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Sintering of β-Thorium−Uranium(IV) Phosphate−Diphosphate Solid Solutions from Low-Temperature Precursors

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Pure and single phase thorium−uranium(IV) phosphate-diphosphate β-TUPD (orthorhombic form) dense pellets were prepared by two wet chemical routes from low-temperature precursors. The first method was based on the "direct evaporation" of a mixture containing tetravalent actinides and phosphoric acid while the second one involved the initial precipitation of the thorium−uranium(IV) phosphate−hydrogenphosphate hydrate (TUPHPH). Both methods led to single phase sintered samples following a two-step procedure using a uniaxial pressing at room temperature and then a heat treatment at high temperature. The dilatometric study and the determination of the linear shrinkage of the pellets showed that the best densification of the samples prepared via the "precipitation" method was obtained after heating the raw pellet at 1250 °C for 5 h, for initial uranium amount lower than 44.5 wt %(U). For samples prepared via "direct evaporation", the heat treatment must be prolonged for at least 15 h at this temperature. Moreover, the complete characterization of the samples (EPMA, and so forth) confirmed that the homogeneity of the samples was significantly improved when using TUPHPH as a precursor, probably due to the better reactivity of the initial powder (higher specific surface area, smaller grain size, and so forth). Several leaching tests were performed in various acidic media and in natural waters on β-TUPD sintered samples. All the corresponding normalized dissolution rates remained low (10^{-6} to 10^{-5} g/(m^2 day)) even in aggressive media which confirms the high chemical durability of β-TUPD, thus enhancing the potential use of this ceramic in the field of the efficient immobilization of tetravalent actinides.

Introduction

The disposal of nuclear waste for an underground repository is currently considered as a likely option for the immobilization of long-lived radionuclides. In these conditions, it can be necessary to stabilize these radionuclides in solids highly resistant to aqueous alteration (e.g., ceramics) in order to delay their release in water. Considering some interesting properties of several phosphate-based matrices such as apatites,[1−3] monazites[4−11] and associated brabantites,[12,13] NZP,[14−16] or zirconium phosphates,[17] the synthesis and the characterization of thorium and uranium phosphate compounds were studied for several years.[18−23] These

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prospective studies revealed the existence of a material of very high chemical durability, the β-thorium phosphate−diphosphate: β-$Th_4(PO_4)_4P_2O_7$ or β-TPD, orthorhombic form (called TPD until now since the low-temperature monoclinic variety or α-TPD was not put in evidence).[23] In several of our already published works, we evidenced that this solid is well-appropriated for the immobilization of small amounts of trivalent actinides and large quantities of tetravalent actinides since it allows the formation of solid solutions $Th_{4-x}M_x(PO_4)_4P_2O_7$ with uranium(IV), neptunium(IV), and plutonium(IV) by replacement of thorium.[24−26] The preparation of pure β-TPD and associated solid solutions with tetravalent actinides, through several wet and dry chemical methods, was previously reported.[24−26]

Because of safety considerations, and to avoid any contamination by dust, the immobilization of radionuclides such as ^{239}Pu ($T_{1/2} = 2.5 \times 10^4$ years) and ^{237}Np ($T_{1/2} = 2.1 \times 10^6$ years) must be performed in sintered samples. For this reason, the preparation of dense pellets of pure β-TPD was studied and already described using a conventional way of preparation (i.e., mainly via the "direct evaporation" of a mixture of concentrated solutions containing the cations and the phosphate ions).[27] By this chemical route, dense pellets exhibited relative apparent and effective densities of 93−97% and 95−99% of the calculated value, respectively, which led to open and closed porosities of 2−5% and 1−5%, respectively.

More recently, to improve the homogeneity of the samples prepared, we reported a new way of preparation of β-TPD and β-TUPD solid solutions (β-$Th_{4-x}U_x(PO_4)_4P_2O_7$ or β-$Th_{4-x}U_xP_6O_{23}$) through the precipitation of low-temperature precursors, at 150 °C, in closed containers.[28,29] These well-crystallized solids were extensively characterized and identified as the thorium phosphate−hydrogenphosphate hydrate ($Th_2(PO_4)_2(HPO_4)\cdot H_2O$, TPHPH) or associated thorium−uranium(IV) phosphate−hydrogenphosphate hydrate ($Th_{2-x/2}U_{x/2}(PO_4)_2(HPO_4).H_2O$, TUPHPH) from 90 °C to about 170 °C. Between 200 and 250 °C, it was progressively transformed into the monoclinic α-form of the thorium phosphate−diphosphate (α-TPD or α-TUPD).[28,29] These phases were stable up to about 950 °C and then turned into β-TPD or β-TUPD solid solutions (orthorhombic form), extensively reported in the literature.[28,29]

We report in this paper the preparation of dense pellets of β-TUPD solid solutions. Two kinds of chemical routes were considered for the synthesis of the β-TUPD precursor: "direct evaporation" of a mixture of concentrated solutions, on the one hand, and "precipitation" of the thorium−uranium(IV) phosphate−hydrogenphosphate hydrate (TUPHPH), on the other hand.

The variation of the specific surface area of the powder and the associated linear shrinkage of the pellets was followed versus the heating temperature. Both properties were correlated to the grain size distribution and to the general densification of the solid. Most of the pellets were prepared using a two-step procedure involving a uniaxial pressing at room temperature and then a heat treatment at 1200−1250 °C for several hours. Several other pellets of β-TPD and associated β-TUPD solid solutions were prepared by hot-pressing experiments. The effects of pressing, heat treatment, and grinding on the densification of the pellets were also examined. The main results are presented in this paper.

Because of the properties required to ensure the long-term immobilization of actinides in the ceramic, its chemical durability was carefully studied. That of powdered β-TPD and β-TUPD solid solutions was already demonstrated.[30−33] We report in this paper the preliminary results dealing with the chemical durability of β-TUPD sintered samples in several aggressive media (e.g., 0.1 M HNO_3 or 0.1 M H_2SO_4) or in natural waters (Hydroxydase and Brides waters (trademarks)).

Experimental Section

Preparation of Powdered β-TUPD Samples. Thorium chloride solution was from Rhône-Poulenc (France) while uranium chloride solution was prepared by dissolving uranium metal chips in 4 M HCl. Other chemical reagents were supplied by Merck and Aldrich-Fluka.

All the β-TUPD precursors were prepared using wet chemistry method from thorium and uranium(IV) chloride solutions and concentrated phosphoric acid. The preparation of the powdered precursor of β-TUPD solid solutions (β-$Th_{4-x}U_xP_6O_{23}$) involved two different wet chemistry methods.

The first one, called "direct evaporation", described in previous published works,[27] started from a mixture of concentrated solutions of thorium chloride (0.6−1.5 M), uranium(IV) chloride (0.7 M), and phosphoric acid (5 M) in the mole ratio $(Th + U)/PO_4 = 2/3$ and $U/Th = x/(4-x)$ for several x values.[21,25,34] After the complete evaporation of the mixture at 100−150°C on a sand bath, the residue was ground manually, heated at 400−500 °C for 2 h, and then finally heated at 1250 °C for 10 h under inert atmosphere (argon) to prevent the oxidation of uranium(IV) into uranyl.

