Morphology dependent sintering path of nanocrystalline ThO₂

T. Wangle^{1,2,3}, M. Belis^{1,4}, V. Tyrpek^{1,4}, J. Pakarinen¹, T. Cardinaels^{1,5}, T. Delloye³, J. Vleugels²,
M. Verwerft¹

¹ Belgian Nuclear Research Centre (SCK CEN), Institute for Nuclear Materials Science, Boeretang 200, B-2400 Mol, Belgium

² KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, P.O. Box 2450, B-3001 Heverlee, Belgium

³ Solvay, 20 rue Marcel Sembat, 69197 St Fons, France

⁴ Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, Prague 2, Czech Republic

⁵ KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. 2404, B-3001 Heverlee, Belgium

Keywords: thoria, thorium oxide, thorium oxalate, sintering, morphology

Abstract: Thorium is most commonly precipitated as oxalate, because of the high efficiency regardless of precipitation conditions. Thorium oxalate readily decomposes into fine-grained ThO₂ during heating, but keeps the macrostructure of the oxalate platelets. To assess the effects of precipitate macrostructure on the sintering behavior, different platelet morphologies were prepared and sintered. There are two factors which influence the sintering: the presence of holes within the platelets and the size of the platelets. Small platelets or precipitates with holes generally sinter to thorium dioxide pellets of a higher density and smaller grain size.

I. Introduction

Thorium dioxide is a candidate fuel for several types of nuclear reactors. Hania and Klaassen [1] extensively reviewed the preparation, properties and use of thorium oxide as a nuclear fuel. The production process, however, still needs to be further developed to meet high industrial efficiency and standards. ThO₂ is a refractory ceramic with the highest oxide melting point reported for binary oxides at 3665±70 K [2] or 3624±86 K [3]. As such, the temperature needed to efficiently sinter ThO₂ to closed porosity (desired densities of ≥ 95%) often exceed the 1700-1750 °C achievable in commercial high-volume continuous furnaces. One may expect to improve sinterability by introducing defects on the cation or anion lattice. At elevated temperatures (T > 2000 K), a narrow non-stoichiometry domain develops under highly reducing atmospheres [4, 5]. Electrical conductivity measurements indicated that deviation of stoichiometry starts already at 1673 K [6]. Alternatively, sintering-enhancement can be achieved by suitable dopants that induce anion or cation lattice defects. Previous reports have shown that the addition of divalent M²⁺ (Ca, Mg) [7], trivalent M³⁺ (Y, Al) [8-11], or pentavalent M⁵⁺ (V, Nb, Ta) [12] cations to ThO₂ can increase the sinterability significantly. In mixed oxides (Th_{1-y}U_y)O_{2+x} and (Th_{1-y}Pu_y)O_{2-x} deviations from stoichiometry readily occur as the substituting cations, U and Pu are also in valence states other than (IV). [13, 14]. The formation of defects on anion or cation sites in the fluorite crystal structure of ThO₂ promotes the diffusion of the sintering-limiting cation. This diffusion rate is a function of the square of the deviation from stoichiometry (x) in fluorite UO_{2±x} [15] and in fluorite ThO_{2±x}. In ThO₂ without additives, this deviation is determined by the presence of impurities and the oxygen potential in the sintering atmosphere. Thus, both heavily reducing and oxidizing atmosphere can be used to promote sintering above about 1400 °C.

Additionally, the morphology of the ThO₂ plays a significant role in the packing density and sintering behavior. Most commonly, ThO₂ is prepared from oxalates, according to eq. (1).

Because the precipitation forms strong thorium-carboxyl complexes, the precipitation efficiency is very high regardless of precipitation conditions. The efficiency made it the method of choice for larger scale

powder-pellet manufacturing campaigns conducted in the USA [16, 17], Canada [18], and India [19], but milling was required to reach high density. Milling is undesirable as it produces radioactive dust. This safety hazard can be removed if different ways are found to improve sinterability. It has been shown that the nature of the ThO₂ precursor plays a significant role on the green and sintered densities which can be achieved, because the original morphology of the precipitate is maintained as the precursor decomposes into ThO₂ [20-24]. For actinide (IV) oxalates, the shape of the precipitate is determined by the stacking of oxalate hexahydrate platelets. Several authors compared the packing and sintering characteristics of oxalate based ThO₂ with that of ThO₂ derived from nitrate [25-27], hydroxide [25, 28], chloride [26], carbonate [25, 29], oxycarbonate [26], as well as benzoate and tannate [29] compounds. Besides the type of ThO₂ precursor, the precipitation conditions of the oxalate precursor can cause the green and sintered densities of pellets to vary significantly. Kantan et al. [25] showed that ThO₂ prepared from oxalates precipitated at 1-60 °C can reach densities of 87-95% after 1 h at 1500 °C, with the best densities obtained for the lower precipitation temperature (10-20 °C) based powders. White et al. [30] showed that precipitation temperature (10 or 70 °C), digestion time (15 or 360 min) and the form of agitation during precipitation (mechanical or mixed mechanical-ultrasonic) can all influence the green and sintered density. Among the conditions investigated by White et al., the precipitation temperature was most significant, as it produced the most striking differences in the precipitate. The platelets formed at 70 °C were significantly larger than those formed at 10 °C. The green density of the material precipitated at 70 °C was significantly higher than that precipitated at 10 °C, whereas the sintered density was opposite. In addition to the effects mentioned, the addition sequence during batch synthesis also plays a large role, as the two different oxalate platelet shapes – randomly stacked platelets with a wide size distribution versus platelets of uniform size stacked into cubes – affect the early stage sintering, and change the sintering rate above 1200 °C [24]. Removing the oxalate structure entirely by decomposition in an autoclave has also been used to improve the sinterability and produce extra small grain size sintered thoria [31].

Despite the large variations in density that can be achieved, the sintering of oxalate based actinide (IV) oxides takes place in two stages [14, 24, 32-35], which are determined by the bimodal inter- and intragranular agglomerate/platelet porosity in the green pellet. The two types of porosity present in such a green pellet are the porosity between the individual nanometric ThO₂ grains formed in a platelet during oxalate decomposition and the porosity determined by the stacking of these platelets.

