UCRL-CR-139073-PT-1

Interim Report on Task 1.2: Near Equilibrium Processing Requirements – Attrition Milling Part 1 of 2 To Lawrence Livermore National Laboratory for Contract B345772

M. W. A. Stewart, E. R. Vance, R. A. Day, E. Eddowes and S. Moricca

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

April 30, 2000

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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materials division

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Part 1 of 2

To Lawrence Livermore National Laboratory for Contract B345772

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30 April 2000

R00m012

Australian Nuclear Science and Technology Organisation
Private Mail Bag 1, Menai, NSW 2234

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DATE ISSUED
30 April 2000

ISSUED TO
Lawrence Livermore National Laboratories

REPORT NUMBER
R00m012

JOB NUMBER
709m

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1 SUMMARY

The objective of Task 1.2 has only partly been achieved as the work on Pu/U-formulations and to a significant degree on Th/U-formulations has been performed under grinding/blending conditions that did not replicate plant-like fabrication processes, particularly in the case with the small glove-box attritor. Nevertheless the results do show that actinide-rich particles, not present in specimens made via the alkoxide-route (equilibrium conditions), occur when the grinding process is not efficient enough to ensure that high-fired PuO_2, ThO_2 and UO_2 particles are below a critical size. Our current perception is that the critical size for specimens sintered at 1350°C for 4 hours is about 5 μm in diameter. The critical size is difficult to estimate, as it is equal to the starting diameter of actinide oxides just visible within brannerite regions.

Our larger scale attritor experiments as well as experience with wet and dry ball milling suggests that acceptable mineralogy and microstructure can be obtained by dry milling via attritor and ball mills. This is provided that appropriate attention is paid to the size and density of the grinding media, grinding additives that reduce caking of the powder, and in the case of attritors the grinding speed and pot setup.

The ideal products for sintering are free flowing granules of ~ 100 μm containing constituents ground to about 1 μm to ensure homogeneity and equilibrium mineralogy.

The following six ceramic formulations were examined in this attrition milling study:

- Ce/Ce/Zr, Th/U/Hf and Pu/U/Hf baseline
- Th/U/Hf-baseline ceramic plus process impurities
- Th/U/Hf-doped zirconolite-rich composition
- Th/U/Hf-doped brannerite-rich composition
- Th/U/Hf-doped composition originally designed to have ~ 10 % perovskite in addition to the normal baseline phases
- ~ 10 % phosphate Th/U/Hf-doped batch.

These samples were prepared by oxide-route via wet and/or dry attrition milling.

Preliminary work with the Ce/Ce/Zr-baseline formulation indicated that dry ball milling could be successfully carried out in large pots (750 – 1500 cc) with 5 mm diameter zirconia media. When the small 110 cc quick-change pots with 2 mm diameter media were used, the initial results for dry attrition milling of Th/U-doped were not successful. The powder tended to form a cake on the bottom of the mill pot (this is sometimes referred to as a foot) and on the walls of the pot. By the combination of breaking up this cake every 10 minutes (called 1 pass), increasing the mill speed, modifying the milling pot and using additives to aid milling we were able to successfully dry attrition mill Th/U and Pu/U-doped samples in the small pot.

The efficiency of the milling method has a direct effect on the final sintered samples. Incomplete milling leads to an inhomogeneous microstructure. The main effects of incomplete milling are:

a) Unreacted actinide oxides remain in the microstructure, usually surrounded by brannerite. The phase composition also alters due to the actinide being tied up in the unreacted oxide, e.g., the pyrochlore has less actinide and additional phases, such as zirconolite may form because of this or localised inhomogeneity.

b) Incomplete breakup of the "large" agglomerates in the green powder produces porosity.

c) Localised concentrations of uranium oxide can produce porosity, particularly if it has been calcined in air and later releases oxygen on sintering.

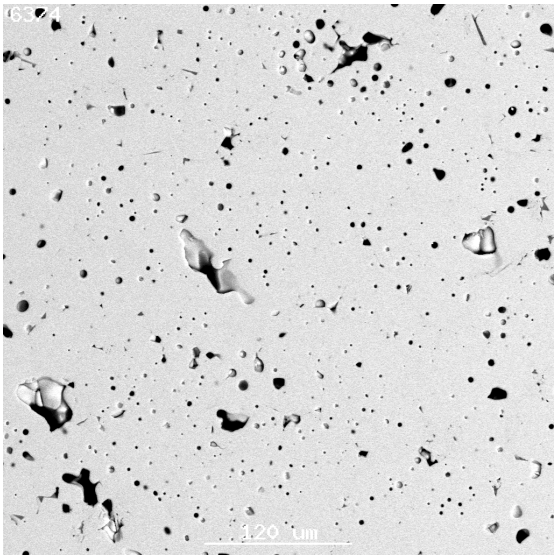
Occasionally, some unreacted hafnia was detected.

Overall, the attrition milled samples produce comparable results to the wet and dry ball milled samples of the same composition. The phases formed in samples of each of the compositions tested were the same as the ball milled samples. The formulations formed the phases expected/nominated when attrition milled. The exception was the nominally ~ 10 % perovskite batch, which did not form perovskite (the same result occurred in the ball milled samples). The baseline ceramics, essentially formed pyrochlore as the main phase with 10 – 20 vol. % brannerite and ~ 5 vol. % Hf-doped rutile. When impurities were added 2M zirconolite and a silicate phase formed. The zirconolite-rich ceramics and brannerite-rich samples were as expected richer in zirconolite and brannerite than the baseline. The phosphate doped samples were similar to the baseline except that they contained the phosphate phase whitlockite (nominally, $Ca_3(PO_4)_2$). The partitioning of the elements in the attrition milled samples is the same as in the ball milled samples. The U, Pu and Th partitioned as expected – mainly into the pyrochlore, brannerite and zirconolite. The amounts in the minor phases, rutile and whitlockite, were small. The Th/U-doped dry attrition milled samples contained some residual ThO_2. In these sample the UO_2 appears to have completely reacted with the precursor elements to form brannerite and pyrochlore. The only UO_2 detected was in the very poorly milled batches. The ThO_2 is present in poorly milled samples as large "unreacted" lumps. In most samples, some actinide oxide regions can be found at the centre of some brannerite grains.

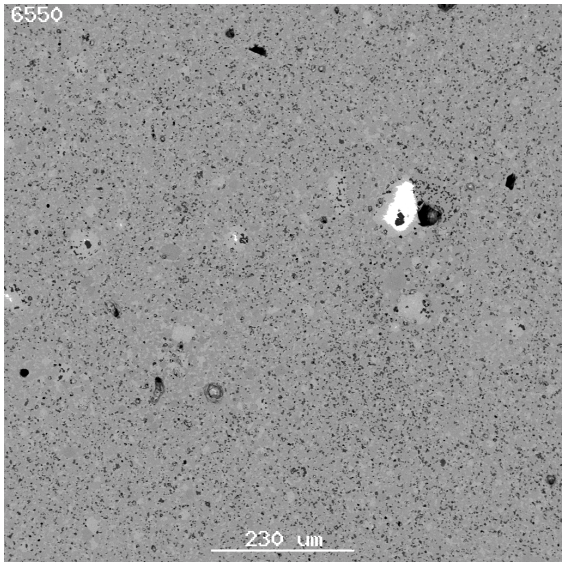
Pu-doped sintered samples (1350°C /4 hours/air) were made from dry attrition milled baseline powder. These samples all contained some PuO_2. The amount of PuO_2 decreased with the milling time/number of passes through the mill. The sample milled for 10 minutes (1 pass) contains PuO_2 grains up to ~ 100μm across. These are surrounded by a thin layer of brannerite. The microstructure of the samples becomes more homogeneous as the milling time/number of passes increases, with the porosity decreasing as the PuO_2 and precursor element agglomerates are progressively milled to a smaller size. After 100 minutes dry attrition milling (10 passes) residual PuO_2 is present mainly as small regions inside brannerite grains with a few residual grains ~ 20 μm across. The Pu-doped samples are comparable to previous dry ball milled samples [1] except that they appear to be more porous. This may in part be due to burnout of the organic milling aids added to assist this dry attrition milling.

The attrition milling results show that dry attrition milling is a feasible process. The microstructures that form (Fig. 1) are satisfactory for the milling setups used. Many of the problems encountered were in part due to the need to scale down the attrition milling to handle the radioactive batches, particularly the Pu-doped batches. Dry attrition milling of large non-radioactive batches worked well.