The second method, called the "precipitation process", respected the same stoichiometric conditions and involved the initial precipitation of thorium−uranium(IV) phosphate−hydrogenphosphate hydrate (TUPHPH) of general formula $Th_{2-x/2}U_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$ in a closed PTFE container on a sand bath ($\theta = 90-160$°C, 3 h to 2 weeks) or in Parr Instrument Company autoclaves ($\theta = 150-160$°C, 4 weeks) as already mentioned for pure TPHPH.[22,28] The crystallized solids prepared in this way were separated from the supernatant by filtration or centrifugation (4000 rpm), washed several times with deionized water and then with ethanol in order to eliminate the remaining acid, dried in an oven ($\theta =$ 100°C), ground manually, and then characterized.

High-temperature treatments of the samples were performed up to 1300 °C (with a rate of 5 °C/min) in alumina boats

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under inert atmosphere (argon) in a Pyrox HM40 or in an Adamel FR 20 furnace.

Sintering and Characterization of the β-TUPD Samples. The initial pressing was performed between 100 and 800 MPa with a Graseby/Specac press supplied by Eurolab using tungsten carbide dies purchased by Siametir in order to get rectangular or cylindrical pellets.

The dilatometric experiments were performed with a TMA 92-16 apparatus from Setaram working in argon atmosphere from room temperature to 1300 °C.

The relative apparent and effective densities of the sintered samples were evaluated using helium or water pycnometry ($\rho_{wat} = 0.997$ g/cm^3 at 25°C) after immersion and outgassing of the sample in the fluid, while the determination of the dimensions of the pellets led to the geometrical density. For measurements with helium, a multipycnometer from Quantachrome was used. These experimental densities were compared to the values calculated for β-$Th_{4-x}U_x(PO_4)_4P_2O_7$ from crystallographic data[25] according to the following formula:

$$d = \frac{4923.1 + 19.9 \times x_U}{949 - 10 \times x_U} \qquad (1)$$

High-temperature sintering experiments were carried out using a high-temperature furnace equipped with a 10-tons uniaxial press from ECM Infrafour Physitherm. The powder was ground in an agate mortar and then put in a graphite die. To avoid any carburization of the powder, a papyex sheet (from Carbone Lorraine) covered with boron nitride (BN) was inserted between the matrix and the powder. BN acted as a diffusion barrier for carbon. The experimental heating/pressing sequence was the following: heating to 150 °C (step of 1 h) and then to 800 °C (step of 15 min) in a vacuum with a rate of 10 °C/min, and then finally up to 1150 °C in argon atmosphere with the same heating rate (step of 4 h) under pressure between 15 and 30 MPa.

Electron probe microanalyses (EPMA) were carried out using a Cameca SX50 apparatus working with 15 kV voltage and a 10 nA current beam. ThO_2 (Mα ray of thorium), UO_2 (Mβ ray of uranium), and $SmPO_4$ (Kα ray of phosphorus) were used as monitors. The grain size distribution of the powdered samples was studied with a Coulter LS 230 laser particle size apparatus while the specific surface area was determined using the BET method (nitrogen adsorption at 77 K) with a Coulter SA 3100 apparatus.[35] TGA and DTA experiments were done with a Setaram TG 92-16 apparatus under inert atmosphere (argon) with a heating rate of 2−5 °C/min. SEM micrographs were carried out with a Hitachi S2500 scanning electron microscope.

Leaching Tests. High-density polyethylene (HDPE) containers of low adsorption properties were used to perform the leaching experiments at 25 °C. After washing the samples (0.1 M HNO_3 or HCl, 1−7 days) to avoid the presence of crystal defects, minor phases, or small particles which could induce perturbations on the normalized dissolution rates during the first days of experiment, the leaching tests were achieved at 25 °C by mixing 200 mg of sintered sample with 5 mL of acidic solution. At regular intervals, a small volume of the leachate (100 μL) was taken and then renewed by fresh solution. After centrifugation at 13 000 rpm to prevent the presence of colloids, the concentrations of thorium and uranium were determined in the leachate by inductively coupled plasma-mass spectrometry (ICP-MS) using a Fisons Plasma Quad apparatus. From these results, the normalized leaching N_L (expressed in g/m^2) and the associated normalized dissolution rate R_L (in g/(m^2 day)) were determined considering the following equation:

$$R_L(E_i) = \frac{dN_L(E_i)}{dt} = \frac{d}{dt}\left(\frac{C_{E_i} \times V \times M_{E_i}}{x_{E_i} \times S}\right) \text{ where } E_i = \text{Th, U} \qquad (2)$$

In this expression, C_{E_i} is the concentration of the element E_i in the leachate, V, the volume of leachate, x_{E_i}, the mass ratio of E_i in the solid, and S, the effective surface area of the solid.

Results and Discussion

Preparation and Characterization of Powdered β-TUPD Samples. All the precursors of β-TUPD solid solutions (β-$Th_{4-x}U_xP_6O_{23}$) were prepared via “direct evaporation” or the “precipitation process” as described in the Experimental Section. From electron probe microanalyses (EPMA), the raw samples appeared homogeneous and single phase. The elementary weight percents and (Th + U)/P and U/(U + Th) mole ratios were in good agreement with that expected, considering the general formula.[29] Nevertheless, as will be described in the following sections, the partial oxidation of small amounts of uranium(IV) into uranium(VI) was observed during this “precipitation process”.

The behavior of the samples prepared via “direct evaporation” was followed by XRD versus the heating temperature. The samples appeared poorly crystallized below 800 °C. Several intermediates such as α-$Th_{1-y}U_yP_2O_7$ or $Th_{2-z}U_z(PO_4)(P_3O_{10})$ (previously known as β-$Th_{1-z}U_zP_2O_7$)[36] were observed between 800 and 1000 °C. The crystallization of β-TUPD solid solutions began above 850 °C. Pure and single phase samples of β-$Th_{4-x}U_xP_6O_{23}$ were prepared at 1250 °C for $x \leq 2.8$. Nevertheless, we observed some great variations in the U/(U + Th) mole ratio while (Th + U)/P remained constant. Moreover, for $Th_2U_2P_6O_{23}$, some remaining α-$Th_{1-y}U_yP_2O_7$ was still present in the solid as a minor phase at this temperature. It was transformed into β-TUPD by extending the holding time or by heating the sample above 1250 °C for several hours.

The same study was devoted to samples prepared via the “precipitation process”. The well-crystallized TUPHPH was transformed into single phase α-TUPD (monoclinic) after heating between 200 and 250 °C.[28,29] Above 900−950 °C, this later compound turned into β-TUPD (orthorhombic) which was found to be stable up to 1300 °C. In this way, pure and single phase β-TUPD solid solutions were prepared for $x \leq 2.8$.[29] No additional diffraction line was found in the XRD diagrams, excluding the presence of α-$Th_{1-y}U_yP_2O_7$, $Th_{2-z}U_z(PO_4)(P_3O_{10})$, $Th_{2-w}U_wO(PO_4)_2$, or $Th_{1-r}U_rO_2$.