This paper addresses the sintering behavior of ThO₂ based on thorium oxalate with numerous morphotypes, as prepared under different precipitation conditions [36]. The influence of the morphology and size of the oxalate precursor on the intermediate and final stage sintering behavior of ThO₂ is described.

II. Experimental

II.1 Powder preparation

Several precipitation conditions were chosen based on previous small scale experiments [36] to provide a large variation in oxalate shapes. The precipitation conditions are summarized in Table 1. The initial thorium feed solution was provided by Solvay, with a composition of 1.9 mol/l Th(NO₃)₄ with 1.6 mol/l free HNO₃. The solution was measured to be ≥99.95% pure Th on a trace metal basis by ICP-MS. Solid oxalic acid dihydrate (Sigma Aldrich, p. a.) was used to prepare oxalic acid solutions. The chemicals were diluted with demineralized water and used without further purification. All tests were performed to yield approximately 1.25 g of calcined ThO₂.

For most experiments, the feed solution was diluted to a 0.1 mol/l Th⁴⁺ concentration, while oxalic acid was dissolved to give a 0.2 mol/l solution. At room temperature, the pH of the 0.1 mol/l Th⁴⁺ unadjusted solution was 1.3. Both addition sequences were used: “direct strike” (oxalic acid solution dropped into thorium solution) and “reverse strike” (thorium solution dropped into oxalic acid solution). Precipitation

was performed at ambient temperature, except for materials #1 and #4. In those experiments, both solutions were kept at 5 °C (#1) or 60 °C (#4) with an ice bath or heated water bath, respectively. For material #3 and #7, the pH of the thorium solution was adjusted during dilution of the feed solution with diluted solutions of ammonia (28% Sigma Aldrich) or nitric acid (70% Sigma Aldrich). The suspension was digested for 10 min after addition was complete.

The prepared oxalates were calcined in air at 3 °C/min to 700 °C, with a 2 h dwell in a Nabertherm LT 9/13/P330 muffle furnace.

Table 1 – Precipitation conditions for the different oxalate precipitate morphologies. The / sign means values were neither adjusted nor measured. For experiments with 0.1 mol/l Th⁴⁺ feed solution the pH corresponds to approximately 1.3, whereas the pH is slightly higher for lower Th concentrations. Measurements below pH 1 are outside of the calibration range and should be considered as only approximate.

Material [#]	c(Th) [M]	c(Ox) [M]	pH	Temperature [°C]	Strike
1	0.10	0.20	/	5	Direct
2	0.10	0.20	/	25	Reverse
3	0.10	0.20	0.5	25	Direct
4	0.01	0.20	/	60	Reverse
5	0.10	1.00	/	25	Reverse
6	0.10	0.02	/	25	Reverse
7	0.10	0.02	2.3	25	Reverse

II.II Compaction and sintering

Approximately 1 g of calcined powder was loaded without further manipulations into a 6.9 mm diameter steel die coated with stearic acid, giving a green pellet height of ~5 mm. The green pellets were uniaxially pressed in an Atlas Auto 8T single-side semi-automatic press at 300 MPa. Pellets were sintered in a Netzsch DIL 402/C/7 dilatometer in an Ar + 5% H₂ atmosphere with a small admixture of Ar + 0.5% O₂ to provide an oxygen potential of -420 kJ/mol at 1625 °C. The furnace was heated to 1625 °C, the maximum temperature of the dilatometer, at 5 °C/min with a dwell time of 1 hour. Shrinkage was measured against a dense, 5 mm α -Al₂O₃ pellet standard. The pellets sintered in the dilatometer were fractured for microstructural investigations of the pellets during the intermediate stage of sintering. The density of both green and sintered pellets was measured geometrically.

A preliminary investigation of the final stage of sintering was investigated by further re-sintering a large piece of the pellets from dilatometry, which remained after microstructural investigation. The sintering was performed in a Linn HT 1800 Moly high temperature furnace. The furnace was heated to 1750 °C at 5 °C/min with a dwell of 8 hours. The sintering atmosphere had an oxygen potential of -420 kJ/mol at 1750 °C. Based on the re-sintering results, four materials (#1, #3, #5 and #6) were selected for direct sintering. Green pellets were prepared in an identical manner to those for dilatometry and were sintered by heating directly to 1750 °C at 5 °C/min with a dwell of 8 hours at -420 kJ/mol. In all cases, the oxygen potential was set to -420 kJ/mol for both furnaces to ensure the effect of atmosphere on the sintering was kept constant. The relative densities of the fragments and the pellets sintered at 1750 °C were also measured by immersion assuming a theoretical density of 10 g/cm³ for ThO₂.

II.III Analysis techniques

Solution pH was measured using a WTW pH 3100 meter equipped with a glass electrode. Brunauer Emmett Teller (BET) surface area analysis was performed with a Micromeritics Tristar® II 3020. The powders were degassed at 250 °C for 3 h under vacuum. XRD analysis was performed with a Philips X'Pert Pro diffractometer provided with a Cu LFF tube and operated in Bragg-Brentano parafocusing geometry and θ - θ configuration. Powders were measured on a single crystal zero-background Si holder. A few drops of an isopropanol suspension were placed on the holder and allowed to dry. Profile

matching was performed using the JANA2006 software [37]. The crystallite size together with the non-dimensional strain ε_0 was calculated using the Hall–Williamson formula [38]. Scanning electron microscopy (SEM) was performed on powders and fractured pellets coated with Pt (5 nm) using a Jeol JSM 7100FA SEM field-emission microscope. The directly sintered pellets were embedded in Technovit 5071 and polished to a mirror finish. Afterwards, the resin was removed by dissolution in acetone and the pellets were thermally etched by heating for 3 h at 1450 °C in synthetic air. These etched pellets were coated with Pt. All micrographs were obtained in secondary electron mode. Platelet and grain sizes were measured from these images. For the etched pellets, grain sizes were calculated using the linear intercept method, where the grain size (G) was calculated from the number of grain boundaries (N) along a defined length of line (L) as $G = \frac{\pi L}{2N}$. Several images from each pellet were used for calculation, with >500 intercepts used. The average grain size and its variations (reported as 2σ) were calculated from these data. High resolution transmission electron microscopy was performed on ThO₂ powders dispersed on holey carbon grids and dried in ambient conditions on a Jeol 3010.

