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New generation nuclear fuel structures: Dense particles in selectively soluble matrix

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ABSTRACT

We have developed a technology for dispersing sub-millimeter sized fuel particles within a bulk matrix that can be selectively dissolved. This may enable the generation of advanced nuclear fuels with easy separation of actinides and fission products. The large kinetic energy of the fission products results in most of them escaping from the sub-millimeter sized fuel particles and depositing in the matrix during burning of the fuel in the reactor. After the fuel is used and allowed to cool for a period of time, the matrix can be dissolved and the fission products removed for disposal while the fuel particles are collected by filtration for recycle. The success of such an approach would meet a major goal of the GNEP program to provide advanced recycle technology for nuclear energy production. The benefits of such an approach include (1) greatly reduced cost of the actinide/fission product separation process, (2) ease of recycle of the fuel particles, and (3) a radiation barrier to prevent theft or diversion of the recycled fuel particles during the time they are re-fabricated into new fuel. In this study we describe a method to make surrogate nuclear fuels of micrometer scale W (shell)/Mo (core) or HfO_2 particles embedded in an MgO matrix that allows easy separation of the fission products and their embedded particles. In brief, the method consists of physically mixing W–Mo or hafnia particles with an MgO precursor. Heating the mixture, in air or argon, without agitation, to a temperature is required for complete decomposition of the precursor. The resulting material was examined using chemical analysis, scanning electron microscopy, X-ray diffraction and micro X-ray computed tomography and found to consist of evenly dispersed particles in an MgO + matrix. We believe this methodology can be extended to actinides and other matrix materials.

1. Introduction

The ultimate disposition of spent nuclear fuel (SNF) remains a major technical problem for the nuclear industry worldwide. It must be solved before nuclear energy will be a more broadly accepted energy technology. The US Global Nuclear Energy Partnership (GNEP) was founded to support the expansion of civilian nuclear power production worldwide. One major goal of this program is to develop and deploy advanced recycle technology that efficiently partitions SNF to recover the energy value of the actinides and prepares the fission products (FPs) for disposal. Currently there is no fuel that permits ready separation of fission products and radioactive actinides in SNF.

Here we report on a preparation method for a surrogate fuel that is designed to allow the fission products and actinides to be readily separated after the fuel is used for energy production. Sub-millimeter sized particles of the surrogate fuel material are dispersed in an inert matrix that makes up the bulk of the solid. During irradiation, the bulk of the fission products will escape from the fuel particles and come to rest in the matrix material. The chosen matrix material dissolves readily in solutions where the fuel particles will not dissolve. In this way, a large fraction of the fission products can be readily separated from fuel particles to be recycled while the solution containing the fission products is processed for disposal.

Specifically, we developed a highly scalable, rapid and inexpensive means to create a matrix consisting of MgO containing well-dispersed sub-millimeter sized particles of W (shell)/Mo (core) or HfO_2. Both materials are surrogates for UO_2 or PuO_2 nuclear fuels. The process is simple: create a physical mixture of surrogate particles and a salt that decomposes to MgO. Heat the mix in air or an inert gas until the salt is fully decomposed. The product is a evenly dispersed heavy metal or metal oxide (fuel surrogate) in a matrix of MgO. MgO has been extensively investigated as a matrix material for dispersion fuels where the dispersed fuel particles are large (>100 μm) and retain nearly all the fission products within their own structure.

The technology introduced here enables the 'selective dissolution' design concept. A properly executed design will leave the bulk of the fission products in the ceramic matrix readily separable from the actinide fuel particles by selective dissolution of the matrix.

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The actinide fuel particles are readily recycled for further energy production (with the addition of new fuel material to make up for the actinides fissioned in the reactor). The actinide particles for recycle still retain a small fraction of the FPs and must be handled remotely, but this also provides a substantial radiation barrier to diversion or theft of this material while it is re-fabricated into new fuel and returned to the reactor for further energy production. The small fraction of the fission products that deposit in the fuel particles is not enough to be a significant poison in the re-fabricated fuel, but is enough to make diversion and theft of this material very difficult.