[1] M W A Stewart, E R Vance, R A Day and A Brownscombe, *Interim Report on Task 1.2: Near Equilibrium Processing Requirements*, ANSTO Materials Division Report No. R99m012, 1 April 1999, Materials Division, ANSTO, Lucas



(a)



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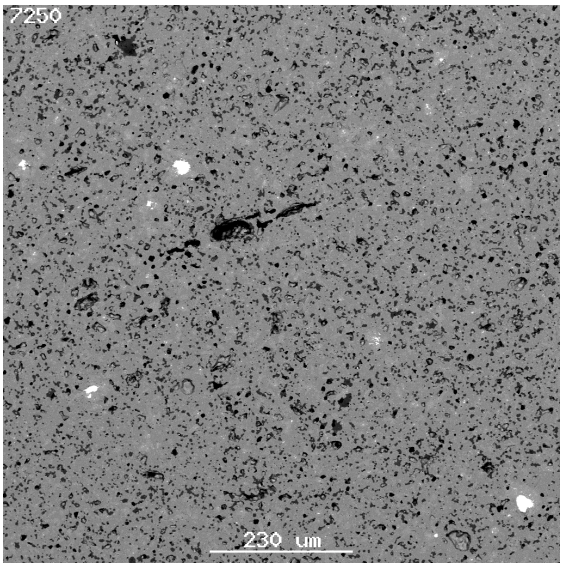
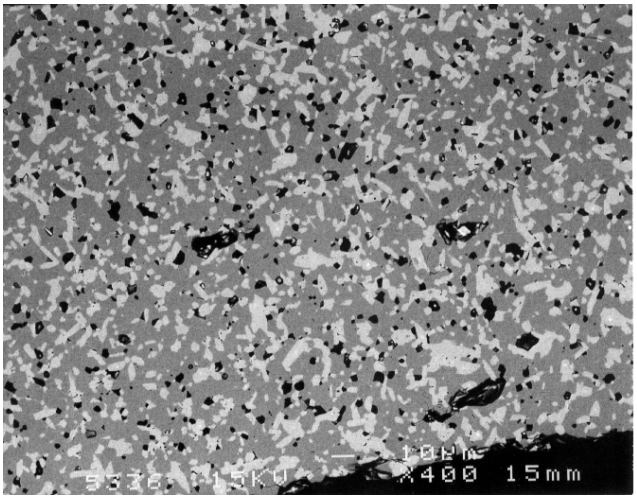


(c)



(d)

Figure 1: Backscatter electron micrographs illustrating the sorts of microstructures achieved by dry milling. (a) Ce/Ce/Zr-baseline formulation, attrition milled 1 kg scale; this sample is mainly pyrochlore. (b) Th/U/Hf-baseline attrition milled on a small-scale. (c) Pu/U/Hf-baseline attrition milled on a small-scale. (b) Th/U/Hf-baseline ball milled on a small-scale. The white regions in (b) – (c) are actinide oxide, In all the samples the matrix is pyrochlore with brannerite (lighter-grey) and some rutile (dark-grey). All the samples contain porosity.

2 INTRODUCTION

2.1 Previous Work on Wet and Dry Ball Milling

In previous interim reports [1,2] the results on Th/U/Hf-doped and Pu/U/Hf-doped ceramics of the six compositions (see section 1 above) that had been processed via wet and dry ball milling, were given. The following conclusions from this work were reached:

1. Caking is a problem during dry ball milling. The Pu/U-doped batches dry-milled better than the Th/U-doped batches to give less heterogeneous powders. The only Th-doped dry-milled batch (out of the initial six) that exhibited what may be considered a satisfactory microstructure was the baseline + impurities batches (B1-4). In these batches the liquid phase formed on sintering, reduced the effect of heterogeneous distribution and agglomeration in the green pellet. On firing, the Th/U-doped oxide-route dry-milled pellets had a lower density and higher porosity due to the aggregates and agglomeration in the powder. However, later work [2,3] on the baseline composition, which involved breaking up the cake as it formed and adding isopropyl alcohol, produced a ceramic with a satisfactory microstructure.

2. Wet ball milling produced more homogeneous samples than dry ball milling.

3. Incomplete milling leads to inhomogeneity in the microstructure. The main effect is that unreacted actinide oxides remain in the microstructure. These are usually surrounded by brannerite. The phase composition also alters due to the actinide being tied up in the oxide, e.g., the pyrochlore has less actinide than the original design. In some cases, the phase ratios will change. The formation of additional phases can also occur, but these tend to be well characterised phases such as zirconolite due to localised insufficient actinide availability, leading to an excess of Hf, and in one case perovskite. If sintering aids are present, e.g., as in the baseline + impurities batch, the effect of processing variables is reduced and the samples are more homogeneous, due to liquid phase sintering.

4. The effect of temperature on density varies with composition. For the 4 hour sintering times, at the sintering temperatures tested (1300, 1350 and 1400°C), most of the pellets made from the batches reach a maximum density at about 1350°C. Above this temperature pore and grain growth occurs, which lead to a decrease in density. Pore and grain growth also occurs at extended sintering times. In the samples with the impurity additions, warping of the pellets occurred, due to partial melting, in the 1350°C and 1400°C sinters. Previous work[4] indicated that 1325°C is an optimum sintering temperature for these materials.

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[2] M W A Stewart and E R Vance, *Interim Report on Task 3: Immobilization Process/Equipment – Task 3.4: Non-destructive Evaluation*, ANSTO Materials Division Report No. R00m011, 30 April 2000, Materials Division, ANSTO, Lucas Heights, Australia.

[3] MWA Stewart, ER Vance, BD Begg, RA Day, S Leung and DS Perera, *Bi-monthly Progress Report October-November 1999 to Lawrence Livermore National Laboratory for Contract B345772, Task 1 Form Development* ANSTO Materials Division Report No. R99m064, 2 December 1999, Materials Division, ANSTO, Lucas Heights, Australia.

[4] E.R. Vance, M.W.A. Stewart, R.A. Day, K.P. Hart, M.J. Hambley and A. Brownscombe, Pyrochlore-rich Titanate Ceramics for Incorporation of Plutonium, Uranium and Process Chemicals, ANSTO Report, Materials Division,

5. Samples fired in air were similar to the samples fired in Ar. Samples sintered in hydrogenous atmospheres were different to those sintered in air or Ar. The reducing conditions promote the formation of zirconolite and perovskite at the expense of pyrochlore and brannerite.

6. When sufficiently milled the formulations formed the phases expected when sintered in air and Ar:

   - The baseline ceramics formed pyrochlore as the main phase with 10 – 25 vol. % brannerite and 3 – 7 vol. % Hf-doped rutile.

   - The baseline + impurities ceramics formed mainly pyrochlore plus ~ 15 vol % 2M zirconolite, ~ 10 – 20 vol. % brannerite, 1 - 3 vol. % Hf-doped rutile and ~ 1 - 2 vol. % of an intergranular silicate phase. The impurities lead to grain growth –via liquid phase sintering.

   - The zirconolite rich ceramics formed an approximately equal mixture of zirconolite and pyrochlore with ~ 15 – 20 vol. % brannerite and sometimes a little (< 5 vol. %) Hf-doped rutile.

   - The brannerite-rich samples consist of an approximately equal mixture of brannerite and pyrochlore; sometimes ~ 2 – 3 vol. % Hf-doped rutile was present.

   - The nominally ~ 10 % perovskite samples did not contain perovskite, rather the additional Ca formed pyrochlore with Ca occupation in the A site (using the general formula $A_2B_2O_7$ to represent the pyrochlore structure) close to one formula unit. The phases formed in addition to the main pyrochlore phase depend on whether the sample was Th/U or Pu/U-doped. For Th/U-doped batches, 5 - 20 vol. % brannerite and 5 – 10 vol. % Hf-doped rutile were present. In the Pu/U-doped samples pyrochlore and less than 5 vol. % rutile were the only phases present.

   - The phosphate doped samples typically consisted mainly of pyrochlore with 15 - 20 vol. % brannerite, 5 – 10 vol. % whitlockite and 3 – 7 vol. % Hf-doped rutile. The whitlockite (nominally, $Ca_3(PO_4)_2$) contains Gd, Hf, U, Th and Ti.