III. Results and discussion

The primary oxalate precipitation conditions caused both the shape (see Figure 1) and size (see Table 2) of the ThO₂ agglomerates to vary widely. The oxalates precipitated and grew into two general shapes. Square platelets formed in material #1, #2 and #5; these squares are distorted into rectangles (ratio of sides 0.75-0.85) in #4. Axially symmetrical octagons formed in #3, #6, and #7. In addition to these large platelets, there is a minor fraction of small square platelets (again distorted into rectangles in #4) in all materials except for #1. In #1, the size distribution does not allow to differentiate two fractions. In addition to the differences in oxalate growth, holes were formed within the oxalate platelets in the direct strike materials (#1 and #3). Such morphology was observed during precipitation with a high amount of free nitric acid [20, 36]. In a direct strike precipitation, the acidity of the solution in which the precipitation occurs (which contains free HNO₃ from the starting solution), is significantly higher than in a reverse strike. The increasing solubility of the oxalates of Th⁴⁺ [39-42] and Np⁴⁺ [43] with increasing acidity, together with the coarse nature of the holes suggests that the holes are formed by a local precipitation-dissolution equilibrium. The precipitation of Th(C₂O₄)₂ forms HNO₃, see eq. (1), the local overconcentration of HNO₃ that this produces dissolves some of the Th(C₂O₄)₂ for precipitation elsewhere. These take the form of a large, uneven, circular central hole in #1. In contrast, #3 displays an even square hole in the center, accompanied by four smaller, uneven holes near the short sides of the octagon. Despite the concentrations and addition rate being identical to our previous work at milligram scale [36], the direct strike grades (#1 and #3) produced in the present study at gram scale, differ from their small scale equivalent published earlier. The absolute addition rates were equal, but the relative addition rates were not. This results in a different local acidity evolution during precipitation and different dissolution behaviors. This results in differences for both #1 – where at milligram scale the acid etches the edges of the platelet to make an ellipsoid – and for #3 – where at milligramscale the acid etches a large central hole.

Figure 1 – The morphologies of ThO₂ prepared by calcining the respective oxalates. The material number is indicated in the top left corner, for which the precipitation conditions are listed in Table 1. Scale bars correspond to 2 μm.

Table 2 – Weight loss during oxalate calcination and the approximate size ranges of the platelets after calcining to ThO₂. The samples consist of a major fraction of square or octagonal platelets with a minor fraction of small square platelets. For material 1, the minor fraction was indistinguishable from the major fraction.

Material [#]	Weight loss [%]	Major fraction		Minor fraction
		Size range [μm]	Thickness range [μm]	Size range [μm]
1	49.6	0.6-1.2	0.2-0.4	/
2	49.1	3.5-6.1	0.2-0.5	1.7-2.5
3	49.0	3.3-4.0	0.3-0.8	0.7-3.7
4	48.2	5.6-11.3	0.4-0.8	0.4-0.7
5	49.3	1.0-1.3	0.1-0.2	0.4-0.7
6	49.2	3.6-7.3	0.1-0.4	0.9-2.7
7	49.2	3.8-8.8	0.2-0.5	1.7-2.7

Figure 2 – Transmission electron microscopy of calcined powders. A snapshot of #2 (A) and #3 (B) is shown, together with the electron diffraction pattern (C) and close-ups (D, E) of #2 confirming the polycrystalline character of the ThO₂ powders obtained by oxalate conversion. The calcined powder is composed of nanometric ThO₂, randomly oriented within the original oxalate platelets.

Upon calcination, the identical calcination conditions result in comparable ThO₂ crystallite sizes, as summarised in Table 3. The calcined ThO₂ was generally too thick for a detailed observation of the grain structure by TEM, with the exception of unevenly stacked platelets (as shown on the edges of the platelets in Figure 2A) or at the edges of holes (Figure 2B). The platelets are composed of randomly oriented ThO₂ nanocrystals (see Figure 2C). The observed crystallite sizes from TEM (Figure 2D, E) are in the same range as those determined by X-ray line broadening (see Table 3). The differences in morphology instead are reflected in the specific surface area of the calcined powders. The highest specific surface areas (23-25 m²/g) were measured for the hole-containing platelets (#1 and #3). A very high surface area was also reported for the oxalate with a central hole studied by Beckett and Winfield [20]. The ThO₂ powders with entire platelets showed no clear trend in the specific surface area as a function of the platelet size.

Table 3 – Specific surface area, crystallite size and strain of calcined ThO₂ powders. The large variation in platelet composition produces ThO₂ powders with a wide variation in specific surface area. The crystallite size and strain however are comparable due to the identical calcination conditions.

Material [#]	Specific surface area [m ² /g]	Crystallite size [nm]	Calculated strain [%]
1	24.82 ± 0.08	31	0.03
2	10.97 ± 0.05	35	0.02
3	23.17 ± 0.11	31	0.03
4	14.93 ± 0.08	33	0.03
5	11.19 ± 0.04	34	0.03
6	9.34 ± 0.03	37	0.03
7	7.74 ± 0.05	36	0.03

The differences in oxalate morphology are reflected in the packing density of the oxides into green pellets (see Table 4). The large platelet samples pack to higher green densities, while the small platelet samples pack to lower green densities. The samples with holes distort these results. A number of green pellets were quite fragile, and pellets produced from powders #2, #5 and #6 showed end-capping during out-pressing. The number of pellets produced from each batch is too small for a statistical comparison of the pressing behavior, but it shows that there are also significant differences in the pellet stability between different platelet types. A further study is needed to conclusively determine which powders have a good green pellet stability.

Table 4 – The pressing characteristics of individual powders together with results achieved after sintering to 1625 °C and after re-sintering of fragments at 1750 °C. The large platelet grades (#2, #4, #6 and #7) have a higher green density, but lower densification (= sintered density – green density) at 1625 °C than the small platelet sized grades (#1, #3 and #5). Upon resintering at 1750 °C, the small platelet grades (#1, #5) sinter to closed density.