TGA and DTA Experiments. To perform the optimal sintering of β-TUPD, TGA and DTA experiments were carried out for both kinds of processes. We already discussed the results obtained when heating pure β-TPD prepared through “direct evaporation”.[27] The total weight loss (≈14%) mainly occurred below 400 °C and was correlated to the elimination of volatile products (water, remaining acid, and so forth). It was found to be complete after heating at 1250 °C. The same behavior was observed for β-TUPD solid solutions prepared by the same method. For samples prepared via the “precipitation process”, the total weight loss was observed between 150 and 400 °C. As it was already described for pure TPHPH,[28] it corresponds to the dehydration of TUPHPH between 170 and 200 °C and then to the condensation of hydrogenphosphate groups into diphos-

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Table 1. Variation of the Specific Surface Area of Powdered β-$Th_{4-x}U_xP_6O_{23}$ Samples versus the Heating Temperature Prepared from a Residue of Evaporation ($x = 0.6$ and 1.2) or from the Precipitation of TUPHPH ($x = 1.0$, 1.6, and 1.9)

	specific surface area[a] (m^2/g)		specific surface area[b] (m^2/g)		
θ (°C)	$x = 0.6$	$x = 1.2$	$x = 1.0$	$x = 1.6$	$x = 1.9$
150	3.6 ± 0.2	2.6 ± 0.2		15.3 ± 0.8	10.6 ± 0.2
400	5.1 ± 0.2	3.5 ± 0.2	10.1 ± 0.5	16.8 ± 0.8	10.3 ± 0.2
600	4.6 ± 0.2	3.0 ± 0.1	10.0 ± 0.5	13.6 ± 0.7	9.7 ± 0.2
700	4.6 ± 0.2	2.4 ± 0.1	9.5 ± 0.5	9.5 ± 0.5	9.4 ± 0.2
800	2.5 ± 0.2	1.6 ± 0.1	8.6 ± 0.5	12.1 ± 0.6	7.7 ± 0.2
900	1.7 ± 0.1	1.4 ± 0.1	6.0 ± 0.4	12.2 ± 0.6	6.2 ± 0.2
1000	2.2 ± 0.1	1.7 ± 0.1	3.6 ± 0.3	6.3 ± 0.6	5.5 ± 0.2
1100	0.8 ± 0.1	0.7 ± 0.1	1.6 ± 0.2	2.7 ± 0.5	4.8 ± 0.1
1200	0.3 ± 0.1	0.3 ± 0.1	0.5 ± 0.2	1.0 ± 0.2	2.9 ± 0.1
1250	0.1 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	1.1 ± 0.1
1300	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1		

[a] β-TUPD prepared via "direct evaporation". [b] β-TUPD prepared via the "precipitation" process.

phate entities between 180 and 250 °C leading to the formation of α-TUPD. The crystallization of β-TUPD occurs between 900 and 950 °C.[29] It was correlated to a small exothermic peak while no additional weight loss was observed. This temperature is consistent with that observed when synthesizing pure β-TPD through "direct evaporation" (938 °C) or from an amorphous precursor (860 °C).[27,37] No weight loss was recorded up to 1300 °C, excluding the decomposition of β-TUPD below this temperature.

Granulometric and BET Studies. The variation of the grain size distribution of powdered β-TUPD prepared using both methods was followed versus several parameters such as heat temperature and holding time. The particle size distribution of β-TUPD prepared by direct evaporation and then heating at 1250 °C is found to be heterogeneous and spread from 1 to 40 μm, with an average grain size equal to 10−20 μm. The grain size distribution remains almost unchanged from 150 to 900 °C. It is composed by two populations spread from 0.1 to 0.5 μm (average grain size of 0.25 μm) and from 2 to 4 μm (average grain size of 3.5 μm). Both seem to correspond to the same grain population since the particles appear as multilayered and elongated aggregates of 0.1−0.3 μm thick and several micrometers in length. Above 1100 °C, the average grain size of the powder slightly increases up to 10−20 μm (this value being reached after heating at 1250 °C).

The specific surface area (SA) of the powder was also followed for several initial conditions after heating the samples between 400 and 1300 °C for 10−14 h (Table 1). The specific surface area of the precursors prepared via "direct evaporation" is found to about 3 m^2/g while it is higher (10−17 m^2/g) for samples obtained through the "precipitation process". For both ways, the SA value does not vary significantly when heating the sample between 400 and 800 °C. For the "precipitation process", it decreases significantly above 900 °C due to the crystallization of β-TUPD and to the swelling of the grains and then to the reactive sintering of β-TUPD. After heating at 1250 °C, the solids synthesized by both ways exhibit a low SA value (0.1−0.4 m^2/g). It does not decrease significantly when increasing the holding time up to 60 h at this temperature (0.2 m^2/g).

Variation of the Linear Shrinkage versus Temperature. The procedure developed to prepare β-TUPD pellets was based on two successive steps. For both chemical methods of synthesis, the solid was initially heated with a rate of 2−5 °C/min up to 400 °C and held for 2−4 h in order to eliminate the major part of remaining water or volatile products. It was then heated at high temperature to turn into β-TUPD. The first study was dedicated to the variation of the linear shrinkage versus the heating temperature through a complete dilatometric study. The dimensional changes of cylindrical pellets ($\varnothing = 8$ mm) pressed at 500 MPa and then heated with a rate of 5 °C/min for both kinds of samples are presented in Figure 1 while the linear shrinkage reported for several compositions of β-TUPD solid solutions prepared by the "precipitation process" is gathered in Table 2.

For this process (Figure 1a), the variation of the thickness of the pellet versus the heating temperature consists of three parts. The first contraction corresponds to low variations between 200 and 400 °C (shrinkage of 0.3−0.4%) and is correlated to the dehydration of TUPHPH and then to the condensation of hydrogenphosphate groups leading to the formation of α-TUPD. Two important dimensional changes are observed above 800 °C. The first one, located between 850 and 1000 °C, can be assigned to the crystallization of β-TUPD and is associated with the small exothermic peak, observed in the DTA curve.[29] The substantially greater shrinkage is observed between 1000 and 1250 °C. It is correlated to the swelling of the grains and to the sintering of β-TUPD (densification and improvement of the cohesion between the grains) which leads to the significant decrease of the specific surface area previously described.

For pellets prepared via "direct evaporation", the results are consistent with that published for pure β-TPD.[27] The shrinkage occurs in several successive steps between 400 and 1000 °C probably due to the formation (and then to the transformation) of the intermediate phases evidenced by XRD. Moreover, the sintering occurs for higher heating temperature and longer holding time than for samples prepared through the "precipitation process". This difference probably results from the heterogeneity and in the lower specific area of the precursors prepared through "direct evaporation".

