<9%). The homogeneous distribution of the particles/grains of $(U,Zr,Y)O_2$ in the matrix was confirmed by the ceramography. The X-ray diffraction analysis (XRD) showed the formation of homogeneous $(U,Zr,Y)O_2$ solid solutions and no appreciable interactions between the $(U,Zr,Y)O_2$ phase and inert matrix materials (spinel or corundum).

1. Introduction

For the incineration of the excess plutonium on the basis of the present LWR technology, the rock-like oxide (ROX) fuel has been proposed as a new once-through type fuel concept [1,2]. The ROX fuel was originally composed of yttria-stabilized zirconia (YSZ), spinel ($MgAl_2O_4$) and corundum (Al_2O_3), although corundum could be excluded from the viewpoint of its irradiation behavior. Recently YSZ particle dispersed fuel concept has been studied in Japan Atomic Energy Research Institute (JAERI) to accommodate the swelling of the inert matrix materials [3].

The ROX fuel has an advantage in the high-annihilation rate of target materials such as plutonium, but there is little information on the irradiation behavior. Furthermore the fuel fabrication technology itself also should be developed. Therefore, three types of uranium-based ROX fuel were fabricated and supplied for the irradiation test in the Japan Research Reactor No. 3 (JRR-3). The present paper describes the fabrication method of the fuel and the results of the characterization tests by ceramography and X-ray diffraction analysis (XRD).

2. Fabrication

Two different kinds of the ROX fuel pellets were fabricated for the irradiation tests. The first one was a homogenous pellet which was a macroscopically homogeneous mixture of $(U,Zr,Y)O_2$ solid solution and an inert matrix material. The second was particle-dispersed pellet which consisted of $(U,Zr,Y)O_2$ particles in an inert matrix such as spinel or corundum. In addition to the above types, single phase pellets of $(U,Zr,Y)O_2$ were also prepared. The compositions of the pellets are shown in Table 1. Enrichment of ^{235}U was 19.6% and the fissile density was arranged to be 4 at.% of metal elements.

2.1. Fabrication of $(U,Zr,Y)O_2$ particles for particle-dispersed pellets

The $(U,Zr,Y)O_2$ particles for the fabrication of particle-dispersed pellets were made by an external sol–gel

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Table 1
Compositions (in mol%) of the uranium ROX fuel

Material	YSZ[a]–Spinel	YSZ[a]–Corundum	YSZ[a]
YSZ[a]	20.0	16.5	80.0
UO_2 (19.6%EU)	37.1	30.6	20.0
Al_2O_3	–	52.9	–
$MgAl_2O_4$	42.9	–	–

YSZ[a]: 88 mol% ZrO_2 + 12 mol% Y_2O_3.

process as shown in Fig. 1. The starting materials were uranyl nitrate [$UO_2(NO_3)_2{\cdot}6H_2O$], zirconium nitrate [$ZrO(NO_3)_2{\cdot}2H_2O$] and yttrium nitrate [$Y(NO_3)_3{\cdot}6H_2O$]. At first, zirconium and yttrium nitrates were dissolved in the uranyl nitrate solution with the uranium concentration of 2.0 mol l^{-1}. Then polyvinyl alcohol (PVA) and tetrahydrofurfuryl alcohol (THFA) were added into the solution for adjusting the viscosity.

The feed solution was dropped into ammonia solution from a needle with a vibrator which controlled the size of droplets. The size of the gel spheres formed was controlled to be around 800 μm in diameter so that the size could become about 250 μm after sintering.

The gel spheres were washed with water to remove ammonium nitrate and then with alcohol to remove moisture at the sphere surface. The spheres were dried at 353 K for an hour and pre-calcined at 773 K for 3 h in