Material [#]	Green density [%]	End-capping green pellet	Sintered density (1625 °C) [%]	Densification (1625 °C) [%]	Grain size (1625 °C) [μm]	Re-sintered density (1750 °C) [%]
1	44.4	No	75.3	30.9	0.2-0.5	97.1
2	47.6	Yes	66.2	18.6	0.3-0.7	92.5
3	40.9	No	68.8	27.9	0.5-1.0	93.5
4	49.4	No	65.5	16.1	0.3-0.6	93.3
5	44.6	Yes	68.5	23.9	0.2-0.6	95.1
6	49.2	Yes	68.2	19.0	0.2-0.7	93.0
7	50.0	No	69.1	19.1	0.2-0.8	93.8

Regarding the compaction, two distinctions can be made between the platelet types. The first concerns the presence of holes (#1 and #3). If the structure of the platelets is also broken during pressing the voids in the platelets do not negatively impact the green density. In grade #1 this is most likely the case, since the sintered grain sizes are significantly smaller than the original platelet size. In #3, the platelets maintain their original shape and the voids caused by the holes lead to the lowest green density observed, of 41%. For platelets without holes, the determining factor is the platelet size. Whatever the shape of the platelets, the larger ones (squares in #2, rectangles in #4, octagons in #6 and #7) behave in a similar manner. In contrast to small platelets without holes (#5), the large platelets have a higher green density due to the alignment of platelets (48-50% versus 45% for #5). This is in line with the observations made by White et al. [30], where larger platelets (precipitated at 70 °C) led to higher green densities (62-64%) than smaller platelets (56-59% when precipitated at 10 °C). The powders used by White et al. were calcined at significantly higher temperatures (900 °C, 24 h), which results in denser platelets and higher green densities. In contrast, the low calcination temperature used here (700 °C, 2 h) result in more sinteractive ThO₂ at the cost of lower green densities.

The clear difference between platelets with or without holes, and small or large platelets is maintained during sintering. This is because the platelet morphology is maintained from powder to pellet. The distance between ThO₂ grains within a platelet is significantly smaller than the distance between platelets. The small hole free platelet compact (#5) performs better than the large platelet compacts, achieving significantly more densification (#2, #4, #6, #7) upon sintering at 1625 °C. The higher sinterability of #5 compensates for the 5% lower green density and #5 matches the 68-69% density of #4, #6 and #7 at 1625°C. The hole containing large platelet compact (#3) also sintered better than the large platelet compacts. The high sinterability of #3 up to 1625 °C is reflected in the fact that it also reached a density of 68-69%, despite its 9% lower green density. The compact of small platelets with holes (#1) has the highest sinterability. Its green density is comparable to the other small platelet material (#5), but the density of 75.3 % after sintering at 1625°C is >7% higher than for all other compacts.

1 Amongst the large platelet compacts, #4 with the largest platelet size has one of the highest green
2 densities of 49%, but the densification at 1625°C is not only the lowest of the large platelet compacts
3 but of all compacts.

4
5 Since all pellets underwent the same thermal treatment, calcination at 700 °C and sintering at 1625 °C,
6 the ThO₂ grains inside the platelet features are still comparable (see Figure 3 and Table 4). The different
7 sintering behavior of the different platelet types is also reflected in the microstructure of the fracture
8 surfaces of sintered pellets, shown in **Figure 4**. The ThO₂ grain sizes are all in the 0.2-0.8 µm range,
9 with the exception of #3 which has larger grains. These ThO₂ grains grew primarily within the platelets.
10 Though some platelets break, most pellets are composed of platelets which have experienced significant
11 grain growth, but otherwise remain largely unchanged as shown in Figure 3. Only limited necking
12 between platelets was observed, most likely as there are only few contact points between the platelets.
13 The exception to this is when platelets closely align, in which case the platelets may grow together (as
14 shown in Figure 3). The sintered grain size of #3 (0.5-1.0 µm) is significantly larger than in the other
15 grades, as shown in **Figure 4**. The small platelets of #5 led to a large number of contact points during
16 packing and the resulting pellet shows a higher amount of necking between platelets than the other
17 materials. #1 shows no clear platelets and the symmetrical grains (0.2-0.5 µm) are smaller than the
18 original platelets (0.6-1.2 µm), corresponding to roughly half of the original platelet size. This makes #1
19 the only grade without a platelet structure. Since densification happens first within the original structure,
20 the platelets most likely broke into four separate chunks and the grains correspond to these chunks fully
21 densified. The fracture surfaces of the large-platelet materials (#2, #4, #6 and #7) are similar to each
22 other, largely preserving the initial platelet structure.

24
25 **Figure 3** - Detailed SEM micrograph of a fractured pellet (#4) sintered at 1625 °C. The scale bar corresponds to
26 1 µm. Grain growth occurs predominantly within the original oxalate platelets, with the onset of necking
27 between platelets.

Figure 4 – Fractured surfaces of pellets sintered at 1625 °C. The original platelet structure is provided in the insert in the upper left corner of each micrograph together with the material grade. Scale bars correspond to 1 µm. Please note that due to the large differences in platelet sizes, the magnification in the insert does not match that of micrograph and only serves for easy navigation.

The stacking of the platelets (see fracture surfaces in Figure 4) significantly affects the distribution of the remaining porosity in the pellets sintered at 1625 °C. The more homogeneous distribution of particles/cracked platelets in #1 equally leads to an even porosity distribution. In the other grades, the oxalate platelet morphology is maintained in the sintered oxide pellet. The platelets lead to an uneven distribution of porosity. Regions of significantly larger pores form between the platelets, especially if platelets contact at higher angles. This is less of a problem for #5, where the platelets are small. Despite the reduced alignment in #5, the residual porosity between platelets is fairly small. Larger platelet grades eliminate some of this porosity (relative to #5) by aligning a large amount platelet faces. This is especially pronounced for the thin platelets in #6, but to a lower degree also for the thicker platelets of #2, #4 and #7. This aligning also contributed to the higher green densities of these materials (see Table 4). Observations on the arrangement of platelets in #3 are complicated by the high degree of necking in that material. This led to an increase in the pellet strength and a trans-platelet rather than inter-platelet fracture. Despite the more advanced neck formation, #3 also still has large channels of residual porosity when sintered at 1625°C. This suggests that unlike in #1, the platelets remained intact during compaction and the larger pores caused by poorly aligned platelets have not yet had the opportunity to close. At higher sintering temperatures, this high degree of necking should ease further densification.