While the sintering of the samples prepared by both methods remains incomplete when heating at 1200 °C (with a heating rate of 5 °C/min) even for long holding times ($d_{eff}/d_{calc} = 85-90\%$, even after 70 h), it is found to be complete at 1250 °C. At this heating temperature, the linear shrinkage reaches 12−18% after 10 h, depending on the chemical process considered. From Figure 1a, the sintering of $Th_{2.4}U_{1.6}P_6O_{23}$ appears complete after heating at 1250 °C for 5 h since it reaches a plateau at about 18.8%. This holding time is significantly reduced by comparison to that observed for samples prepared via "direct evaporation" which requires a step of at least 10−15 h at this temperature. This main difference between both processes can be directly correlated to the higher specific surface area

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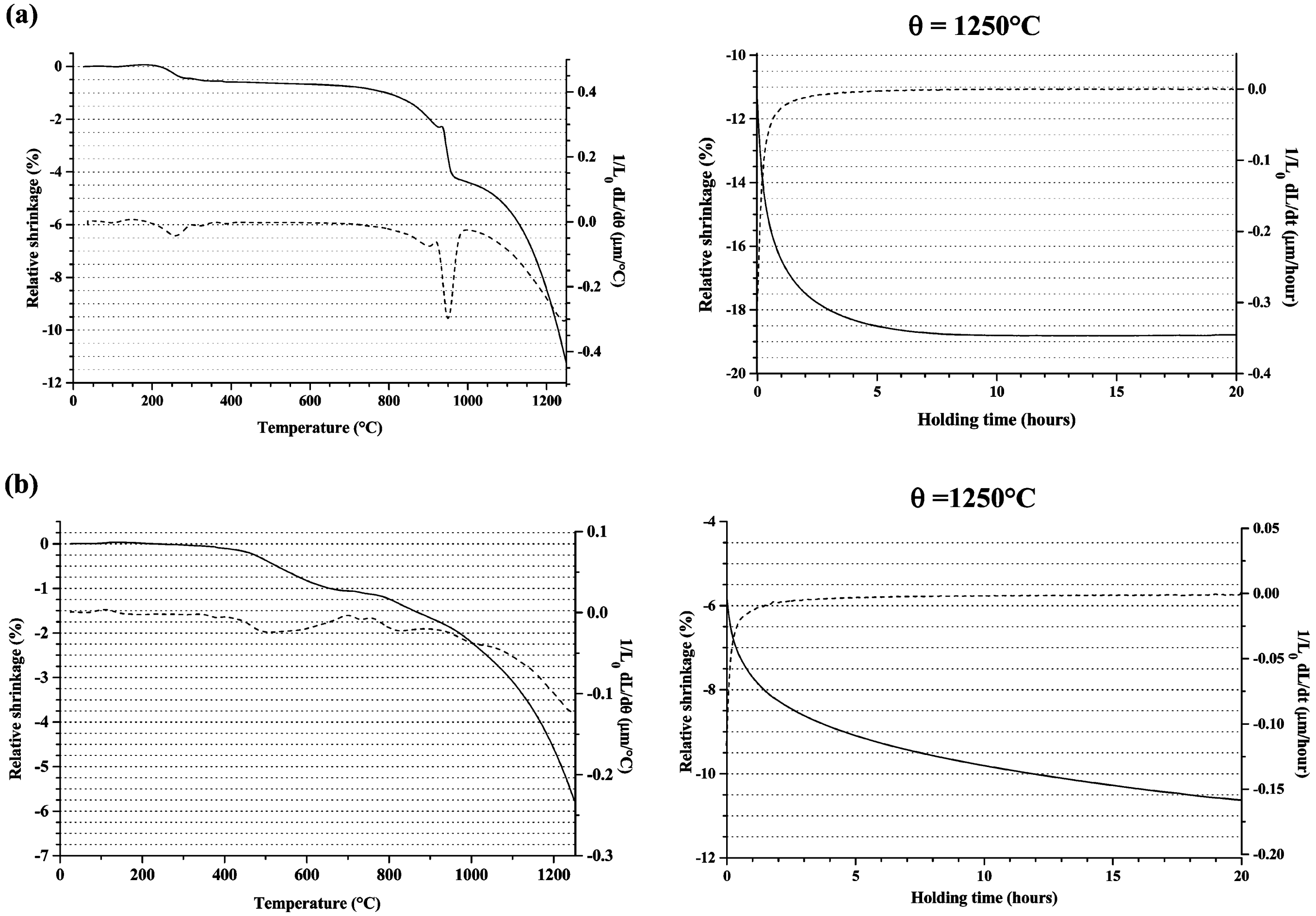

Figure 1. Dilatometric curve of β-TUPD (P = 500 MPa) prepared via the "precipitation process" (a) and through "direct evaporation" (b): relative shrinkage (solid line) and derivative $1/L_0 \times dL/d\theta$ or $1/L_0 \times dL/dt$ (- - -).

Table 2. Variation of the Linear Shrinkage versus the Heating Temperature for β-TUPD Solid Solutions Prepared via the "Precipitation Process"

	$x = 0.2$	$x = 1.6$	$x = 2.0$
Dehydration−Condensation of Hydrogenphosphate Groups			
temperature (°C)	350	250	266
linear shrinkage (%)	0.4	0.4	0.3
Transformation of α-TUPD into β-TUPD			
temperature (°C)	900	948	904
linear shrinkage (%)	2.5	4.2	3.3
Sintering of β-TUPD			
holding time at 1250 °C (h)	linear shrinkage (%)		
0	8.7	11.4	10.1
1	13.8	16.4	11.4
2	14.7	17.5	11.6
5	15.4	18.5	11.7
10	15.7	18.8	11.8
50	16.0	18.8	12.4

(and thus to the higher reactivity) of the precursors prepared by precipitation in a closed container. Finally, as shown from Table 2, the chemical composition of β-TUPD solid solutions (e.g., the uranium weight loading in the sample) does not affect significantly the heating temperature nor the holding time required to get dense pellets. This remark can also be applied to samples prepared through "direct evaporation".

The variation of linear and volumic relative shrinkages was also studied versus the initial pressure when heating at 1250 °C (Figure 2). For all the initial pressing conditions considered (200−800 MPa), the relative linear shrinkage reaches 13−18% (relative volumic shrinkage of 28−42%). These results are in very good agreement with that already obtained for pure β-TPD (Figure 2).[27] Moreover, as it was expected, more important is the initial pressure used, and less important is the relative linear shrinkage. Finally, for all the samples

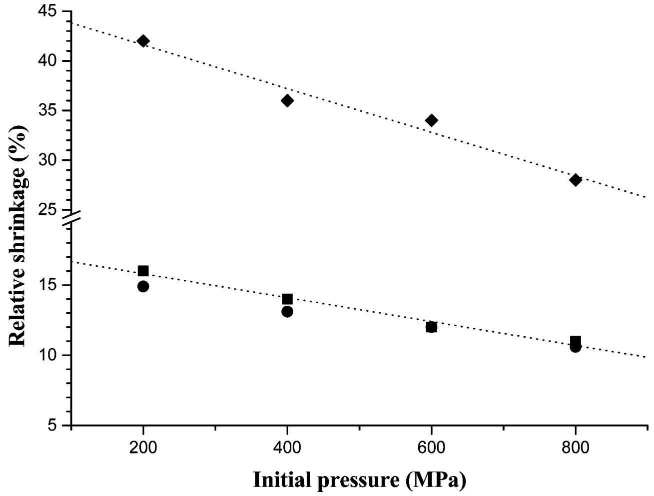

Figure 2. Variation of the relative shrinkage of β-TUPD, prepared through the "precipitation process", versus the initial forming pressure (θ = 1250 °C, 10 h): ◆ volumic, ■ linear; ● results reported for pure β-TPD prepared through "direct evaporation".[27]

Table 3. Influence of the Initial Pressing Conditions on the Final Density of β-TUPD Pellets Prepared via the "Precipitation Process" (θ = 1250 °C, t = 10 h)

initial pressure (MPa)	200	400	600	800
d_{init}[a,c]	2.93 (58%)	3.24 (64%)	3.37 (66%)	3.55 (70%)
d_{geom}[b,c]	4.89 (92%)	4.87 (92%)	4.73 (89%)	4.70 (89%)
d_{eff} (water)[b,c]	5.14 (97%)	5.15 (97%)	5.13 (97%)	5.03 (95%)
d_{eff} (helium)[b,c]	5.28 (99%)	5.27 (99%)	5.31 (100%)	5.31 (100%)

[a] Relative density calculated considering the density of α-TUPD (e.g., 5.08). [b] Relative density of β-TUPD calculated considering eq 1. [c] With an uncertainty of 2%.