   - Traces (< 1 vol. %) of ThO_2 and PuO_2 were found in some samples. Sometimes this was "unreacted" and other times it was partly "reacted". By reacted we mean that it contained significant amounts of the other elements present in the sample (e.g., Ca, Gd, Hf, U, Ti). The term "unreacted" applies, in this work, to lumps of residual material that have not reacted during sintering.

7. The Pu, U and Th partition as expected – mainly into the pyrochlore, brannerite and zirconolite, with some in the whitlockite and rutile. The amounts in the minor phases, rutile and whitlockite, are small however, and the neutron absorbers Hf and Gd can be found in significant amounts in these phases.

8. The results of the Pu-doped samples are similar to the Th/U-doped batches and produced samples with similar microstructures, which indicate that Th is a good surrogate for Pu in the microstructural context. The major difference between Th and Pu was that the Th has a greater tendency to form brannerite and ThO_2 seemed to be less reactive than the PuO_2 during sintering. This results in the Th-doped pyrochlore in the ceramics being slightly deficient in Th.

9. The approach to equilibrium is determined by a number of factors
    - the efficiency of the milling
    - the sintering time
    - the sintering temperature
    - the batch composition.

2.2 Goal of Task 1.2

The purpose of these tests is to compare the products obtained by plant-like fabrication processes to the products under near equilibrium conditions.

2.3 Strategy Adopted

The six formulations tested previously by ball milling (see section 1, above) were all tested

In this section we mainly report on work on attrition milling of small Th and Pu-doped batches (~ 10 g). Larger scale attrition milling (> 1 kg batch size) has been carried out as part of Task 3 on Ce/Ce/Zr-baseline compositions. The large scale attrition milling of Pu-doped batches is precluded at this stage, hence the use of small batch sizes. Based on previous experience[1-4] on ball milling, we initially expect the wet attrition milled oxide-route materials to be more homogeneous than those prepared by the dry attrition milling.

Th was used as a surrogate for Pu in this work. It avoids some of the redox problems encountered if Ce is used and is believed to be a closer analog of Pu at least in the range of compositions tested here. Thorium is not a perfect analogue for Pu, e.g., as the phase $CaThTi_2O_7$ will not form whereas the phase $CaPuTi_2O_7$ will form. This means that the solubility of Th in the pyrochlore is more limited than Pu. In addition, Th appears to have a greater tendency to enter the brannerite structure than Pu.

3 EXPERIMENTAL

3.1 Compositions Tested

Compositions made were based on those forwarded by LLNL[5](Table 1). The Th/U/Hf-doped formulations made were:

- B1-2 – the baseline ceramic
- B1-4 – the baseline ceramic with impurities
- B1-10 – zirconolite-rich
- B1-12 – brannerite-rich
- B1-14 - nominally ~ 10 % perovskite
- B1-16 - ~ 10 % phosphate

and the Pu/U/Hf-doped formulation made were:

- B1-1 – the baseline ceramic

These are formulated around the LLNL-baseline ceramic composed nominally of 95 wt. % pyrochlore ($Ca_{0.89}Gd_{0.22}Pu_{0.22}U_{0.44}Hf_{0.23}Ti_2O_7$) and 5 wt. % titania ($Ti_{0.9}Hf_{0.1}O_2$). In this work, Ce and Th are used as surrogates for Pu and Ce is used as a surrogate for U.

In addition, Ce/Ce/Zr- baseline ceramic was used for preliminary attrition milling tests

3.2 Fabrication Methods

Compositions of the batches are given in Table 1. The raw materials used to make these batches are given in Table 2.

Both wet and dry attrition milling runs were done. Preliminary trials were conducted on a large-scale (~ 1 kg) with oxide-route, Ce/Ce/Zr-baseline composition. Small-scale (10 g batch size) trials were then carried out on Ce/Ce/Zr and then Th/U/Hf-baseline compositions; in preparation for an attempt at small-scale milling of Pu/U/Hf-baseline batches.

3.2.1 Ce/Ce/Zr-doped Oxide-route Powder Preparation

Preliminary attrition milling trials were carried out up to a ~ 1 kg scale using 750 cc and 1400 cc pots, 5 mm diameter yttria-stabilised zirconia media, with both dry and wet attrition milling for 45 minutes at ~ 450 rpm.

The attritor used for the small-scale (10 – 20 g batch size) attrition milling was a Union Process 01-HDT machine that has been modified for use inside a glovebox. This mill is fitted with 750 cc pots. The machine can also operate with Union Process 110 cc quick-change pots. Attrition milling of

[5] Compositions used are based on those forwarded by e-mail from B.B. Ebbinghaus, LLNL, Livermore CA, in Table B1:

the small scale batches was carried out using the 110 cc polyethylene quick-change pots. Approximately 140 g of 2mm diameter yttria-stabilised zirconia media was used. Dry and wet attrition milling were done at 450 rpm for 45 minutes. The batch size in both cases was ~ 10 g.

Table 1: Th/U-doped compositions made for Task 1.2 (given as weight % oxides).

Batch No.	Ce/Ce/Zr Baseline	Pu/U/Hf B1-1 Baseline	Th/U/Hf B1-2 Baseline	Th/U/Hf B1-4 Baseline + Impurities	Th/U/Hf B1-10 Zirconolite -rich	Th/U/Hf B1-12 Brannerite -rich	Th/U/Hf B1-14 ~ 10 % nominal perovskite	Th/U/Hf B1-16 ~ 10 % nominal phosphate
Components	(Wt. %)	(Wt. %)	(Wt. %)	(Wt. %)	(Wt. %)	(Wt. %)	(Wt. %)	(Wt. %)
CaO	12.11	9.95	9.99	9.50	9.26	5.89	12.07	11.64
Gd_2O_3	9.68	7.95	7.98	7.59	6.61	6.34	7.98	8.53
ZrO_2	7.88							
HfO_2		10.65	10.69	10.16	24.26	9.95	10.88	9.72
CeO_2	27.56							
PuO_2		11.89						
ThO_2			11.62	11.09	9.35	12.68	12.04	12.73
UO_2		23.69	23.77	22.60	15.44	28.04	20.83	21.43
TiO_2	42.77	35.87	35.96	34.21	33.93	37.10	36.19	32.59
Al_2O_3				0.48	1.13			
B_2O_3				0.16				
$CaCl_2$				0.63				
CaF_2				0.42				
Cr_2O_3				0.08				
Fe_2O_3				0.14				
Ga_2O_3				0.54				
K_2O				0.31				
MgO				0.42				
MoO_2				0.27				
Na_2O				0.13				
NiO				0.12				
P_2O_5								3.35
SiO_2				0.44				
Ta_2O_5				0.18				
WO_2				0.47				
ZnO				0.07				
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 2: Raw materials used for the oxide batches.

Element	Raw Materials for Batches (raw material, source, catalogue number)
Ca	$Ca(OH)_2$, AR grade, BDH Ltd. 90131
Gd	99.9 %, Gd_2O_3, -325 mesh, Cerac Speciality Inorganics, G-1015
Zr	99.7 %, ZrO_2, Electonic Grade (EG), Harshaw/Fitrol Partnership
Hf	99.95 % HfO_2, -325 mesh, Cerac Speciality Inorganics, H-1011
Ce	99.9 % CeO_2, -325 mesh, Cerac Speciality Inorganics, C-1064
Pu	Calcined (1050°C), Pu nitrate (see table 3)
Th	Calcined (1050°C or 850°C), $Th(NO_3)_4.5H_2O$, Merck, 1.08162
U	Calcined (1050°C or 850°C), $UO_2(NO_3)_2.6H_2O$, depleted (~ 0.318 % U235), BDH, Batch FF296, 10289
Ti	> 99.1 % TiO_2, pigment grade anatase, Tioxide Pty. Ltd., AHR select 100375.
Al	99.6 % Al_2O_3, Degussa AG, Aluminium Oxide C
B	H_3BO_3, Ajax Chem., Unilab 102
Cl	$CaCl_2$, BDH, AR grade 27587,
Cr	Cr_2O_3, BDH, AR grade 218330
F	CaF_2, BDH, AR grade 540823
Fe	99 % + Fe_2O_3, Aldrich Chem., 31005-0
Ga	99.999 % Ga_2O_3, Chemat Tech., RG-304
K	KOH, Merck, 5033
Mg	MgO, Johnson Matthey, Specpure J.M. 130
Mo	99.995 % MoO_3, BDH, 16669
Na	NaOH, Merck, 6498
Ni	NiO, Johnson Matthey, Specpure J.M. 895
P	85% H_3PO_4, Ajax Chem.,
Si	Ludox HS-40 colloidal silica, 40% suspension in water, Aldrich Chem., 42081-6
Ta	99.9 % Ta_2O_5, A.D. MacKay Ltd.
W	99.9 % WO_3, BDH, 30543
Zn	99.9 % ZnO, Aldrich Chem., 20553-2

Dry attrition milling of a composition was done first. A few drops of iso-propyl alcohol were added before dry milling. After dry attrition milling the media were separated from the powder using a sieve. Any powder sticking to the pot was also scraped from the pot. The media and pot were then reused, without cleaning, for wet attrition milling. Approximately 15 ml of deionised water was added to the mill for wet attrition milling. After wet attrition milling the media were separated from the slurry by a sieve. Water was used to wash the remaining slurry from the media and pot. The media and pot were then thoroughly cleaned and dried for next dry attrition milling run.