There are issues that must still be resolved. A short list includes these questions; (i) can the fuel be created in the complex shapes that may be required for advanced fuels? (ii) Can evolving gases be readily removed? (iii) Ultimately, MgO may not be the preferred matrix material therefore, is the process flexible enough to be successfully used with other ceramics? Finally, (iv) is it necessary to control the void density? None of these questions is completely answered in this initial work, but some encouraging results are included. Notably, (i) the ceramic compact does conform to the container in which it was formed and (ii) void size and density was found to be a function of easily controllable parameters. Selection of the correct void density, for example enough to insure percolation, might be used to insure gas diffusion. Alternatively, molds structured to encourage gas transport might be considered. Finally, we do not believe that the MgO chemistry is unique. It is likely the 'shake and bake' approach can be broadly applied.

2. Experimental

Production-Physical mixtures of both W (shell)/Mo (core) or HfO_2 and magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) salt were prepared. Approximately 200 mg of one of the mixtures was then placed in the vessel shown in Fig. 1.

Notably, the atmosphere in the vessel can be controlled, and the temperature read with a thermocouple embedded in the powder. Various maximum temperatures were tried. Indeed, as the salt purportedly decomposes at 130 °C the initial efforts were made at 150 °C. However, experience indicated, confirmed by thermal gravimetric analysis (TGA), that full decomposition required, at a minimum, that the material be heated to 425 °C for 1 h. Hence,