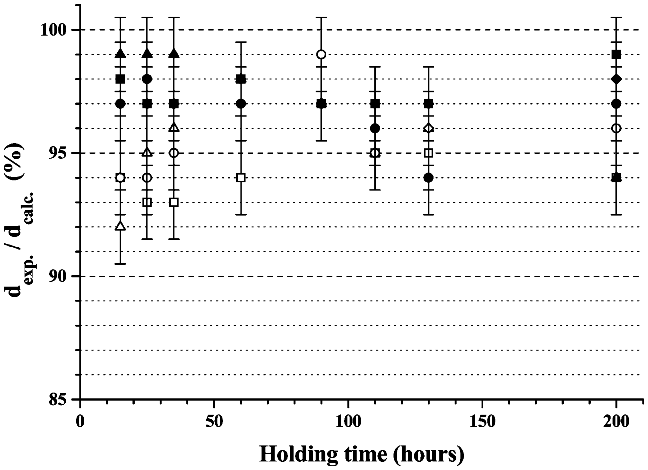

Figure 3. Influence of the initial pressing and heating conditions on the final densities of β-TUPD pellets prepared via "direct evaporation" (θ = 1250 °C): apparent (open symbols) and effective (solid symbols) relative densities for initial pressing at 100 MPa (□/■), 300 MPa (△/▲), 500 MPa (◇/◆), and 800 MPa (○/●).

prepared (cylindrical pellets, ∅ = 10 mm), the final geometrical and effective densities seem to be independent of the initial pressing conditions ($d_{geom}/d_{calc} = 89-92\%$; $d_{eff}/d_{calc} = 97-100\%$) after heating for 10 h at 1250 °C (with a heating rate of 5 °C/min, Table 3 and Figure 3). In these conditions, the initial pressing does not play any important role in the final densification of the pellets prepared provided that the heat treatment is achieved at this last temperature.

Density of the Pellets. As already reported, all the samples were pressed at room temperature between 100 and 800 MPa and then finally heated between 1200 and 1250 °C for a few hours. This procedure was applied with success to various compositions of β-TUPD solid solutions. The dimensions and the corresponding relative densities of β-$Th_3UP_6O_{23}$ pellets are gathered in Table 4 for several initial conditions. From these results, the pellets appear poorly densified after heating at 1200 °C ($d_{geom}/d_{calc} \approx 70-80\%$) which is consistent with the results of the dilatometric study. Complementary observations by SEM confirmed that the open porosity remains high at this temperature while the cohesion between the grains is rather poor (see Figure 5a,b). On the contrary, the samples prepared at 1250 °C appear well-densified even after only 3 h of holding time ($d_{geom}/d_{calc} \approx 91-95\%$). The influence of the holding time (at 1250°C) on the final density of β-$Th_{2.4}U_{1.6}P_6O_{23}$ pellets was also studied. In this way, the evolution of the dimensions of the pellets was followed from 2.5 to 50 h at this temperature (Table 5). For all the conditions considered, the densification appears rather good. On the basis of the results obtained, the open and close porosities are evaluated to 2−4% each. Both values seem to be sufficient to ensure the decrease of the normalized leaching rate during the dissolution tests (due to the low specific area of the sample) and to allow the elimination of helium produced in situ by the disintegration of α-emitter radionuclides, mainly actinide isotopes in this case.

Characterization of the Sintered β-TUPD Samples. All the sintered samples were extensively characterized by EPMA. The results obtained for various chemical routes, chemical compositions, initial pressures, heating temperatures, or holding times are gathered in Table 6. From this table, it appears that, for all the initial conditions, the elementary weight percent and the corresponding mole ratios are consistent with that calculated considering the chemical formula of β-TUPD. Nevertheless, we observed that the samples

Table 4. Relative Density and Dimensions of β-$Th_3UP_6O_{23}$ Pellets for Several Heating Temperatures and Holding Times (P = 150 MPa)

heating temperature (°C)	400[a]	1200[b]	1200[b]	1250[b]	1250[b]
holding time (h)		10	12	3	10
average diameter (mm)	10.13 ± 0.01	9.50 ± 0.03	9.50 ± 0.01	9.00 ± 0.01	8.56 ± 0.01
average thickness (mm)	0.51 ± 0.01	0.57 ± 0.01	0.50 ± 0.01	0.43 ± 0.01	0.46 ± 0.01
geometrical density	3.36 ± 0.04	4.25 ± 0.05	3.72 ± 0.07	4.82 ± 0.03	5.02 ± 0.07
d_{geom}/d_{calc}	66.0 ± 1.5%	81.0 ± 1.0%	70.0 ± 1.0%	91.0 ± 1.5%	95.0 ± 1.5%
d_{He}		4.31 ± 0.09		4.79 ± 0.05	5.07 ± 0.06
d_{He}/d_{calc}		82.0 ± 1.0%		91.0 ± 1.5%	96.0 ± 1.5%

[a] Relative density calculated considering the density of α-TUPD (e.g., 5.08). [b] Relative density of β-TUPD calculated considering eq 1.

Table 5. Variation of the Dimensions and Associated Relative Density of β-TUPD Pellets (x = 1.6) Prepared through the "Precipitation Process" versus the Heating Time for θ = 1250 °C and P = 300 MPa

holding time (h)	0[a]	2.5[b]	5[b]	10[b]	20[b]	35[b]	50[b]
average diameter (mm)	8.08 ± 0.01	6.94 ± 0.01	6.88 ± 0.01	6.90 ± 0.01	6.88 ± 0.01	6.87 ± 0.01	6.86 ± 0.01
diameter shrinkage (%)		14.1	14.9	14.6	14.9	15.0	15.1
average thickness (mm)	2.04 ± 0.02	1.79 ± 0.01	1.74 ± 0.01	1.77 ± 0.01	1.77 ± 0.01	1.77 ± 0.01	1.77 ± 0.01
thickness shrinkage (%)		12.3	14.7	13.2	13.2	13.2	13.2
volumic shrinkage (%)		35.2	38.1	37.1	37.1	37.1	38.1
d_{geom}	3.23 ± 0.03	4.78 ± 0.05	4.98 ± 0.06	4.88 ± 0.05	4.85 ± 0.05	4.88 ± 0.05	4.89 ± 0.05
d_{geom}/d_{calc} (%)	63.6 ± 1.5	90.0 ± 1.5	94.0 ± 1.5	92.0 ± 1.5	91.5 ± 1.5	92.0 ± 1.5	92.0 ± 1.5
d_{H_2O}/d_{calc} (%)			96.0 ± 1.5	96.0 ± 1.5	97.0 ± 1.5	97.0 ± 1.5	97.5 ± 1.5

[a] Relative density calculated considering the density of α-TUPD (e.g., 5.08). [b] Relative density of β-TUPD calculated considering eq 1.