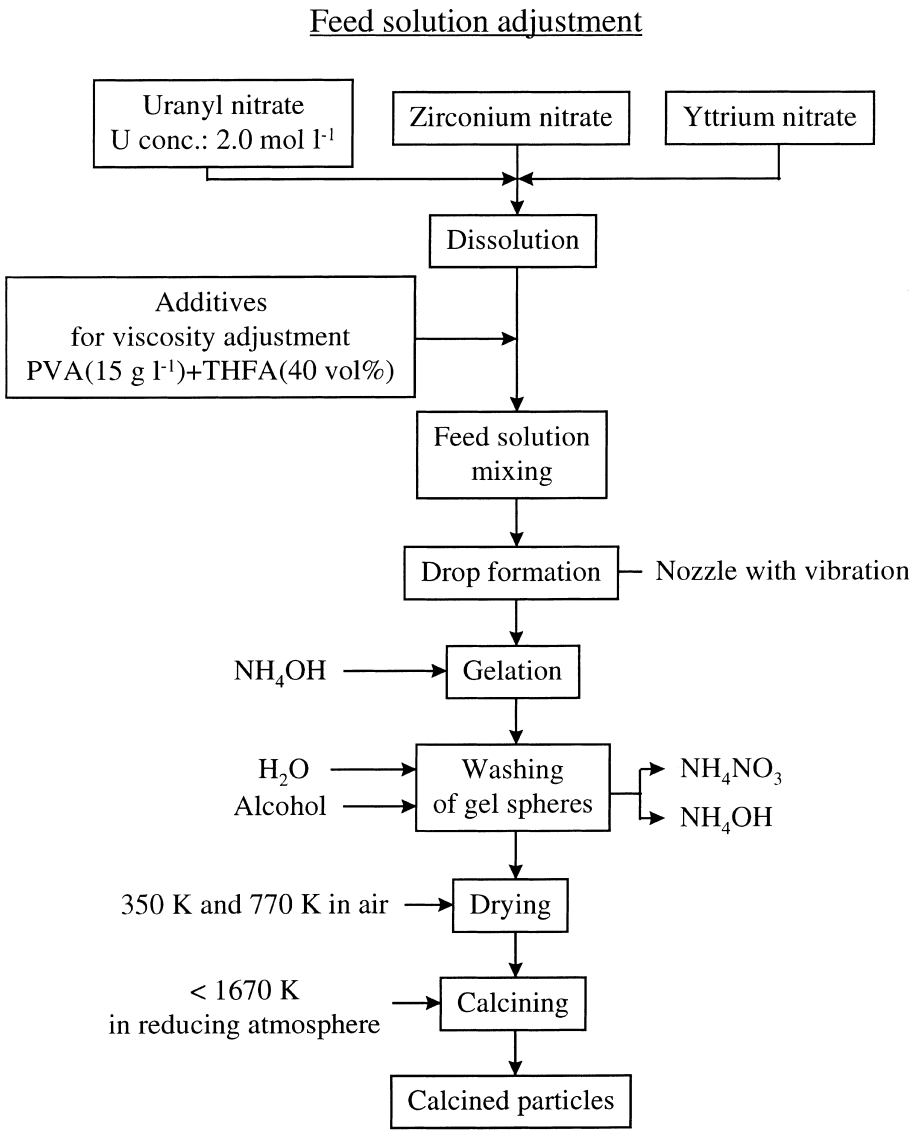

Fig. 1. Flow diagram for fabrication of $(U,Zr,Y)O_2$ particles with an external sol–gel process. PVA and THFA: see text.

air to remove additives in the gel spheres. The heating rate for pre-calcination was of great importance to avoid crack formation of the pre-calcined particles. A satisfactory result was obtained by employing the heating rate of 25 K h^{-1} above 370 K. Calcination was performed at 1270–1670 K for 3 h in a stream of 75%H_2/25%N_2 mixed gas.

It was found from a preliminary test on the sintering characteristics of particle-dispersed pellets that the usage of completely sintered particles might easily result in the formation of cracks in the matrix or wide gaps between particles and the matrix, because of the difference in the shrinkage rates between the sintered particles and inert matrix materials during sintering. In the present studies, therefore, the calcined particles which had not sintered were used in this stage of pellet fabrication.