Figure 5 – Shrinkage rates of the different powder compacts during heating at 5 °C/min to 1625 °C. The onset of sintering occurs around 700 °C, reaches a local maximum around 900 °C, followed by a drop in sintering rate to a plateau at 1000-1200 °C.

Dilatometry of the oxide compacts (see Figure 5) shows a general sintering behavior. The onset of sintering takes place around the calcination temperature (700 °C). The sintering rate reaches a (local, in the case of #5) maximum at 900 °C, followed by a gradual decrease to a plateau level between 1000 and 1250 °C. Beyond the plateau, the sintering rate further reduces until the maximum temperature of 1625 °C is reached. The sample with the least densification (#4) shows an identical densification profile up to 1625°C as the other large platelet compacts (#2, #6 and #7). The smallest platelet compact (#5) also follows the same profile until 1300 °C, where a sharp increase in the sintering rate occurs and the sintering rate exceeds the local maximum at 900 °C.

The hollow platelet containing compacts behave differently. The densification rate of #3 continues to increase past the maximum of the larger platelet grades and reaches a maximum densification rate at 950 °C. After this maximum, the sintering rate remains very high up to about 1250 °C. Beyond 1250 °C, the sintering rate reduces to 1625 °C. The holes present in the platelets seem to form a more sinter-active internal surface in the powder compacts which promotes surface diffusion. This then leads to the closing of the holes or to greater neck formation on platelet contact. The small hollow platelet compact (#1) reached a comparable maximum sintering rate comparable to #3, but already at 900 °C. The maximum shrinkage rate of these hollow platelet grades is higher than for all the other grades. In contrast to #3, the high densification rate drops quickly to the values obtained for the large-platelet compacts in the 1200-1300 °C window. Beyond 1300 °C, the sintering rate of #1 rises again as it did for the finer platelet grade #5. This grade lacks a sintering rate plateau after its first maximum as well as lacking a platelet structure in the sintered pellet (see fracture surface in Figure 4). The plateau is most likely the onset of necking between platelets. The large porosity present between platelets delays the onset of the two-step porosity typical of actinide (IV) oxides from oxalate [24, 32-35]. The two-step shape is caused by bimodal porosity in the pressed pellet, one within platelets and one between them. The sintering rate peak around 900 °C is the typical peak caused by the sintering ThO₂ grains within platelets (these grains can be seen in Figure 2D). The second sintering rate peak depends upon the closing of porosity between platelets. In the small platelet grades (#1, #5) the onset of sintering between platelets can be seen in the range 1400-1625 °C. In the large platelet grades, closing porosity between platelets is a difficult task and the onset of the second sintering peak is pushed to a temperature above used in dilatometry.

Upon re-sintering of the pre-sintered (1 h at 1625 °C) pellets at 1750 °C for 8 h, the pellets reached high densities of 92-97% (see Table 4). The ranking of the different materials based on their relative density in the intermediate stage of sintering (1625 °C) was maintained after re-sintering at 1750 °C. The large-platelet-based ceramics (#2, #4, #6 and #7) reached a density of 92-94%. The large amount of open porosity of #3 was not eliminated by re-sintering at 1750 °C and the final density (93.5%) was comparable to that of the large-platelet-based materials. The smaller porosity in #5 leads to a slightly higher density (95%) after re-sintering. As for sintering at 1625 °C, a highest density of 97% was obtained for #1. The large platelet based ceramics (#2, #4, #6 and #7) are similar (good packing, modest sinterability) but substantially different than #1 (subpar packing, excellent sinterability throughout), #3 (poor packing, excellent neck formation), and #5 (subpar packing, good sinterability).

Since a substantial amount of the thermodynamic driving force for densification might be lost in an interrupted sintering cycle, pellets of the calcined oxalates with good sinterability (#1, #3, # 5), along with #6 as a representative of the large-platelet based materials were sintered in a single step at 1750 °C for 8 hours. The direct sintering shows effectively the same results (Table 5) in terms of density as the re-sintering cycle (Table 4), with #1 reaching the highest density (96.7% direct, 97.1% re-sintered), #5 reaching a lower, but still good density (95.7% direct, 95.1% re-sintered) and the large platelet based #6 reaching the lowest density (93.4% direct, 93.0% re-sintered). These similarities in direct and re-sintered density did not hold for #3 (95.6% direct, 93.5% re-sintered), where a substantial higher amount of porosity is eliminated upon direct sintering.

Table 5 – Sintered density, grain size and pore size of the pellets sintered at 1750 °C. No green pellets showed end-capping. #6 has a slightly lower density and significantly larger sintered grain size.

Material [#]	Sintered density (1750 °C) [% TD]	Sintered grain size [μm]	Pore size [range, μm]
1	96.7	1.39 ± 0.34	0.1 - 0.7
3	95.7	1.63 ± 0.46	0.2 - 1.0
5	95.6	1.37 ± 0.40	0.1 - 1.0
6	93.4	10.5 ± 4.0	0.5 - 3.5

In addition to the differences in density between the ceramics, there is also a significant difference in the produced microstructures, as illustrated in **Figure 6**. The ceramics with better densification (#1, #3 and #5) sintered to closed porosity while maintaining a relatively smaller grain size (1-2 μm). The porosity of #1 was predominantly intergranular, with most 0.1-0.7 μm diameter pores located at the intersections of three or more grains. Intragranular pores are also observed, though in very small numbers. The porosity of #3 was comparable, with slightly larger pores of 0.2-1.0 μm diameter and several elongated ovoid pores. #5 had a greater number of intragranular pores than #1 and #3, but intergranular 0.1-1.0 μm pores were still predominant. The pores of #6 were significantly larger, in the 0.5-3.5 μm range. A large number of pores was intragranular, and a higher number of the intergranular pores are between only two grains.