3.2.2 Th/U/Hf-doped Oxide-route Powder Preparation

3.2.2.1 High-fired ThO_2 and UO_2

These Th/U-doped batches were made via the oxide-route using high-fired ThO_2 and UO_2. This high-fired ThO_2 and UO_2 was made by calcining thorium nitrate pentahydrate and uranyl nitrate at 1050°C for 4 hours, in air. Batches of the 6 formulations (Table 1) were made using oxide-route precursor chemicals (Table 2).

The attrition milling parameters were the same as the Ce/Ce/Zr-baseline above (section 3.2.1). After the milling results of B1-2, B1-4, B1-10 and B1-12 (see below in section 4.2), the last two of these batches (compositions B1-14 and B1-16) were passed through a 150 µm sieve. The residue was crushed in a mortar and pestle until it too passed through the sieve. This was to simulate pre-milling the high-fired actinide oxides.

The non-radioactive elements were mixed together in a plastic jar taken to the uranium laboratory where UO_2 and ThO_2 were added. The powders were blended by tumbling the jar. The powders were then dry or wet attrition milled for 45 minutes (see below). After attrition milling the samples were calcined in air at 750°C for 1 hour.

To try to improve milling the dry attrition milled baseline (B1-2) batch that contained high-fired ThO_2 and UO_2 was re-milled. The attrition re-milling of this powder batch was carried out for 45 minutes the same way as previously, but with stoppages at 10, 20 and 30 minutes. At these stoppages the powder and media were removed and the cake that formed on the bottom of the mill broken up, the mill setup again, the media and then the powder added and milling restarted. Approximately 0.5 ml of iso-propanol was added at the start and at each stop.

3.2.2.2 Pre-ground, High-fired ThO_2 and UO_2

A second lot of Th/U-doped batches were made using pre-ground, high-fired ThO_2 and UO_2. This was done by wet ball milling for 16 hours in nylon jars with 10 mm diameter yttria-stabilised zirconia media. Water was used in milling the ThO_2 and iso-propanol for the UO_2. Compositions (Table 1) made by this method oxides using oxide-route precursor chemicals were:

- B1-2 – the baseline ceramic
- B1-4 – the baseline ceramic with impurities
- B1-10 – zirconolite-rich
- B1-12 – brannerite-rich

The non-radioactive elements were mixed together in a plastic jar taken to the uranium laboratory where UO_2 and ThO_2 were added. The powders were blended by tumbling the jar. The powders were then dry and wet attrition milled for 45 minutes (see below). After attrition milling the powders were calcined in air at 750°C for 1 hour.

3.2.2.3 Pre-ground, Low-fired ThO_2

A third series of Th/U-doped batches were made using ThO_2 that had been fired to only 850°C, then pre-ground as above. The UO_2 in these batches was the pre-ground, high-fired material used above. This work was done with oxide-route powders of the B1-2 (the baseline ceramic) composition.

The following attrition milling setups were used:

(1) The first attrition milling setup was with uncalcined precursor powder. In this setup, the attrition milling was carried out for 45 minutes the same way as the high-fired batches above (110 cc quick-change pot, 450 rpm). The difference was that at 10, 20 and 30 minutes the mill was stopped the powder and media removed and the cake that formed on the bottom and walls of the pot was broken up. The mill setup again and the media and powder added for further milling. Approximately 0.5 ml of iso-propanol was added at the start and at each stop. Powder samples were taken after 10, 20 and 30 minutes milling. Sintered samples were made from these powdered samples plus the final 45 minutes (4 passes) powder. This batch was calcined

at 950°C after the attrition milling.

(2) The second attrition milling setup used calcined precursor powder (950°C, 1 hour, air). In this setup the batch was milled with a modified 110 cc quick-change pot for 45 minutes, with stops every 10 minutes to break up the cake that formed on the base and walls of the pot (as per the first runs in the preceding paragraph). The mill speed was 500 rpm. This is 50 rpm faster than the setup in (1). Powder samples were taken after 10, 20, 30 and 45 minutes milling. Sintered samples were made from these powdered samples plus the final 65 minutes (6 passes) powder.

(3) The third setup used the modified pot as above. The attritor was run at 600 rpm with organic chemicals added to the powder to improve the milling. A sintered sample was made from the powder milled for 65 mins (6 passes). This setup gave near-optimal conditions within the limitations of the attrition mill equipment.

(4) The forth setup used the modified pot at 600 rpm as above (3), but with wet attrition milling, using 15 ml of deionised water, for 65 minutes without stopping. This was to give a comparison with wet ball milled samples.

3.2.3 Pu/U/Hf-doped Sample Preparation

The Pu-doped attrition milling was done on a small-scale - 10 g batch size. The work on the Ce/Ce/Zr-doped and Th/U/Hf-doped batches, discussed above, was carried out in an attempt to optimise the attrition milling parameters before Pu-doped batches were attempted.

The PuO_2 had been high-fired at 1050°C for 4 hours in air. The baseline composition B1-1 with oxide-route precursor powders was used. The batch size in both cases was ~ 10 g. The precursor, minus the PuO_2, was passed through a 150 μm sieve, with the residue being crushed in a mortar and pestle till it passed through the sieve. An ultrasonic bath and acetone washing was used to help the powder pass through the sieve. After sieving, the powder was dried and then calcined at 750°C for 1 hour in air. It was then taken to the actinide suite where the PuO_2 was added. The PuO_2 was blended by tumbling for 5 minutes. The powder was then attrition milled.

Attrition milling was carried out with the same Union Process 01-HDT machine Th/U/Hf and Ce/Ce/Zr-doped batches above. Attrition milling was carried out the modified 110 cc polyethylene quick-change pot at 600 rpm. Approximately 140 g of 2mm diameter yttria-stabilised zirconia media was used. Milling aid chemicals were added to the powder prior to milling. The milling was carried out for 100 minutes (10 passes) with stops every 10 minutes where the powder and media were removed and the cake that formed on the bottom and walls of the pot broken up. The mill was then setup again and the media and powder added for further milling. Iso-propanol was added at each stop. Powder samples were taken after 1 (10 minutes) and 6 (60 minutes) passes. Sintered samples were made from these powdered samples plus the final 100 minutes (10 passes) powder.

3.2.4 Cold-pressing and Sintering

Pellets were prepared by cold pressing ~ 0.5 g of powder in a 10mm diameter steel die at ~ 60 MPa. Dies were lubricated with oleic acid. The green pellets were sintered in alumina tube furnaces. The sintering atmosphere used was air (open furnace tube ends), the sintering time was 4 hours and the sintering temperature was 1350°C. The heating and cooling rates were 5°C/min.

3.3 Analysis

3.3.1 Density

After sintering, the densities of the samples were measured using Archimedes' method, in water for the Ce/Ce and Th/U-doped samples, and octanol for the Pu/U-doped samples, via the evacuation technique.

3.3.2 X-ray Diffraction

X-ray diffraction (XRD) was carried out using either a Siemens D500 diffractometer employing Co K-alpha radiation, or a Scintag X1 Advanced Diffractometer System, with Cu K-alpha radiation.

The Pu/U-doped samples were mounted in resin and polished to a 0.25-1.0 μm diamond finish. XRD was carried out on this polished surface.