The particle size distribution of $(U,Zr,Y)O_2$ spheres after sintering was checked by an image analyzer. Fig. 2 shows the appearance and size distribution of the particles obtained by sintering the pre-calcined particles at 2020 K for 4 h in a stream of 75%H_2/25%N_2 mixed gas. It is indicated that the particles have the average diameter of 250 μm and have a relatively narrow size distribution. The sphericity, which is defined as a ratio of any two orthogonal diameters, is a quality measure of sintered particles. The sphericity of the particles was between 1.00 and 1.10. Particles with a poor sphericity might cause crack formation and increase in damaged volume of the matrix during irradiation. It is easily understood that particles those are true spheres (i.e. the sphericity equals unity) have the minimum surface area and, therefore, can reduce damaged volume of the matrix by fission fragments to the minimum extent.

XRD analysis confirmed that the sintered spheres were a homogeneous solid solution of $(U,Zr,Y)O_2$. Cross sectional images of the sintered particles observed by optical microscopy showed that a very small void volume fraction of 1% was attained by these heat treatments.

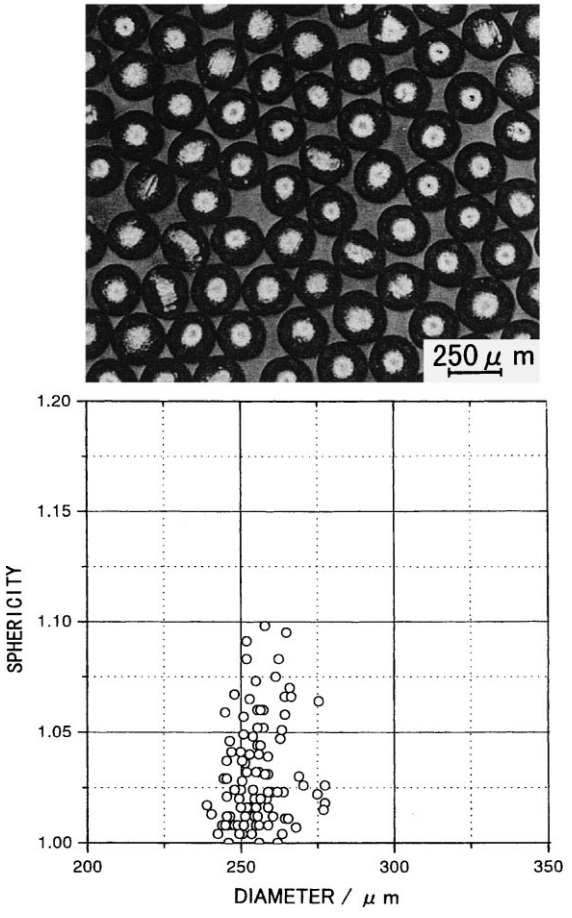

Fig. 2. Typical aspects of $(U,Zr,Y)O_2$ sintered particles and particle size distribution.

2.2. Fabrication of the pellets

The flow diagram of the fabrication of the pellets is shown in Fig. 3. As for $(U,Zr,Y)O_2$ single phase pellets, the powders of UO_2, ZrO_2 and Y_2O_3 were blended and milled in an agate mortar for 30 min. The mixture was pelletized at a pressure of about 200 MPa. Sintering was carried out at 2020 K for 4 h in a high-temperature furnace with tungsten mesh heaters in a stream of 75%H_2/25%N_2 mixed gas. The other two homogeneous pellets, $(U,Zr,Y)O_2$ + spinel and $(U,Zr,Y)O_2$ + corundum, were fabricated using UO_2, ZrO_2, Y_2O_3 and $MgAl_2O_4$, or UO_2, ZrO_2, Y_2O_3 and Al_2O_3 as starting powders. The rest procedure was the same as that for $(U,Zr,Y)O_2$ single phase pellets.

For the fabrication of the particle-dispersed pellets, special attention was paid to keep homogeneous dispersion of particles in the matrix at the green pellet fabrication process. The calcined $(U,Zr,Y)O_2$ particles were put in a slurry of spinel or corundum and were dispersed homogeneously by gentle stirring. Then the mixture was compacted into green pellets at about 200 MPa. Sintering was carried out at 2020 K for 4 h in a stream of 75%H_2/25%N_2 mixed gas.