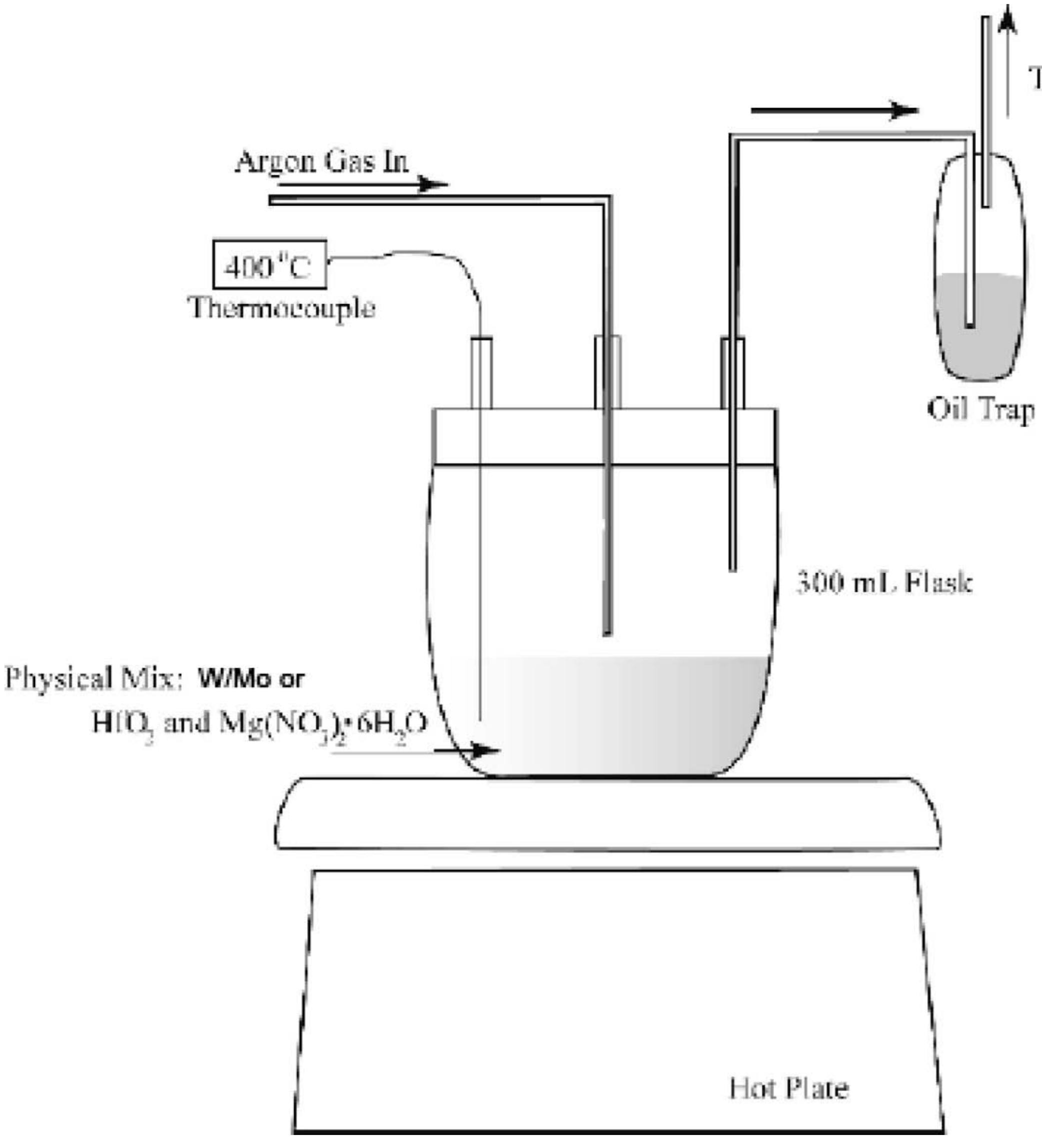

Fig. 1. *Simple batch apparatus*: Sample salts mix (HfO_2 and magnesium nitrate hexahydrate) is placed in flask. No stirring. Thermocouple placed near center of salt mix. Heat to 400 °C, or higher, in low flow rate of argon, and hold for 2 h in flowing Ar or dry air. Cool and remove.

in most cases discussed below, the precursor was heated for at least 1 h at 425 °C. (In a couple of cases, the sample was heated to 500 °C). The heating protocol for the samples analyzed below is as follows: The samples were heated under air from room temperature to about 300 °C at a rate of 10 °C per minute. Frothing was readily apparent. Once the temperature reached 300 °C the frothing ceased and the samples appeared solid. The heating rate was changed to approximately 4 °C per minute. At about 350 °C a brown/yellow gas, presumably NO_2, was observed in the flask above the sample. Once the temperature reached 425 °C, the reaction was deemed complete and the sample removed from the hot plate and allowed to cool. Argon and oxygen were both tried as the flowing gas, and the results indistinguishable.

After cooling in flowing gas, the samples were readily removed from the beaker, completely intact, by simply prying around the borders between sample and container with a small (ca. 1 cm across) flat topped scrapper. The samples (Fig. 2) were hard brittle material, hence cut in half using a hand held jigsaw with a diamond tipped blade. No crumbling was observed as a clean cut was produced.

Analytical-X-ray diffraction (XRD) data was collected using a Bruker D8 Advance diffractometer using Cu Kα radiation and operating at 40 kV and 40 mA. Data was collected from 10° to 70° 2θ in using a step size of 0.02° and a count time of 5 s/step in detector scan mode with the X-ray source fixed at 8°. A Hitachi scanning electron microscope (SEM) was used to image the samples. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed simultaneously using a Netzche Model STA 449 C instrument. Digital X-ray radiographs and computed tomography data sets were collected using an Xradia (Concord, CA) micro X-ray computed tomography instrument. The source for this instrument is a Hamamatsu microfocus tungsten source. Images were collected using Olympus microscope objectives with scintillators mounted on front and projected onto a four mega pixel CCD camera. The samples were either mounted using a vacuum tip, or by setting on a stage. Finally, chemical analysis was performed at a commercial laboratory, Galbraith Laboratories (Knoxville, TN).

3. Results

3.1. Decomposition

Two visual observations, suggesting chemical processes, occurred at specific temperatures during heating. First, the material was seen to become plastic in appearance at ~100 °C, forming a froth (that is, frothing began when the sample reached, or nearly reached the nominal decomposition temperature of ~90 °C). Bubbles on the order ~1 cm across were observed forming and popping. This frothing action, without the need for mechanical agitation, appears to be sufficient to keep the sample well mixed. This frothing action presumably accounts for the homogeneous dispersion of the surrogate (hafnia or W/Mo) in the final cooled material. It also suggests an origin of the void spaces found in the sample (Fig. 2). Secondly, at ~400 °C, a brown/orange gas was seen to evolve from all mixtures very quickly.

Analysis using TGA/DSC of a small amount of sample (ca. 50 mg) suggested that the frothing occurred due to gas evolution from the material. As shown in Fig. 3, there is steady weight loss observed about 100 °C to about 300 °C. At this point weight loss slows, and a plateau in weight is observed from about 300 °C to almost 400 °C. From about 400 to 500 °C a sharp, rapid weight loss is observed. The sample weight then stabilizes.