Table 6. Results of EPMA for β-TUPD Sintered Samples ($x = 1.0$ and 1.6, $\theta = 1250$ °C)

		expt					expt	
	calcd[a]	direct evaporation			precipitation	calcd[b]	precipitation	
holding time (h)		15	15	15	10		2.5	10
initial pressure (MPa)		500	500	700	500		300	300
Th (wt %)	46.8	46.9 ± 1.3	46.8 ± 1.4	47.0 ± 2.5	48.5 ± 0.4	37.3	40.9 ± 0.3	40.3 ± 0.6
U (wt %)	15.9	15.6 ± 1.1	15.8 ± 0.9	16.1 ± 2.0	14.3 ± 0.3	25.5	21.6 ± 0.5	22.3 ± 0.2
P (wt %)	12.5	12.7 ± 0.4	12.6 ± 0.5	12.4 ± 0.2	12.5 ± 0.1	12.5	12.6 ± 0.1	12.6 ± 0.2
O (wt %)	24.7	24.8 ± 0.2	24.8 ± 0.6	24.5 ± 0.3	24.7 ± 0.2	24.7	24.9 ± 0.2	24.8 ± 0.2
mole ratio U/(U + Th)	0.25	0.24 ± 0.02	0.25 ± 0.02	0.25 ± 0.04	0.22 ± 0.01	0.40	0.34 ± 0.01	0.35 ± 0.01
mole ratio (Th + U)/PO_4	0.67	0.65 ± 0.03	0.66 ± 0.03	0.68 ± 0.04	0.67 ± 0.01	0.67	0.65 ± 0.02	0.66 ± 0.02

[a] Calculated considering the formula β-$Th_3UP_6O_{23}$. [b] Calculated considering the formula β-$Th_{2.4}U_{1.6}P_6O_{23}$.

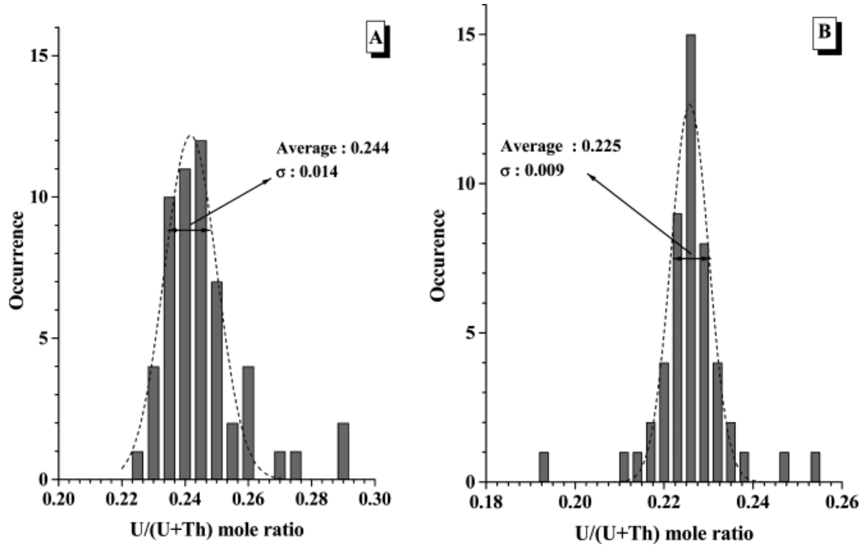

Figure 4. Statistical variations of the U/(U + Th) mole ratio in β-$Th_3UP_6O_{23}$ solid solutions prepared through “direct evaporation” (A) or via the “precipitation process (B)”.

prepared via the “precipitation process” were uranium depleted (of about 8−10 mol % of initial uranium) by comparison to the expected composition. This result is explained by the presence of small amounts of uranium(VI) in the initial solution used and to the low oxidation of uranium(IV) into uranyl during the “precipitation process”. We verified that uranyl ions do not precipitate in our operating conditions. On the contrary, the (U + Th)/PO_4 mole ratios are in good agreement with the expected stoichiometry of β-TUPD. These results were confirmed by XRD analyses which showed that only the diffraction lines of β-TUPD (orthorhombic form) [23,38] are observed excluding the presence of secondary crystallized phases.

Moreover, to confirm the better homogeneity of the samples prepared via the “precipitation process”, especially concerning the U/(U + Th) mole ratio, statistical EPMA experiments were carried out on β-$Th_3UP_6O_{23}$ samples prepared by both methods. For both kinds of sintered samples, 50 analyses were performed, and the variations of the U/(U + Th) mole ratio were carefully examined. The results are reported in Figures 4a (pellet prepared through “direct evaporation”) and Figure 4b (pellet obtained via the “precipitation” process). As was expected considering both ways of the developed synthesis, the samples homogeneity is significantly improved when using the “precipitation process” (0.225 ± 0.009) instead of “direct evaporation” (0.244 ± 0.014), resulting in the precipitation of TUPHPH homogeneous solid solutions as initial precursors.

SEM Observations. Either powdered or sintered β-TUPD samples were observed using scanning electron microscopy (Figure 5). Figure 5a,b correspond to the surface and to the inside of a broken sintered β-TUPD sample heated at 1200 °C for 12 h, respectively. From these micrographs, the solid remains poorly densified at this temperature which is consistent with the results obtained from the dilatometric study. For these operating conditions, the grains are of submicrometric scale and form bigger agglomerates (several micrometers of average diameter) without any global cohesion. The corresponding specific surface area of the sample remains rather high (SA ≈ 2.5 m^2/g).

On the contrary, when increasing the temperature to 1250 °C (Figures 5c,d, respectively), the surface and inner view of the β-TUPD pellet appear very dense even after only 2.5 h of holding time. Correlatively, the specific surface area decreases significantly down to 0.03 m^2/g and was lower than the detection limit of the apparatus when heating the samples for 10 h. The surface and the inside of the pellet remain homogeneous, and the observations are consistent with that achieved for pure β-TPD prepared via “direct evaporation”. The samples appear as a brittle material in which only few open and closed pores are detected. Between both temperatures, the swelling of the grains is also evident, since their dimensions reach several microme-