It is worthwhile to note here that adjustment of shrinkage rate of the calcined particles to that of matrix materials is of great importance to obtain high-density pellets. Property changes of the calcined particle depend on both calcined temperature and chemical composition of the gel particles. The shrinkage rates of the calcined particles were measured as a function of calcining temperature prior to the fuel pellet fabrication. The calcining temperature of the pre-calcined particles was determined so as to meet the shrinkage rate of the matrix material determined separately.

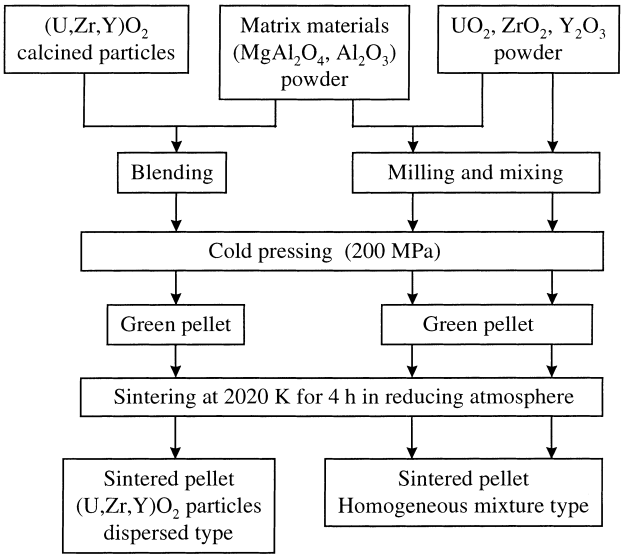

Fig. 3. Flow diagram for fabrication of the ROX fuel pellets.

3. Ceramography and XRD of the pellets

Fig. 4 shows the typical aspects of the ROX pellets fabricated in the present studies. No cracking or fragmentation was observed. The dimensions and densities of the pellets are shown in Table 2. The density derived from dimension and weight measurements was between 5.6 and 6.0 g cm^{-3}. The void volume fraction was estimated by an image analyzer using SEM images of the sintered pellets. The observed void volume fraction was 2–9%.

Microstructures of sintered pellets were examined by optical microscopy after polishing the surface of pellets using diamond pastes. Fig. 5 shows optical microscope images of typical pellets. Fig. 5(a) indicates

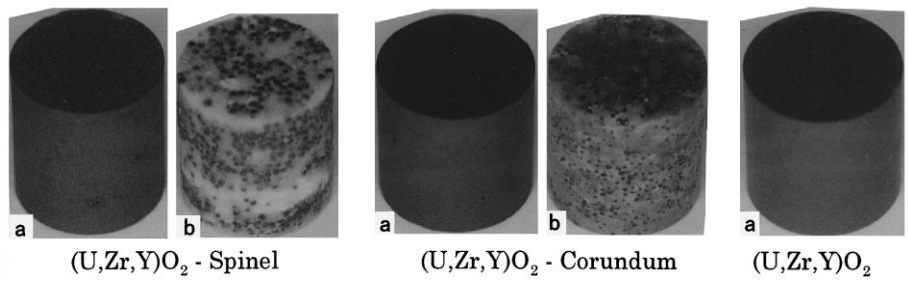

Fig. 4. Typical aspects of the ROX fuel pellets. Pellet size, diameter: 5.35 mm; height: 5.5 mm. (a) Homogeneous mixture type. (b) Particle dispersed type.

Table 2
Characteristics of the sintered pellets

Composition	$(U,Zr,Y)O_2$–Spinel		$(U,Zr,Y)O_2$–Corundum		$(U,Zr,Y)O_2$
Type of pellet	Homog.	Particle	Homog.	Particle	Homog.
Diameter (mm)	5.35	5.35	5.35	5.35	5.35
Height (mm)	5.5	5.5	5.5	5.5	5.5
Density (g cm^{-3})	5.7	5.6	5.9	5.8	6.0
Void volume (%)	7	9	2	2	9