The following types of XRD were carried out on the Ce/Ce and Th/U-doped samples: the as fired top surface of the pellet; a ground face of the pellet; and a small sample of powder from the pellet with or without tungsten metal as an internal reference standard. This powdered sample was a thin film on a resin base. Some samples were also done on a zero background silicon base.

3.3.3 Scanning Electron Microscopy

The samples were examined by scanning electron microscopy (SEM) using either JEOL JSM6400 or JEOL JSM6300 machines, both of which are fitted with energy dispersive x-ray spectrometry (EDS) instruments for quantitative analysis.

Image analysis was carried out manually, using visual estimation diagrams to determine the percentages of the various components present.

4 RESULTS AND DISCUSSION

The images from the SEM analyses, EDS analysis results and a summary of the XRD results are given in Appendices A to E. Electronic copies of the raw XRD data files are included on a disk with this report.

4.1 Ce/Ce/Zr-doped Samples

The SEM/EDS and XRD results on this material are in Appendix A.

The larger sample pots (750 cc and 1440 cc) enabled attrition milling in both wet and dry modes. Examples of the microstructures seen in typical samples made via wet and dry attrition milling are given in Figs. A-1 and A-2, Appendix A. The samples are composed of > 99 % pyrochlore with a small amount (<< 1 vol. %) of what is believed to be whitlockite. The dry milled sample exhibits some compositional variation of the pyrochlore across the sample whereas the wet milled sample has a uniform pyrochlore composition. The dry milled sample has more porosity than the wet milled sample.

The small pot could not be made to work using dry attrition milling under the parameters tested. The powder formed a cake on the bottom and walls of the mill. Little if any milling occurred.

Wet attrition milling however, worked well. The powder was agitated in the mill and the resulting pellet had a uniform microstructure, which consisted mainly (> 99 %) of pyrochlore (Fig. A-3, Appendix A).

4.2 Th/U-doped Samples

4.2.1 Results on Samples Made Using High-Fired ThO_2 and UO_2

4.2.1.1 Results on Samples of Composition B1-2, B1-4, B1-10 and B1-12 With the High-fired ThO_2 and PuO_2 Used as Made

Lumps of black UO_2 and white ThO_2 were observed by eye in the dry and wet milled powders. This plus the mottled colour and the rough surface appearance of the sintered pellets made from the dry attrition milled powders suggests that the dry attrition milling has not been effective in homogenising the starting powder or grinding the UO_2 and ThO_2. The wet milled sintered pellets appear to be more homogeneous than the dry milled samples, but there was still some colour variation across these pellets. The densities of these dry attrition milled pellets are much less than those of the wet attrition milled samples (Table 3). The densities are lower than the equivalent wet and dry ball milled samples (Table 3)

The SEM results are given in Appendix B, Figures B-1 to B-8, and the XRD results are summarised in Appendix B, Table B-1. Due to the heterogeneous microstructures full EDS analysis was not done on these samples, though the EDS system was used to identify the phases.

B-7. Large lumps of residual ThO_2, about 20 to 250 μm across, can be seen in the microstructure. Smaller amounts of ThO_2 can be found inside some of the brannerite grains. Only a few grains of UO_2 were observed in the samples, even though black particles of UO_2 were visible in the milled powders, indicating that the ThO_2 is much less reactive than the UO_2. The wet milled samples were more homogeneous than the dry milled samples, but residual unreacted ThO_2 and significant porosity, which is often associated with agglomerates in green powders, indicated that the milling is incomplete.

No unexpected phases formed (Table B-1, Figs., A1-B-8, Appendix B). Some zirconolite, probably the 4M polytype, was found in the dry milled baseline ceramic. This is present because the large lumps of unreacted ThO_2 shifts the composition of the rest of the sample towards zirconolite.

These results suggest that the 2 mm diameter grinding balls may not provide insufficient grinding force to mill the larger agglomerates of UO_2 or ThO_2 with the attrition mill parameters used. The results also indicate that little milling is occurring during the dry attrition milling process; the powder dropped to the bottom of the pot and formed a cake. The large particles of UO_2 or ThO_2 may also settle on the bottom of the mill during wet attrition milling. Pre-grinding of the UO_2 or ThO_2 may help solve this problem.

4.2.1.2 Results on Samples Made Using the High-Fired ThO_2 and UO_2 that had been Hand Ground in a Mortar and Pestle

The samples examined in this section were made using the high-fired ThO_2 and UO_2 reported on in the previous section. In light of the poor microstructures achieved when using the high-fired ThO_2 and UO_2 it was decided to pre-grind the powders prior to attrition milling. A mortar and pestle was used. The powder was passed through a 150 μm sieve. This aim of this work was to simulate a grinding stage prior to attrition milling the actinide oxides and precursor chemicals. The results are given in Appendix B.

The dry attrition milled sample of composition B1-14, (nominally 10 % perovskite ceramic) was heterogeneous, highly agglomerated and porous (Fig. B-9). Phases observed were pyrochlore, brannerite, rutile, hafnia, thoria and zirconolite. The composition was variable across the sample so EDS analysis was not attempted.

The wet attrition milled B1-14 sample consists mainly of pyrochlore, with some brannerite a small amount of rutile and some residual thoria (Table B-1, Fig. B-10). This is slightly different to the wet ball milled samples sintered in air (reported elsewhere [1,2]), which had ~ half as much brannerite and only a trace of thoria (< 1 vol. %). The brannerite and residual thoria suggest that this attrition milling has not been as efficient as the wet ball milling.

As for the B1-14 sample above, the dry attrition milled sample of composition B1-16 (10 % phosphate-doped ceramic) was heterogeneous, highly agglomerated and porous (Fig. B-11). Phases observed were pyrochlore, brannerite, rutile, hafnia, thoria and zirconolite. The composition was variable across the sample so EDS analysis was not attempted.

The wet attrition milled B1-16 sample consists mainly of pyrochlore, with some brannerite a small amount of rutile and residual thoria (Table B-1, Fig. B-12). The wet ball milled samples sintered in air (reported elsewhere [1,2]), were similar, but had no residual thoria. This residual thoria implies that this attrition milling has not been as efficient as the wet ball milling route used previously [1].

Table 3: Densities * as measured by Archimedes' method of sintered Th/U-doped pellets produced from the attrition milled powders.

Pellet No. /composition	Th and U Type	Attrition Milling Wet or Dry +	Bulk Density (g/cm^3)	Theoretical Density $ (%)	Apparent Porosity (%)	Ball Milled Density Results #	(g/cm^3)
						Dry	Wet
B1-2						***B1-2***	
oxide-route							
Calcined after attrition milling							
mws99-0585	high-fired oxide	dry	4.31	73.0	17.2	4.9	5.3 - 5.6
mws99-0586	high-fired oxide	dry	4.34	73.6	17.0		
mws00-0651	high-fired oxide	re-milled dry 90 min/4 passes	5.06	85.8	7.2		
mws00-0652	high-fired oxide	re-milled dry 90 min/4 passes	5.09	86.3	6.1		
mws99-0587	high-fired oxide	wet	4.89	82.8	8.3		
mws99-0588	high-fired oxide	wet	4.91	83.3	10.0		
mws99-0606	high-fired pre-ground oxide	wet	5.52	93.6	1.1		
mws99-0666	low-fired pre-ground oxide	dry 10 min/1 pass	4.35	73.8	20.8		
mws99-0667	low-fired pre-ground oxide	dry 20 min/2 passes	4.69	79.6	13.5		
mws99-0668	low-fired pre-ground oxide	dry 30 min/4 passes	4.79	81.2	11.0		
mws99-0669	low-fired pre-ground oxide	dry 45 min/4 passes	5.02	85.1	6.4		
mws99-0670	low-fired pre-ground oxide	dry 45 min/4 passes	5.03	85.2	6.7		
Calcined before attrition milling		***Modified Pot***					
mws99-0671	low-fired pre-ground oxide	dry 10 min/1 pass	4.05	68.7	27.8		
mws99-0672	low-fired pre-ground oxide	dry 20 min/2 passes	4.74	80.3	13.2		
mws99-0673	low-fired pre-ground oxide	dry 30 min/4 passes	5.00	84.7	7.8		
mws99-0680	low-fired pre-ground oxide	dry 45 min/4 passes	5.16	87.4	4.5		
mws99-0681	low-fired pre-ground oxide	dry 45 min/4 passes	5.09	86.2	6.4		
mws99-0674	low-fired pre-ground oxide modified attritor	dry 65 min/7 passes	5.22	88.4	4.4		
mws99-0677	low-fired pre-ground oxide modified attritor	dry 65 min/7 passes	5.20	88.2	4.6		
mws99-0683	low-fired pre-ground oxide	dry – optimised 65 min/6 passes	5.46	92.6	0.4		
mws99-0683	low-fired pre-ground oxide	dry – optimised 65 min/6 passes	5.46	92.6	0.3		
mws99-0688	low-fired pre-ground oxide	Wet 65 min	5.54	93.8	4.3		
mws99-0688	low-fired pre-ground oxide	Wet 65 min	5.38	91.3	3.8		