Figure 6 – Thermally etched polished cross-sections of pellets #1, #3, #5 and #6 sintered for 8 h at 1750 °C. Scale bars correspond to 5 μm , except for #6 for which the scale bar is 10 μm . Ceramics #1, #3 and #5 have a small grain size and correspondingly small pores, whereas ceramic #6 has a significantly larger grain and pore size.

No clear recommendation can be made regarding the optimum oxalate morphology, as fuel requirements are multifaceted. The present sintered density requirement for UO_2 fuel is 95-97% [44], a density which can be reached best for ThO_2 by #1 (small < 1.2 μm hollow oxalate platelets), though #3 (larger up to 4 μm hollow oxalate platelets) and #5 (small < 1.5 μm oxalate platelets) may also suffice. A competing requirement concerns grain sizes. For conventional UO_2 -based fuels, a larger grain size leads to lower fission gas release [45, 46]. The effect of the fuel grain size is so pronounced that – despite the formation of release-promoting precipitates – dopants are often added to UO_2 [47] and MOX fuel [48] to increase grain sizes. For an equivalent ThO_2 -based fuel, this gas release is expected to be similar [49] or

lower [50], despite the slightly larger noble gas production [51]. While this may make smaller grain sizes less problematic, the grain sizes of grades #1, #3 and #5 are an order of magnitude below those in commercial fuels ($\sim 5\text{--}7\text{ }\mu\text{m}$ [47]). ThO₂ ceramic #6 (and presumably also the other large $>4\text{ }\mu\text{m}$ oxalate platelet based ceramics) achieves a grain size comparable to commercial fuels, but at the cost of a lower sintered density. Clavier et al. [52] removed the platelet morphology by milling and found grain growth to become the dominant mechanism at about 92% density. The platelet morphology appears to play a crucial role in the grain boundary diffusion and grain boundary migration (grain growth) during densification of ThO₂. When the platelets are small or separated into several zones by holes, the homogeneously distributed residual porosity acts as a barrier to grain growth (an example of Zener pinning). When the platelets are large their stacking produces larger and less homogeneously dispersed porosity, which acts as a barrier to densification. The surface energy that could lead to densification is instead diverted and leads to significant grain growth.

Since 1750 °C is at the upper limit for commercial furnaces and longer heating times cannot achieve much, judicious powder engineering is required instead to produce a powder which is both dense and large-grained. The simple direct pressing of powder used here produced a modest green density, even for the large platelet materials. In part this is due to the high amount of porosity present within the platelets. This porosity within platelets can be significantly reduced by calcining at higher temperatures. At these higher calcination temperatures, crystallites within the platelets sinter together and grow larger. These leads to lower densification later, but significantly shrinks the platelet sizes [33] and improves the green density [24]. Beyond calcination changes, improvements in agglomeration such as the precompaction used by White et al. [30] may suffice to either increase the density of the large platelet materials $>95\%$ or to complete densification earlier with the more sinteractive oxalates (#1, #3 and #5) and promote subsequent grain growth. Mixing in a fraction of some large platelet oxalates to a small platelet grade may be enough limit pining and ensure sufficient grain growth without significantly hindering sintering.

A potential alternative method for promoting early sintering is to switch to sintering in oxidizing atmosphere. At lower temperatures the conductance of ThO₂ [6] is improved more by defect effects in oxidizing rather than reducing atmosphere. These same defects will promote early stage sintering. This is especially relevant for the large platelet samples which achieve suitable grain sizes, as their sintering suffers at low temperatures (see dilatometry in Figure 5).

IV. Conclusions

The morphology of the oxalate platelet – be it square or octagon – has little effect on the sinterability of the produced ThO₂. Instead two factors determine the sinterability: the platelet size and the presence of holes within them. As soon as the platelet size exceeds $3\text{ }\mu\text{m}$, the platelets begin to show preferential stacking during pressing and reach similar green and sintered densities. Upon sintering at 1750 °C for 8 h in an oxygen potential of -420 kJ/mol , pellets produced from oxalates with large platelets do not reach the desired density of $\geq 95\%$ of the theoretical density, but produce $10\text{ }\mu\text{m}$ sintered grain sizes similar to that of commercial UO₂ fuel. The presence of holes in large platelets changes the sintering considerably. Although these holes reduce the green density, they significantly improve the sinterability allowing to reach the desired 95% density but with a small $\sim 1\text{ }\mu\text{m}$ grain size. Smaller platelet sizes ($\sim 1\text{ }\mu\text{m}$) have an even worse green packing densities ($\sim 44\%$) due to the lack of preferential stacking, but the sinterability is significantly improved. These platelets break during green pellet pressing and then sinter to 97% density, with a small sintered grain size ($\sim 1\text{ }\mu\text{m}$).

Acknowledgement

The authors would like to acknowledge Yves Heymans for polishing, Peter Dries and Koen Vanaken for assistance with dilatometry and many other technical matters. This work was partially funded by Solvay under contract CO-90-15-3832-00.