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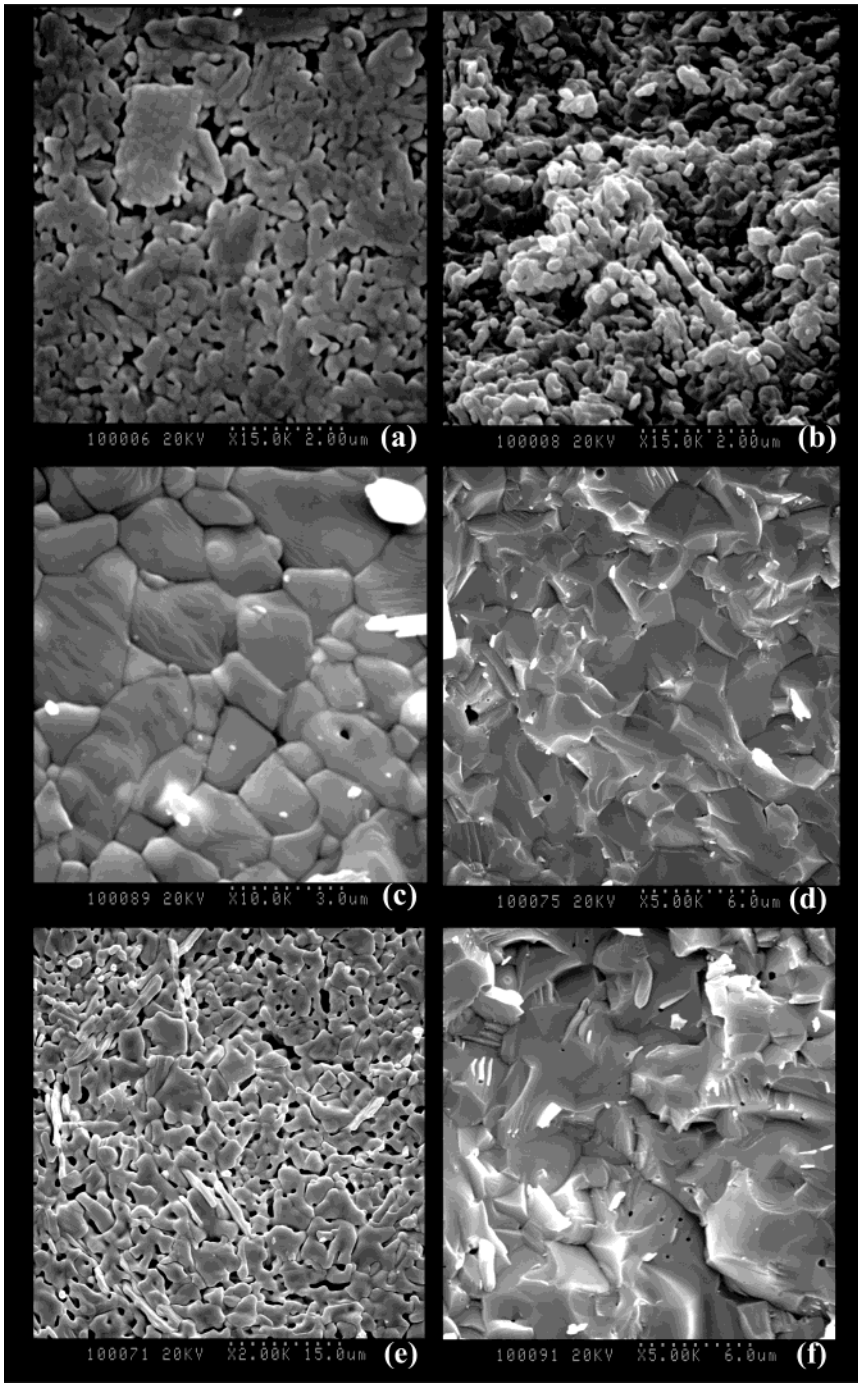

Figure 5. Scanning electron micrographs of sintered β-TUPD heated at 1200 °C for 12 h (a, surface; b, inside) or at 1250 °C for 2.5 h (c, surface; d, inside) and for 50 h (e, surface; f, inside).

ters at 1250 °C while some grain boundaries are clearly observed.

Finally, the increase of the holding time at 1250 °C (up to 50 h, Figure 5e,f) modifies the surface of the material, probably due to the local decomposition of phosphate and then to the formation of $U_{2-w}Th_wO(PO_4)_2$ at the surface of the sample by volatilization of P_4O_{10} while the inside of the pellet is not modified. A significant modification of the surface results from volatilization since the microstructure reveals a pore/grain boundary breakaway, inducing the degradation of the cohesion between the grains. Moreover, in these conditions, the presence of phosphate-depleted secondary phases formed at the surface of the solid could degrade significantly the chemical durability of the pellets during the leaching tests and enhance the specific surface area of the solid.

Hot Pressing Experiments. To complete this study, several pellets (∅ = 13 mm) were prepared through hot-pressing experiments, performed at 1150 °C for 4 h (heating rate of 10 °C/min in argon atmosphere) and for several pressing conditions (15−30 MPa). The results obtained are gathered in Table 7 for several β-TPD (2 tests) and β-TUPD (3 tests) samples. For each sample, the geometrical density reaches 96−99% of the calculated value which corresponds to a global porosity of 1−4%. Results of helium and water pycnometries (after outgassing the samples in the fluid) lead to a density of

Table 7. Relative density of β-TPD and β-TUPD ($x = 1.6$) Samples Prepared through Hot-Pressing Experiments

	β-TPD-1	β-TPD-2	β-TUPD-1	β-TUPD-2	β-TUPD-3
initial pressing (MPa)	15	30	30	27	27
d_{geom}[a]	5.11 (98%)	5.12 (99%)	5.14 (97%)	5.09 (96%)	5.07 (96%)
d_{eff} (water)[a]	5.02 (97%)	5.15 (99%)	5.26 (99%)	5.25 (99%)	5.26 (99%)
d_{eff} (helium)[a]	5.11 (98%)	5.18 (100%)	5.34 (100%)	5.32 (100%)	5.31 (100%)

[a] Relative density calculated considering eq 1, with an uncertainty of 2%.

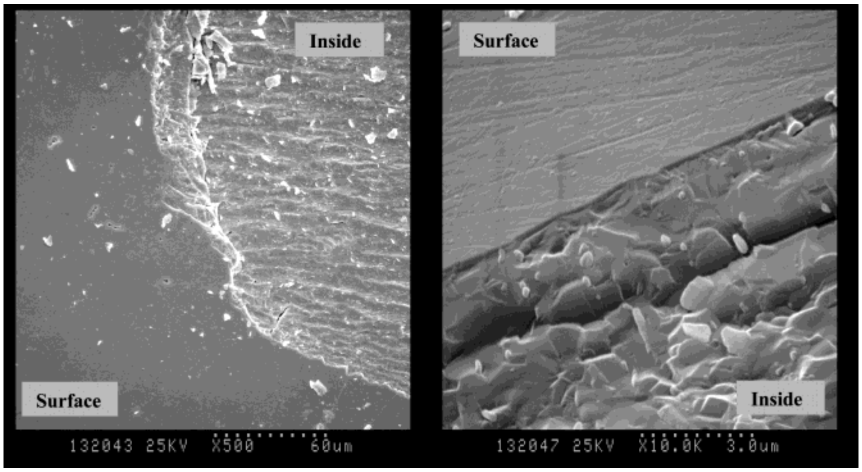

Figure 6. Scanning electron micrographs of sintered β-TUPD prepared by hot pressing experiments (15−30 MPa, $\theta = 1150$ °C, 4 h).

Table 8. Normalized Dissolution Rates R_L(Th), $R_L(U)_i$, and $R_L(U)_t$ (Expressed in g/(m^2 day)) of β-TUPD Sintered Samples during Leaching Tests in Acidic Media and in Natural Waters at 25 °C

leachate	R_L(Th)	$R_L(U)_i$	$R_L(U)_t$
0.1 M HNO_3	$(2.4 \pm 0.1) \times 10^{-5}$	$(4.6 \pm 0.3) \times 10^{-5}$	$(2.0 \pm 0.1) \times 10^{-5}$
0.1 M HCl	$(4.1 \pm 0.5) \times 10^{-6}$	$(1.94 \pm 0.03) \times 10^{-5}$	$(4.7 \pm 0.5) \times 10^{-6}$
0.1 M H_2SO_4	$(2.2 \pm 0.4) \times 10^{-5}$	$(4.0 \pm 0.1) \times 10^{-5}$	$(2.2 \pm 0.2) \times 10^{-5}$
Hydroxydase water (trademark)	$<10^{-6}$	$(3.9 \pm 0.1)\ 10^{-6}$	$(2.4 \pm 0.3)\ 10^{-6}$
Brides water (trademark)	<LoD[a]	$(1.08 \pm 0.02)\ 10^{-5}$	<LoD[a]

[a] Limit of detection.