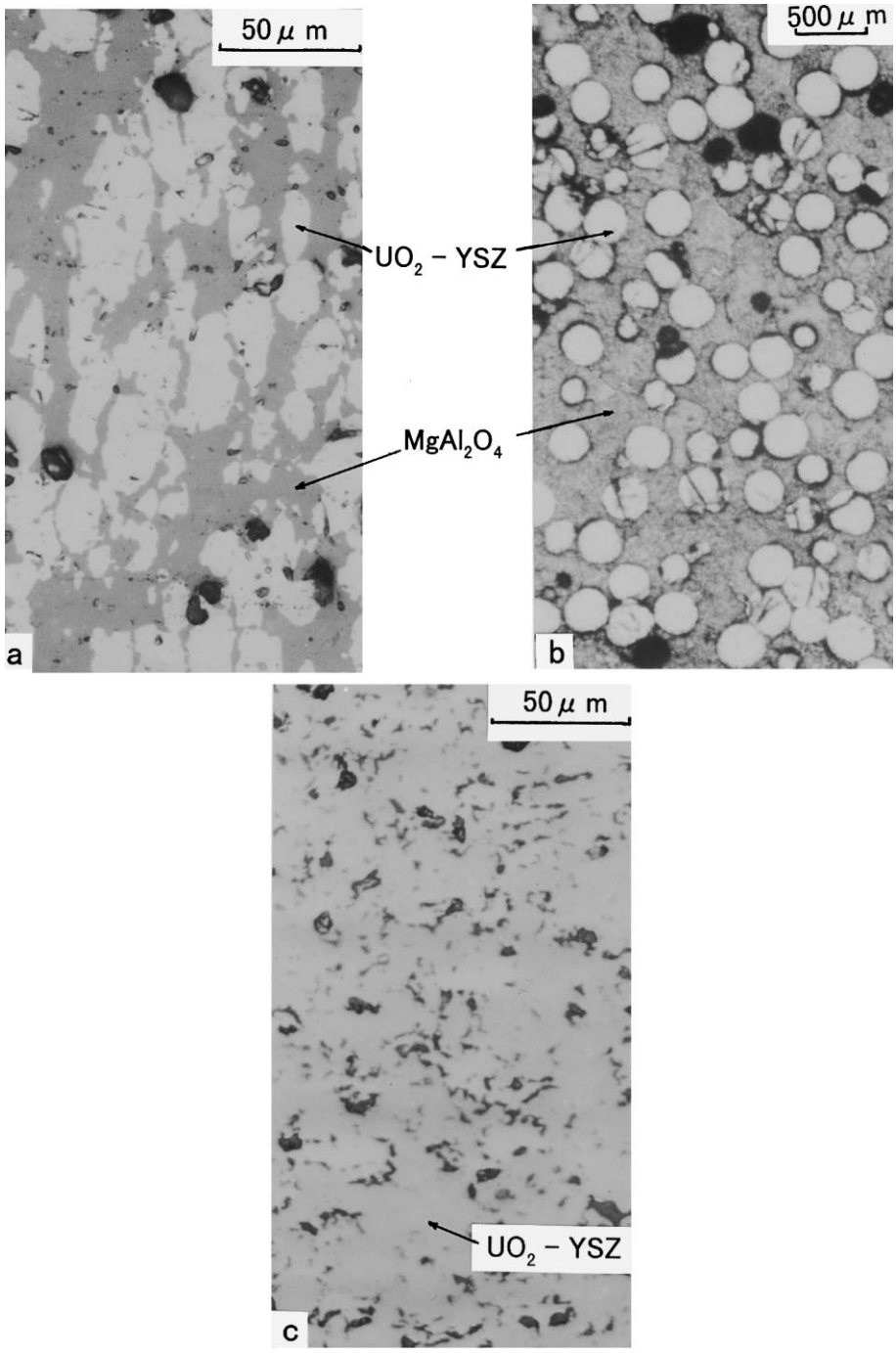

Fig. 5. Microstructures of the ROX fuel pellets obtained by the optical microscopy. (a) Homogeneous mixture type of $(U,Zr,Y)O_2$–spinel. (b) Particle dispersed type of $(U,Zr,Y)O_2$–spinel. (c) Homogeneous type of single $(U,Zr,Y)O_2$ phase.

the microstructure of the homogeneous pellet with $(U,Zr,Y)O_2$ and spinel, where white $(U,Zr,Y)O_2$ grains with a size of 10–50 μm were homogeneously distributed in the spinel matrix (gray part). Each grain is clearly visible and no indication of reaction is observed between $(U,Zr,Y)O_2$ and the spinel. Fig. 5(b) shows the microstructure of the particle-dispersed pellet in which the particles are dispersed in the spinel matrix. It can