References

- [1] P.R. Hania, F.C. Klaassen, 3.04 - Thorium Oxide Fuel, in: R.J.M. Konings (Ed.), *Comprehensive Nuclear Materials*, Elsevier, Oxford, 2012, pp. 87-108.
- [2] T.R. Pavlov, T. Wangle, M.R. Wenman, V. Tyrpekl, L. Vlahovic, D. Robba, P. Van Uffelen, R.J.M. Konings, R.W. Grimes, High temperature measurements and condensed matter analysis of the thermo-physical properties of ThO₂, *Scientific Reports* 8 (2018).
- [3] R. Böhler, A. Quaini, L. Capriotti, P. Çakır, O. Beneš, K. Boboridis, A. Guiot, L. Luzzi, R.J.M. Konings, D. Manara, The solidification behaviour of the UO₂–ThO₂ system in a laser heating study, *Journal of Alloys and Compounds* 616 (2014) 5-13.
- [4] A.B. Lidiard, Self-diffusion of uranium in UO₂, *Journal of Nuclear Materials* 19(1) (1966) 106-108.
- [5] R. Benz, Thorium-thorium dioxide phase equilibria, *Journal of Nuclear Materials* 29(1) (1969) 43-49.
- [6] R.J. Ackermann, M. Tetenbaum, High-temperature thermodynamic properties of the thorium-oxygen system, *High Temperature Science* 13(1-4) (1980) 91-105.
- [7] I. Bransky, N.M. Tallan, Electrical Properties and Defect Structure of ThO₂, *Journal of the American Ceramic Society* 53(11) (1970) 625-629.
- [8] K. Ananthasivan, S. Balakrishnan, S. Anthonysamy, R. Divakar, E. Mohandas, V. Ganesan, Synthesis and sintering of nanocrystalline thoria doped with CaO and MgO derived through oxalate-deagglomeration, *Journal of Nuclear Materials* 434(1–3) (2013) 223-229.
- [9] I.C. Cosentino, R. Muccillo, Powder synthesis and sintering of high density thoria–yttria ceramics, *Journal of Nuclear Materials* 304(2–3) (2002) 129-133.
- [10] D. Sanjay Kumar, K. Ananthasivan, R. Venkata Krishnan, S. Amirthapandian, A. Dasgupta, Studies on the synthesis of nanocrystalline Y₂O₃ and ThO₂ through volume combustion and their sintering, *Journal of Nuclear Materials* 479 (2016) 585-592.
- [11] A. Baena, T. Cardinaels, J. Vleugels, K. Binnemans, M. Verwerft, Activated sintering of ThO₂ with Al₂O₃ under reducing and oxidizing conditions, *Journal of Nuclear Materials* 470 (2016) 34-43.
- [12] Y. Cherkaski, N. Clavier, L. Brissonneau, R. Podor, N. Dacheux, Densification behavior and microstructure evolution of yttrium-doped ThO₂ ceramics, *Journal of the European Ceramic Society* 37(10) (2017) 3381-3391.
- [13] K. Ananthasivan, S. Anthonysamy, C. Sudha, A.L.E. Terrance, P.R.V. Rao, Thoria doped with cations of group VB-synthesis and sintering, *Journal of Nuclear Materials* 300(2-3) (2002) 217-229.
- [14] N. Hingant, N. Clavier, N. Dacheux, S. Hubert, N. Barre, R. Podor, L. Aranda, Preparation of morphology controlled Th_{1-x}U_xO₂ sintered pellets from low-temperature precursors, *Powder Technology* 208(2) (2011) 454-460.
- [15] N. Hingant, N. Clavier, N. Dacheux, N. Barre, S. Hubert, S. Obbade, F. Taborda, F. Abraham, Preparation, sintering and leaching of optimized uranium thorium dioxides, *Journal of Nuclear Materials* 385(2) (2009) 400-406.
- [16] P.E. Hart, C.W. Griffin, K.A. Hsieh, R.B. Matthews, G.D. White, ThO₂-based pellet fuels - their properties, methods of fabrication, and irradiation performance: a critical assessment of the state of the technology and recommendations for further work, 1979.
- [17] R.B. Matthews, N.C. Davis, Fabrication of ThO₂ and ThO₂-UO₂ pellets for proliferation resistant fuels, Battelle Pacific Northwest Labs., 1979.
- [18] R.W. Jones, H.R. Lee, H. Hahn, J.F. Walker, A. Celli, Thoria Fuel Technology for CANDU-PHW Reactors, *Transactions of the American Nuclear Society* 27 (1977) 303-304.