97−100%, i.e., to 1−3% and 0−2% of open and closed porosity, respectively. These values are confirmed by SEM observations of the surface and inside of the sample (Figure 6) which exhibits a low open porosity essentially located at the edge of the cylindrical pellets.

Chemical Durability of Sintered β-TUPD during Leaching Tests. In the aim to immobilize tetravalent actinides in the β-TPD structure, the chemical durability of β-TUPD sintered samples was examined through several leaching tests in acidic solutions or in natural waters. The high resistance of powdered samples of β-TPD and associated solid solutions (U, Pu) was already demonstrated in already published works.[30−33] In this paper, we report the first results dealing with the resistance of β-TUPD pellets (various samples prepared whatever the chemical method of preparation) to aqueous alteration and the direct consequences of the sintering process on the chemical durability of the samples. The normalized dissolution rates determined at 25 °C are gathered in Table 8 while the evolution of the normalized leaching in 0.1 M H_2SO_4 acid is given, as an example, in Figure 7. A more detailed and complete study will be published soon, especially pointing out the results obtained far from thermodynamical equilibrium (study of the kinetics of the β-TUPD dissolution),[39] on one hand, and near to the saturation (analysis and characterization of the phases neoformed in the back-end of the initial dissolution), on the other hand. A general scheme involving the successive chemical reactions occurring during the dissolution of β-TUPD will be proposed in a forthcoming paper.[40]

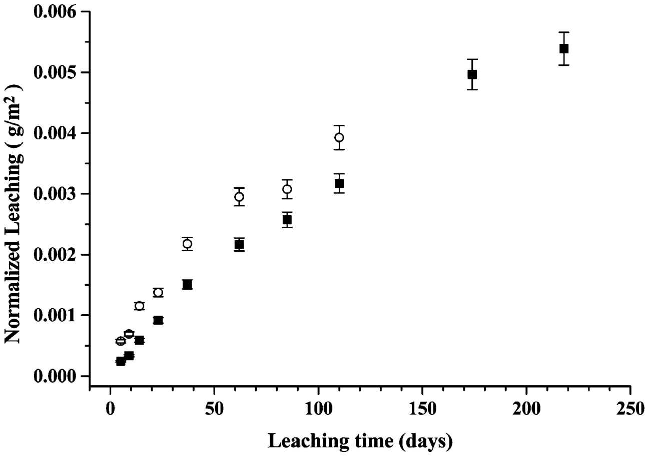

Figure 7. Evolution of the normalized leaching N_L(Th) (○) and N_L(U) (■) of β-$Th_3UP_6O_{23}$ in 0.1 M H_2SO_4 ($\theta = 25$ °C).

As was expected from the characterization of β-TUPD sintered samples (absence of significant amounts of

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[39] Clavier, N.; Dacheux, N.; Ritt, J. To be published.

[40] Dacheux, N.; Clavier, N.; Du Fou de Kerdaniel, E.; Drot, R.; Simoni, E. To be published.

secondary phases which could induce the degradation of the retention properties of the material), the chemical durability of β-TUPD samples is not significantly affected by the sintering process. All the normalized dissolution rates determined from the thorium and uranium amounts in the leachate remained very low at room temperature (10^{-6} to 10^{-5} g/(m^2 day)). Moreover, as was already observed for powdered β-TUPD solid solutions, the R_L(Th) and $R_L(U)_t$ values are almost equal which clearly indicates that the dissolution is congruent (both elements being released with the same normalized leaching rate without any formation of neoformed phase). For uranium, the initial dissolution rate, $R_L(U)_i$, determined during the first days of leaching, is usually found two to three times higher than the $R_L(U)_t$ value. This phenomenon, which is not observed for thorium, can be assigned to the oxidation of small quantities of uranium(IV) into uranyl at the surface of the pellets and the consequent easier dissolution of uranium in this chemical oxidation state.

On the contrary, for leaching tests performed at higher temperature (e.g., $\theta = 90$°C) and/or higher pH values, the normalized leaching, N_L(Th), decreases drastically due to the saturation of the leachate and/or to the precipitation of thorium at the surface of the pellet as the TPHPH while uranium remains in the leachate in the uranyl form. In these experimental conditions, thorium does not appear as a conservative element. Thus, only the normalized dissolution rates $R_L(U)_i$ and $R_L(U)_t$ were considered to evaluate the chemical durability of the β-TUPD samples. More generally, in all the media considered, the normalized dissolution rates appear lower than that determined, in the same conditions, for other ceramics studied in the same objective such as apatites, britholites, zirconolites, synroc, or zircons and of the same order of magnitude as for monazites.[3,4,41−43]

Conclusion

The main results discussed in this paper confirmed the good capability of sintering of β-TPD and associated solid solutions β-TUPD. Dense pellets were prepared through a rather simple procedure involving a uniaxial pressing at room temperature and then a heating treatment at high temperature. The best densification of the pellets prepared through the “precipitation” method was obtained after heating the raw pellet for 5 h at 1250 °C. On the contrary, the heating treatment must be prolonged up to at least 15 h for samples prepared via “direct evaporation”.

While pure β-TUPD samples were prepared through both chemical methods, the homogeneity of the sintered samples was significantly improved by the use of TUPHPH solid solutions as initial precursors. That observation was mainly attributed to the higher reactivity of the initial powder (higher specific surface area, smaller grain size, and so forth).

The results of leaching tests performed on β-TUPD sintered samples confirmed the high resistance of β-TPD and associated solid solutions already described for this material in the powder form. Indeed, no significant modification of the normalized dissolution rate was observed which confirmed the absence of secondary phases of low chemical durability. In these conditions, β-TPD can be considered as a potential ceramic for the efficient immobilization of tetravalent actinides.

Complementary experiments are now in progress in order to study the simultaneous incorporation of trivalent (Am, Cm) and tetravalent (U, Np, Pu) actinides in phosphate based materials. The synthesis, the characterization, the sintering properties, and the chemical durability of β-TPD/(La,Nd,Ce,Gd)−monazite composites are now being examined.

Finally, taking into account the data reported in this paper, the preparation of sintered samples of β-TUPD from TUPHPH was demonstrated. Because of the very low solubility product of TPHPH (e.g., $\log(K°_{S,0}) \approx -67$)[30,44] and that of associated solid solutions with tetravalent actinides TAn^{IV}PHPH (U, Np, Pu), the decontamination of radioactive liquid waste could be performed through a three-step procedure involving the initial precipitation of TAn^{IV}PHPH, uniaxial pressing of the dried powder, and then heat treatment at 1250 °C to get the formation of sintered β-TAn^{IV}PD samples. Through this process, the efficient immobilization of the given tetravalent actinides could be guaranteed.[45,46]

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