B1-4						***B1-4***	
oxide-route							
mws99-0589	high-fired oxide	dry	4.65	78.8	10.8	5.0 – 5.2	5.2 – 5.4
mws99-0590	high-fired oxide	dry	4.42	75.0	14.6		
mws99-0591	high-fired oxide	wet	5.12	86.8	3.0		
mws99-0592	high-fired oxide	wet	5.13	86.9	4.2		
mws99-0608	high-fired pre-ground oxide	wet	5.23	88.6	3.3		
B1-10						***B1-10***	
oxide-route							
mws99-0577	high-fired oxide	dry	3.71	62.9	36.0	4.1	4.1 – 5.9
mws99-0578	high-fired oxide	dry	3.58	60.7	41.0		
mws99-0579	high-fired oxide	wet	4.87	82.5	13.4		
mws99-0580	high-fired oxide	wet	5.02	85.1	6.9		
mws99-0602	high-fired pre-ground oxide	wet	5.32	90.2	0		
B1-12						***B1-12***	
oxide-route							
mws99-0581	high-fired oxide	dry	4.05	68.7	31.3	4.6	5.3 - 5.6
mws99-0582	high-fired oxide	dry	4.04	68.4	31.5		
mws99-0583	high-fired oxide	wet	5.20	88.2	7.2		
mws99-0584	high-fired oxide	wet	5.20	88.2	7.3		
mws99-0604	high-fired pre-ground oxide	wet	5.64	95.6	0.4		
B1-14						***B1-14***	
oxide-route							
mws99-0609	high-fired oxide crushed < 150µm	dry	4.28	72.5	23.1	3.8 – 4.5	4.8 – 5.3
mws99-0610	high-fired oxide crushed < 150µm	wet	4.95	83.8	8.0		
B1-16						***B1-16***	
oxide-route							
mws99-0611	high-fired oxide crushed < 150µm	dry	4.18	70.9	23.7	3.9	4.7 – 5.3
mws99-0612	high-fired oxide crushed < 150µm	wet	5.10	86.4	2.6		

* It should be noted that the processing conditions in this work have not been optimised to produce maximum densities. The powders did not contain additives to assist cold pressing. Nor had the powders been granulated prior to cold pressing.

\+ Milling time is 45 mins unless stated.

$ Given as a guide with the theoretical density taken to be 5.9 g/cm^3.

\# Given for comparison. Taken from Table 5 in: M W A Stewart, E R Vance, R A Day and A Brownscombe, *Interim Report on Task 1.2: Near Equilibrium Processing Requirements*, ANSTO Materials Division Report No. R99m012, 1 April 1999, Materials Division, ANSTO, Lucas Heights, Australia.

The lack of major improvement even with pre-grinding suggests that changes to the to the attrition milling parameters were required to improve the milling efficiency. It also suggests that the "high-fired" thoria may not be a suitable surrogate for attrition milling experiments.

4.2.1.3 Results on the Re-milled High-fired ThO_2 and UO_2-doped B1-2 Composition Sample

This work was carried out after work using the low-fired ThO_2 (see section 4.2.2 below). The aim was to see if increasing the milling time and number of passes would improve the milling of the high-fired ThO_2. The results of SEM/EDS and XRD analyses on this work are given in Appendix B. As discussed in section 3.2.2.1 above, this was done by breaking up the powder cake every 10

minutes, setting up the mill and adding the powder back into the mill.

The dry attrition re-milling combined with a breaking up of the cake has significantly improved the microstructure of the sintered samples (compare microstructures of the sample in Fig. B-13 with those in Fig. B-1).

4.2.1.4 Summary of The Results on the High-fired ThO_2 and UO_2-doped Samples

The problem with these initial trials (section 4.2.1.1) was that the powder passed through the balls in the attrition mill to the bottom of the mill pot relatively quickly and little milling occurred, hence extending the milling time had little effect. The heavy ThO_2 and UO_2 particles may fall even quicker through the mill and hence they may undergo little or no milling at all. Stopping and breaking up the powder cake helped improve milling. Each stop/break-up approximately simulates a pass though a bottom-discharge attrition mill. The results on the re-milled sample suggest that, in this case, it is not the milling time that is critical to the milling efficiency – it is the number of passes through the mill. The number of passes would be equivalent to the milling path length. In a large attrition mill there is a longer milling path. In the small 110 cc pots the milling path is short. Once the powder reaches the bottom of the pot it settles there and undergoes little, if any, further milling. Therefore, using the larger milling pots used in the initial Ce/Ce/Zr-baseline attrition milling trials may improve the dry attrition milling of the high-fired ThO_2 and UO_2-doped samples.

4.2.2 Results on Samples Made Using Pre-ground High-fired ThO_2 and UO_2

The attrition milling of the previous samples (section 4.1.1) that used the high-fired (1050°C) ThO_2 and UO_2 was ineffective (black lumps, presumably of UO_2 and white lumps of ThO_2 were observed in the powders). A second series of powders of compositions B1-2, B1-4, B1-10 and B1-12 were prepared (Table 1). In these batches, the high-fired ThO_2 and UO_2 were pre-ground prior to addition to the precursor. The preparation has been discussed in section 3 above. The measured Archimedes' density of each of these pellets was higher than the equivalent pellets made from the high-fired unmilled ThO_2 and UO_2.

The dry attrition milling was not successful. The results are the same as the high fired ThO_2-doped samples tested above. Large lumps of ThO_2 remained in the samples. Clearly the dry attrition milling setup is not effective. Changes were subsequently made to the dry milling parameters for later work.

The wet attrition milling results of SEM/EDS and XRD analysis of samples made from these compositions are given in Appendix C. The estimated amount of each phase, done manually with the aid of visual estimation diagrams, is given in the EDS Tables B1 to B4.

4.2.2.1 Composition B1-2, Baseline Ceramic

The mineralogy of the sample was:

- ~ 65 - 75 vol % pyrochlore
- ~ 15 - 25 vol. % brannerite
- ~ 5 – 7 vol. % rutile

This attrition milled sample is microstructurally similar to the previous wet ball milled samples [1,2], but contained more rutile (~ 3 vol. % more). Some large lumps of rutile were detected in this sample (Fig. C-1). These were not found in previous work. The density is also similar to the wet ball milled samples (Table 3), though it should be noted that the processing conditions in this work

have not been optimised to produce maximum densities. The powders did not contain additives to assist cold pressing. Nor had the powders been granulated prior to cold pressing.

The composition of each of the phases was constant across each of the samples. The only major difference between the exterior and interior appears to be a thin (~ 20 μm) layer at the surface of the pellet which appears to be deficient in rutile (Fig. C-1(d)). This absence of rutile was not picked up in the XRD, probably due to the small amount of rutile present (< 5 vol. %).

4.2.2.2 Composition B1-4, Baseline Ceramic + Impurities

The mineralogy of the sample was:

- ~ 60 - 70 vol % pyrochlore
- ~ 10 – 15 vol. % 2M zirconolite
- ~ 15 - 20 vol. % brannerite
- ~ 3 -5 vol. % rutile
- ~ 1 – 2 vol. % glass

As above with composition B1-2, this wet attrition milled sample was also microstructurally similar to the previous wet ball milled samples [1,2], but contained more rutile (~ 3 - 4 vol. % more). Large (~ 50 μm) clumps of rutile grains were detected in this sample (Fig. C-2). These were not found in previous wet ball milling work..

No major difference was observed between the compositions of the phases at the interior and exterior of the pellets.

An additional peak at ~ 0.56 nm was observed in the XRD pattern. This peak was more intense in the XRD patterns of the surfaces of the pellets (Appendix C, Table C-7). This peak has been discussed in another report [2]. The deficiency in rutile observed near the surface of the B1-2 composition sample above, was not observed in this sample.