Table 3
Lattice parameters (in nm) of phases in the ROX fuel pellets

Composition	$(U,Zr,Y)O_2$–Spinel		$(U,Zr,Y)O_2$–Corundum		$(U,Zr,Y)O_2$
Type of pellet	Homog.	Particle	Homog.	Particle	Homog.
$(U,Zr,Y)O_2$	$a=0.5360$	$a=0.5363$	$a=0.5395$	$a=0.5388$	$a=0.5200$
$MgAl_2O_4$	$a=0.8061$	$a=0.8058$			
Al_2O_3			$a=0.4770$	$a=0.4781$	
			$c=1.3025$	$c=1.3040$	

be seen that the white $(U,Zr,Y)O_2$ particles are approximately 250 μm in diameter and are uniformly distributed in the spinel matrix. The dark circles are the holes of the particles which may have been removed during polishing. The gaps between the particles and the matrix are not so wide but further improvement is necessary because the gaps may have a tendency to increase the temperature of $(U,Zr,Y)O_2$ particles during irradiation. The microstructure of the pellet with the single $(U,Zr,Y)O_2$ phase is shown in Fig. 5(c). Pores (dark spots) are distributed in the $(U,Zr,Y)O_2$ phase.

Microstructure observation by optical microscopy failed for the pellet with corundum, because grains of corundum were plucked from the surface of the pellet during polishing. The broken surface of the pellet was observed by SEM without any polishing. The result showed that the pellets were very dense and the $(U,Zr,Y)O_2$ particles/grains were uniformly distributed.

XRD analysis was performed on the sintered pellets at room temperature and the results are summarized in Table 3. No phase was observed except the fluorite-type $(U,Zr,Y)O_2$, spinel and corundum. The lattice parameters of the fluorite $(U,Zr,Y)O_2$ phase were comparable to the values evaluated by the assumption of the ideal solid solution of UO_2 and $(Zr,Y)O_2$ [4,5] indicating the formation of homogeneous solid solutions. The lattice parameters of spinel and corundum agreed fairly well with the literature values [6,7]. These findings show that the reaction of the matrix materials (spinel and corundum) with the $(U,Zr,Y)O_2$ phase did practically not occur.

Ten pellets of each fuel were loaded into a stainless steel cladding tube of 6.50 mm outer diameter and of 5.56 mm inner diameter after inspection. Five fuel pins were encapsulated in a irradiation capsule instrumented with flux monitors and thermocouples. Irradiation started in June 1998 in JRR-3 and will be carried out for four reactor cycles (100 full power days). The maximum neutron fluence is expected to be $\sim 1.1 \times 10^{25}$ m^{-2}.

4. Conclusions

Three types of uranium-based ROX fuel were successfully fabricated for the irradiation test in JRR-3 at JAERI. The first one was a particle dispersed type fuel where $(U,Zr,Y)O_2$ particles of 250 μm in diameter were dispersed in a matrix of spinel or corundum. The second one was a homogeneous mixture type fuel of $(U,Zr,Y)O_2$ and spinel or corundum. The third one was a $(U,Zr,Y)O_2$ single phase fuel. The followings are the accomplishments of the present study.

1. A preparation process has been established by an external sol–gel route for a $(U,Zr,Y)O_2$ particle of about 250 μm diameter.
2. Pellets with homogeneous dispersion of $(U,Zr,Y)O_2$ particles can be fabricated by blending the particles with a slurry of an inert matrix.
3. Partially sintered particles must be supplied at the green-pellet fabrication stage in order to obtain crack-free pellets with small void volumes after sintering.
4. The characterization tests showed that the pellets had a small void volume fraction (<9%) and the homogeneous distribution of particles/grains of $(U,Zr,Y)O_2$ in the matrix. The XRD analysis confirmed the formation of homogeneous $(U,Zr,Y)O_2$ solid solutions and no appreciable interactions between the $(U,Zr,Y)O_2$ phase and inert matrix materials (spinel or corundum).

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