- [19] Thorium fuel cycle - Potential benefits and challenges, International Atomic Energy Agency, Vienna, Austria 2005.
- [20] R. Beckett, M.E. Winfield, The Thermal Decomposition of Thorium Oxalate, *Australian Journal of Chemistry* 4(4) (1951) 644-650.
- [21] M. Breyse, B. Claudel, Y. Trambouze, Influence des conditions de précipitation d'un sel sur la texture de son produit de décomposition thermique. Cas de l'oxalate de thorium., *Bulletin de la Société chimique de France* (1) (1965) 201-204.
- [22] V. Tyrpekl, J.F. Vigier, D. Manara, T. Wiss, O.D. Blanco, J. Somers, Low temperature decomposition of U(IV) and Th(IV) oxalates to nanograined oxide powders, *Journal of Nuclear Materials* 460 (2015) 200-208.
- [23] S. Grandjean, B. Arab-Chapelet, A.C. Robisson, F. Abraham, P. Martin, J.P. Dancausse, N. Herlet, C. Leorier, Structure of mixed U(IV)-An(III) precursors synthesized by co-conversion methods (where An = Pu, Am or Cm), *Journal of Nuclear Materials* 385(1) (2009) 204-207.
- [24] T. Wangle, V. Tyrpekl, S. Cagno, T. Delloye, O. Larcher, T. Cardinaels, J. Vleugels, M. Verwerft, The effect of precipitation and calcination parameters on oxalate derived ThO₂ pellets, *Journal of Nuclear Materials* 495 (2017) 128-137.
- [25] S.K. Kantan, R.V. Raghavan, G.S. Tendolkar, Sintering of Thorium and Thoria, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, pp. 132-138.
- [26] Y. Harada, Y. Baskin, J.H. Handwerk, Calcination and Sintering Study of Thoria, *Journal of the American Ceramic Society* 45(6) (1962) 253-257.
- [27] J.M. Pope, K.C. Radford, Physical-properties of some thoria powders and their influence on sinterability, *Journal of Nuclear Materials* 52(2) (1974) 241-254.
- [28] E. De Bona, O. Walter, H. Störmer, T. Wiss, G. Baldinozzi, M. Cologna, K. Popa, Synthesis of nanostructured ThO₂ pellets, *Journal of the American Ceramic Society* 102(7) (2019) 3814-3818.
- [29] V.K. Moorthy, A.K. Kulkarny, S.V.K. Rao, Relation Between the Origin, Powder Characteristics, and Sintering Treatment on the Densification and Microstructures of Urania and Thoria, Third United Nations International Conference on the Peaceful Uses of Atomic Energy, United Nations, New York, 1964, pp. 386-392.
- [30] G.D. White, L.A. Bray, P.E. Hart, Optimization of thorium oxalate precipitation conditions relative to derived oxide sinterability, *Journal of Nuclear Materials* 96(3) (1981) 305-313.
- [31] L. Balice, D. Bouëxière, M. Cologna, A. Cambriani, J.-F. Vigier, E. De Bona, G.D. Sorarù, C. Kübel, O. Walter, K. Popa, Nano and micro U1-xThxO₂ solid solutions: From powders to pellets, *Journal of Nuclear Materials* 498 (2018) 307-313.
- [32] V. Tyrpekl, M. Cologna, D. Robba, J. Somers, Sintering behaviour of nanocrystalline ThO₂ powder using spark plasma sintering, *Journal of the European Ceramic Society* 36(3) (2016) 767-772.
- [33] J. Martinez, N. Clavier, T. Ducasse, A. Mesbah, F. Audubert, B. Corso, N. Vigier, N. Dacheux, From uranium(IV) oxalate to sintered UO₂: Consequences of the powders' thermal history on the microstructure, *Journal of the European Ceramic Society* 35(16) (2015) 4535-4546.
- [34] D. Horlait, F. Lebreton, A. Gauthé, M. Caisso, B. Arab-Chapelet, S. Picart, T. Delahaye, Americium-based oxides: Dense pellet fabrication from co-converted oxalates, *Journal of Nuclear Materials* 444(1-3) (2014) 181-185.
- [35] L. Ramond, D. Horlait, T. Delahaye, G. Jouan, A. Gauthé, B. Arab-Chapelet, S. Picart, Dilatometric study of a co-converted (U,Am)O₂ powder, *Journal of the European Ceramic Society* 36(7) (2016) 1775-1782.
- [36] V. Tyrpekl, M. Beliš, T. Wangle, J. Vleugels, M. Verwerft, Alterations of thorium oxalate morphology by changing elementary precipitation conditions, *Journal of Nuclear Materials* 493 (2017) 255-263.
- [37] V. Petříček, M. Dušek, L. Palatinus, Crystallographic Computing System JANA2006: General features, *Zeitschrift Für Kristallographie* 229(5) (2014) 345-352.
- [38] G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminium and wolfram, *Acta Metallurgica* 1(1) (1953) 22-31.

- 1 [39] P.R. Monson, Jr., R. Hall, Thorium oxalate solubility and morphology, Savannah River Laboratory,
2 1981, p. 15.
- 3 [40] E.M. Pazhukhin, E.A. Smirnova, A.S. Krivokhatskii, Y.L. Pazukhina, S.M. Kochergin, Optimization of
4 conditions of thorium oxalate precipitation. I. Solubility of thorium oxalate in the presence of like
5 ions, Radiokhimiya 27(5) (1985) 606-11.
- 6 [41] A.G. Kurnakova, L.K. Shubochkin, The solubility of $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ in aqueous solutions of HNO_3
7 and $\text{H}_2\text{C}_2\text{O}_4$ at 25° , Zhurnal Neorganicheskoi Khimii 8(5) (1963) 1249-54.
- 8 [42] V. Tyrpekl, R. Lommelen, T. Wangle, T. Cardinaels, K. Binnemans, J. Vleugels, M. Verwerft, Studies
9 on the Thoria Fuel Recycling Loop Using Triflic Acid: Effects of Powder Characteristics, Solution
10 Acidity, and Radium Behavior, Journal of Sustainable Metallurgy 5(1) (2019) 118-126.
- 11 [43] D.T. Rankin, G.A. Burney, P.K. Smith, R.D. Sisson, Jr., Preparation and characterization of oxalate-
12 based $^{237}\text{NpO}_2$ powder, Ceramic Bulletin 56(5) (1977) 478-483, 486.
- 13 [44] Fuel Design Data, Nuclear Engineering International, 2015, pp. 30-37.
- 14 [45] J.A. Turnbull, The effect of grain size on the swelling and gas release properties of UO_2 during
15 irradiation, Journal of Nuclear Materials 50(1) (1974) 62-68.
- 16 [46] I.J. Hastings, Effect of Initial Grain Size on Fission Gas Release from Irradiated UO_2 Fuel, Journal of
17 the American Ceramic Society 66(9) (1983) c150-c151.
- 18 [47] J. Arborelius, K. Backman, L. Hallstadius, M. Limbäck, J. Nilsson, B. Rebensdorff, G. Zhou, K. Kitano,
19 R. Löfström, G. Rönnberg, Advanced Doped UO_2 Pellets in LWR Applications, Journal of Nuclear
20 Science and Technology 43(9) (2006) 967-976.
- 21 [48] R. Thomas, MOX dopé chrome : optimisation du dopage et de l'atmosphère de frittage, Institut
22 de Chimie de la Matière Condensée de Bordeaux Université de Bordeaux 1, 2013, p. 274.
- 23 [49] M.W.D. Cooper, C.R. Stanek, J.A. Turnbull, B.P. Uberuaga, D.A. Andersson, Simulation of radiation
24 driven fission gas diffusion in UO_2 , ThO_2 and PuO_2 , Journal of Nuclear Materials 481 (2016) 125-
25 133.
- 26 [50] Y. Long, Y. Yuan, M.S. Kazimi, R.G. Ballinger, E.E. Pilat, A Fission Gas Release Model for High-Burnup
27 LWR ThO_2 - UO_2 Fuel, Nuclear Technology 138(3) (2002) 260-272.
- 28 [51] J. Belle, R.M. Berman, Thorium dioxide: properties and nuclear applications, 1984, p. 585.
- 29 [52] N. Clavier, R. Podor, L. Deliere, J. Ravau, N. Dacheux, Combining *in situ* HT-ESEM observations
30 and dilatometry: An original and fast way to the sintering map of ThO_2 , Materials Chemistry and
31 Physics 137(3) (2013) 742-749.
- 32
- 33