4.2.2.3 Composition B1-10, Zirconolite-rich Ceramic

The mineralogy of the sample was:

- ~ 35 - 45 vol % pyrochlore
- ~ 35 - 45 vol. % 2M zirconolite
- ~ 10 – 25 vol. % brannerite
- ~ 5 - 7 vol. % rutile
- < 1 vol. % ThO_2

The attrition milled sample has a similar phase composition to the wet ball milled sample reported previously [1,2], except that it has Hf-doped rutile present; rutile was only found in the dry ball milled samples of this composition. The sample is also denser than the wet ball milled samples sintered at 1350°C for 4 hours in Ar or air (4.1 – 4.8 g/cm^3, Table 3). However, it was observed that sintering B1-10 pellets at a higher temperature, or for longer times significantly increased the density, e.g., a density of 5.9 g/cm^3 was achieved on sintering at 1400°C. Hence, it is possible that small variations in the furnace temperature around 1350°C, will have a significant effect on the density of pellets made from this composition.

No major differences were observed between the interior and exterior compositions of the individual phases in the sintered sample. Occasional variations in brannerite composition were observed, presumably due to heterogeneous starting powders

A thin (~ 20 μm) layer at the surface of some pellets appears to be deficient in rutile and brannerite (Fig. C-3). An additional peak at ~ 0.56 nm was observed in the XRD pattern. This peak was more intense in the XRD patterns of the surfaces of the pellets. The surfaces of the pellets produce XRD patterns with more intense zirconolite peaks and less intense rutile peaks than the ground face or powdered samples. Preferred orientation of the zirconolite crystals at the surface may also be occurring.

4.2.2.4 Composition B1-12, Brannerite-rich Ceramic

The mineralogy of the sample was:

- ~ 45 - 55 vol % pyrochlore
- ~ 45 - 55 vol % vol. % brannerite
- ~ 5 vol. % rutile
- << 1 vol. % ThO_2

A region of "unreacted" HfO_2 was found in the sample and this is presumably from an agglomerate that had not been milled effectively.

This attrition milled sample is similar microstructurally to the previously reported [1,2] wet ball milled samples. The density is also similar (Table 3).

No major differences were observed between the interior and exterior compositions of the phases in the pellets. Occasional variations in brannerite composition were observed, presumably due to heterogeneous starting powders.

4.2.2.5 Summary of the Results on the Samples Made Using Pre-ground, high-fired ThO_2 and UO_2

The wet attrition milled samples were similar to the wet ball milled samples reported previously. The small-scale, dry attrition milling was ineffective with the parameters used. The powder appears to settle on the bottom of the pot with little milling of the powder occurring. The difference between the small-scale and large-scale attrition milling has been discussed above (section 4.2.1.4)

The different compositions formed the expected phases, with the Th and U partitioning in the same way as in the wet ball milled samples – mainly into the pyrochlore, brannerite and zirconolite with minor amounts in the rutile and whitlockite.

4.2.3 Results on the Samples Made Using Pre-ground, Low-fired ThO_2 and Pre-ground, High-fired UO_2

As discussed above, the initial small-scale, dry attrition milling trials of the samples containing high-fired ThO_2 was unsuccessful. The powders tended to fall straight to the bottom of the pot and form a cake. The end-result was that little particle size reduction of the coarse particles occurred. Wet attrition milling was however successful and produced samples similar to that of wet ball milled materials. This suggested that given sufficient agitation of the media small-scale dry-attrition milling would work. It has been shown previously [2,6] that breaking up the cake during dry

[6] MWA Stewart, ER Vance, BD Begg, RA Day, S Leung and DS Perera, *Bi-monthly Progress Report October-November 1999 to Lawrence Livermore National Laboratory for Contract B345772, Task 1 Form Development* ANSTO Materials

ball milling and adding a few drops of iso-propanol, significantly improved the homogeneity of the sintered sample. Hence, a new approach was taken in an attempt to improve the small-scale dry attrition milling. The methods were discussed in section 3.2.2.3 above. This work was carried out using the Th/U/Hf-baseline formulation.

4.2.3.1 Results on the Samples Made Using the Unmodified Quick-change Pot

These samples were made by the method described in (1) of section 3.2.2.3 above. The results of SEM/EDS and XRD analyses in this work are given in Appendix D.

The samples consisted of a matrix of pyrochlore with brannerite, rutile and thoria. The thoria was present as large aggregates, which appear to be broken up with increased milling time/number of passes (Fig. D-1). The amount of porosity also decreases. The final sample (after 45 mins/4 passes), while not as homogeneous as wet ball milled samples, is much more homogeneous than the initial dry attrition milled samples (sections 4.2.2, 4.2.1 and Appendix B) and is comparable to satisfactory dry ball milled samples. Regions of this sample (Fig. D-2) have a relatively homogeneous microstructure, similar to the better ball milled samples. The amount and composition of each of the phases present is also consistent with earlier ball milled work (Table D-1) [1,2].

4.2.3.2 Results on the Samples Made Using the Modified Quick-change Pot

These samples were made by the method described in (2) of section 3.2.2.3 above. The samples were made using a batch of the same composition as that reported in the preceding section. For this run changes were made to the attrition mill setup in an attempt to improve the dry attrition milling. The milling was carried out with the cake being broken up every 10 mins and the mill pot was altered to try to reduce “dead zones” – regions where the media is not fluidised.

The results of SEM/EDS and XRD analyses in this work are given in Appendix D. The densities of the sintered samples increase with milling time (Table 3). This corresponds to a steady improvement in the homogeneity of the microstructure with increased milling time (Fig. D-3). The amount and composition of each of the phases present is also consistent with earlier ball milled work (Table D-2). As with the above sample (45 min./4passes sample without the modified pot, Fig. D-2) the regions of the pellets away from the thoria agglomerates are microstructurally homogeneous (Fig. D-3 (e)).

4.2.3.3 Results on the Samples Made Under Near-Optimal Conditions

The results of SEM/EDS and XRD analyses in this work are given in Appendix D. This work was carried out under close to optimal conditions for the small quick-change pot (see section 3.2.2.3 setup (3)).

The densities of the samples attrition milled for 65 mins/6 passes are the highest for the Th/U-doped dry attrition milled baseline compositions (Table 3). The apparent porosity of these samples is low (< 0.5 %). This low porosity can be seen in the relatively homogeneous microstructure (Fig. D-4).

The amount and composition of each of the phases present (Table D-3) is also consistent with earlier ball milled work [1,2]. Phases present included pyrochlore, brannerite, rutile, a few grains of whitlockite, some thoria and one localised cluster of zirconolite grains. Only one big (100 μm) lump of thoria was observed in the entire cross section of the pellet - the milling has been very

effective. As with previous ball milled work small areas of actinide oxide could be found in the centre of some of the brannerite grains, but these are rare in this sample.

4.2.3.4 Results on the Samples Made Via Wet Attrition Milling

The results of SEM/EDS and XRD analyses in this work are given in Appendix D. The milling setup in given in section 3.2.2.3 (setup (4)). The results of SEM/EDS and XRD analyses in this work are given in Appendix D.

The densities of these samples are similar to the optimised dry milled samples of the preceding section though the apparent porosity is higher (~ 4 % compared to 0.4 %) (Table 3).

The amount and composition of each of the phases present (Table D-4) is also consistent with earlier ball milled work. The microstructure is relatively homogeneous (Fig. D-5). The grain size is slightly finer than that of the dry attrition milled sample; compare Fig. D-5 (d) to D-4(c). Phases present included pyrochlore, brannerite, rutile and a few grains of whitlockite. Thoria was only observed as small spots in the centre of a few brannerite grains - the wet attrition milling has been very effective. There are some regions that are deficient in rutile (Fig. D-5(e)).

4.2.3.5 Summary of The Results on the Pre-ground, low-fired Th/U-doped Samples

The initial milling parameters for the 110 cc quick-change milling pots were not effective for dry attrition milling as a cake formed on each run at the base of the pot. The milling procedure was therefore changed to one whereby the mill was stopped every 10 mins and the powder removed and then re-milled. This combined with modifications to the pot, an increase in the milling speed and the use of additives enabled dry attrition milling to be carried out successfully. Wet milling for 45 minutes at the higher speed in the modified pot was also successful. The wet and dry attrition milled samples are similar to those produced by wet ball milling and improved dry ball milling.

4.3 Pu/U-doped Samples

The results of the SEM and XRD analysis are given in Appendix E. The density of the Pu-doped sample milled for 100 minutes was 5.33 g/cm^3. The apparent porosity was 0.4 %. This is comparable to earlier dry and wet ball milling work where the densities were ~ 5.4 g/cm^3 and 5.6 g/cm^3, respectively.

The XRD analysis indicated the presence of pyrochlore, brannerite and rutile in all the samples. There was also a trace of PuO_2 detected in the samples, but the XRD peaks were very small.

All the Pu-doped sintered samples (1350°C /4 hours/air) contained PuO_2 (Figs. E1-E4). The amount and size of the PuO_2 decreased with the milling time/number of passes through the mill (Fig. E-1). The sample milled for 10 minutes (1 pass) contains PuO_2 grains up to ~ 100 µm across. These are surrounded by a thin layer of brannerite. This sample (Figs. E-1 and E-2) also contains substantial porosity and the remnants of green-state agglomerates. The microstructure of the samples becomes more homogeneous as the milling time/number of passes increases, with the porosity decreasing as the PuO_2 and precursor element agglomerates are progressively milled to a smaller size. After 60 minutes milling (6 passes), the PuO_2 is typically less than 50 µm (Figs. E-1 and E-3) and the porosity has been substantially reduced; as has the size of the remnants of the green-state agglomerates. After 100 minutes dry attrition milling (10 passes) residual PuO_2 is

present mainly as small regions inside brannerite grains with a few residual grains ~ 20 μm across (Figs. E-1 and E-4).

There are two types of actinide oxide present. The large "lumps" in the microstructure are "unreacted" PuO_2. The smaller PuO_2 particles inside the brannerite also contain U and a small amount of Ca, Gd and Hf (Table E-1).

The EDS analysis (Table E-1) of the final sample (100 minutes/10 passes) is comparable to previous baseline compositions. The sintering in air has increased the amount of Ca in the pyrochlore, as was observed in the Th/ U-doped samples [1]. The Pu has partitioned, as expected, into the pyrochlore and brannerite. Only a trace was found in the rutile. The PuO_2 inside the brannerite grains has significant amounts of U, and some Ca, Gd, and Hf (Table E-1).

The Pu-doped samples are similar to previous wet and dry ball milled samples [1] except that they appear to be more porous. This may in part be due to burnout of the organic milling aids added to assist the dry attrition milling. These organic milling aids were not used in the previous Pu-doped wet and dry ball milling tests.

4.4 Discussion of Attrition Milling Results

Preliminary work with Ce/Ce/Zr-baseline compositions indicated that dry attrition milling could be successfully carried out in large pots (750 – 1500 cc) with 5 mm diameter zirconia media. When the small 110 cc quick-change pots with 2 mm diameter media were used the initial results for dry attrition milling were not successful. The powder tended to form a cake on the bottom of the mill pot (this is sometimes referred to as a foot) and on the walls of the pot. The smaller diameter meant that for the same rotational speed the velocity of the attritor rotor arms at the walls of the pot was less and hence the media here were not as agitated. Milling at this velocity also resulted into the media on the base of the pot not fluidising. In addition, the smaller diameter media did not have the same impact force and did not break up the agglomerates as well. By the combination of increasing the mill speed, modifying the milling pot and using additives to aid milling we were able to successfully process actinide-doped samples in the small attrition mill. These samples were comparable with the previous wet ball milled samples [1].

Generally, the six formulations tested formed the phases expected. The exception was the nominally ~ 10 % perovskite batch, which as previously with ball milling, did not form perovskite if the sample was properly milled. No significant compositional variations were observed between the exterior and interior of the pellets tested. For the attrition milled samples, sintered at 1350°C in air, the following generalisations are true of the Th/U-doped samples, if the samples are well milled:

- The baseline ceramics, formed pyrochlore as the main phase with 15 – 25 vol. % brannerite and 3 – 7 vol. % Hf-doped rutile.

- The baseline + impurities ceramics formed mainly pyrochlore plus ~ 10 - 15 vol. % 2M zirconolite, ~ 15 – 20 vol. % brannerite, 3 – 5 vol. % Hf-doped rutile and ~ 1 - 2 vol. % of an intergranular silicate glass. The impurities lead to grain growth – probably via liquid phase sintering.

- The zirconolite-rich ceramics formed an approximately equal mixture of 2M zirconolite and pyrochlore with ~ 15 – 25 vol. % brannerite and ~ 5 – 7 vol. % Hf-doped rutile.

- The brannerite-rich samples consist of an approximately equal mixture of brannerite and pyrochlore; and ~ 5 vol. % Hf-doped rutile.
- The nominally ~ 10 % perovskite samples had no perovskite and the additional Ca formed pyrochlore with Ca occupation in the Ca site content close to one formula unit. The additional phases formed were 15 - 20 vol. % brannerite and ~ 5 vol. % Hf-doped rutile.
- The phosphate doped samples typically consisted mainly of pyrochlore with ~ 20 vol. % brannerite, ~ 5 vol. % whitlockite and ~ 5 vol. % Hf-doped rutile. The whitlockite (nominally, $Ca_3(PO_4)_2$) contains Gd, Hf, U, Th and Ti.

The U and Th partition as expected – mainly into the pyrochlore, brannerite and zirconolite, with some in the whitlockite and rutile. The Pu in the baseline composition tested partitions into the pyrochlore and brannerite. The amounts of Pu, U and Th in the minor phases, rutile and whitlockite are small and the neutron absorbers Hf and Gd can be found in significant amounts in these phases. The ThO_2 appears to be harder to break up and react than the UO_2. This may be due to the calcined Th-nitrate forming denser harder agglomerates and/or the fact that ThO_2 is less reactive than UO_2. For instance, Th does not form a pyrochlore, such as $CaThTi_2O_7$, on its own.

Incomplete milling leads to heterogeneous microstructures. The main effect is that unreacted actinide oxides remain in the microstructure. These are usually surrounded by brannerite. The results indicate that high-fired PuO_2, ThO_2 and UO_2 particles need to be below a critical size. Our current perception is that the critical size for specimens sintered at 1350°C for 4 hours is approximately 5 μm in diameter. The critical size is difficult to estimate as it is equal to the starting diameter of actinide oxides just visible within brannerite regions.

Incomplete milling also alters the phase due to the actinide being tied up in the oxide, e.g., the pyrochlore has less actinide. In some cases the phase ratios will change, e.g., more brannerite may form. The formation of additional phases can also occur, but these tend to be well characterised phases such as zirconolite, for example, due to insufficient actinide availability leading to an “local” excess of Hf in the microstructure. Also observed were some grains of hafnia in poorly milled samples.

5 CONCLUSIONS

Wet and dry attrition milling of Ce/Ce/Zr-baseline ceramics was carried out successfully at 750 cc and 1500 cc pot sizes. For the smaller size of 110 cc needed for Pu-doped trials. Dry attrition milling could also be successfully carried out by a combination of an increased mill speed, additives, modifying the milling pot, and by carrying out the milling as a pass-through operation where the powder that settles on the base of the milling pot is removed and passed through the top of the mill again.

The results in this attrition milling work are comparable to the ball milling work. All the compositions tested formed the phases expected. Incomplete milling led to porosity and "lumps" of actinide oxide in the sample. The ThO_2 appears to be harder to break up and react than the PuO_2 or UO_2.

The attrition milling results show that dry attrition milling is a feasible process. Many of the problems encountered were in part due to the need to scale down the attrition milling to handle the radioactive batches, particularly the Pu-doped batches. Dry attrition milling of large non-radioactive batches worked well.

6 ACKNOWLEDGMENTS

Thanks to Dr P A Walls for supplying information on large attrition milling; done as part of Task 3 of this project. Thanks also to Mr. S. Leung for his help with the image analysis and SEM work, Mr G. Thorogood for his advice on XRD and Ms. M.L. Carter for helping out with some of the laboratory work. A special thanks to Mr A. Brownscombe, Dr B.D. Begg and Mr B.O. Hudson for their help in fabricating the Pu-doped samples in a short time frame. Thanks also to T. Hughes and S. Brodala for their general help in the daily operation of the laboratories.