Also marked on Fig. 3 are specific fractional mass loss values, corresponding to particular stoichiometries. The correspondence between these stoichiometries and plateaus in the DSC curve suggest a detailed model of the decomposition. Indeed, it appears that the initial weight loss (from 100 to 300 °C) results from the loss of water. That is, the fractional weight loss observed at the plateau (~55% from 300 to 400 °C) corresponds to full dehydration. The second, and sharper, weight loss (starting at 400 °C) leads to a final weight consistent with the formation of MgO. That suggests NO groups are 'released' from the material once the temperature reaches approximately 400 °C. This interpretation is supported by the observation of an orange/brown gas at elevated temperature (NO_2), and XRD results (below) that show MgO becomes the dominant Mg phase only after the sample has been heated above 400 °C.

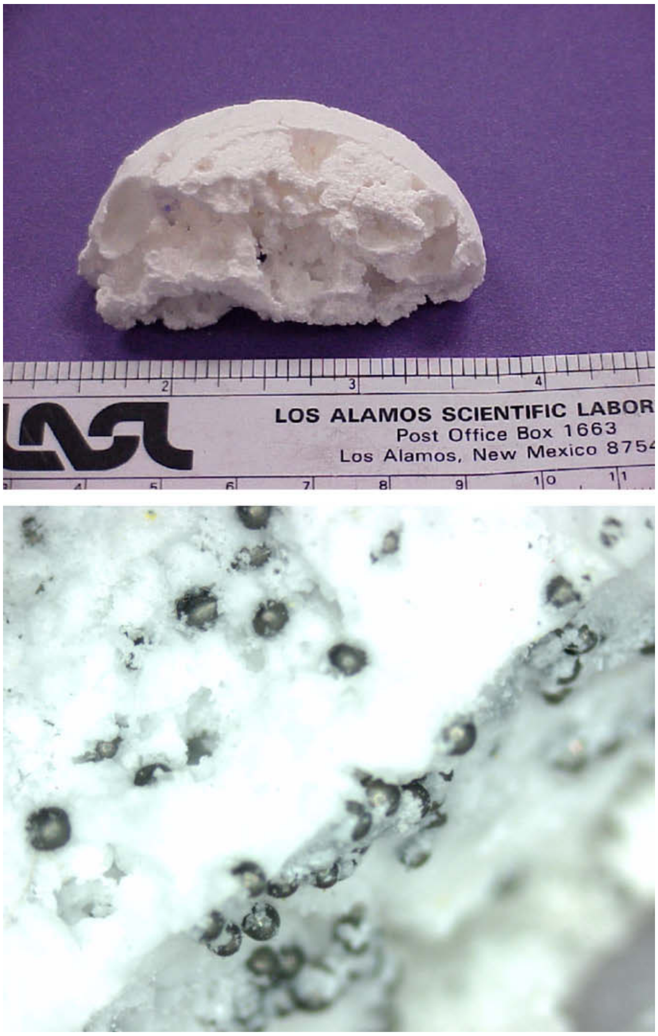

Fig. 2. *Ceramic sample*: TOP – Cutting the surrogate (HfO in MgO) fuel sample (approximately 5.5 cm across, bottom scale) in half reveals large void spaces (ca. 1 cm diameter). Roughly half the volume of the sample appears to be void space. BOTTOM – W/Mn particles (blacks spheres) in MgO matrix. Random distribution apparent in this picture of a random cut through the sample showing particles distributed in two planes nearly at right angles. (Note: particles nominally 500 μm in diameter).

3.2. Post-production analysis

All techniques are consistent with the postulate that the solid 'ceramic' material produced by the heating process consists of MgO with a uniform distribution of surrogate particles.

XRD analysis shows that the only phases present after heating to 425 °C for 2 h in the case of the hafnia surrogate material are

MgO and HfO_2 (Fig. 4). In the case of the W/Mo surrogates only W, Mo and MgO peaks were observed. The relative peak intensities were independent of the position in the sample from which the XRD samples were harvested. Samples taken from the top, middle, and bottom of the samples yielded nearly identical XRD spectra. XRD also indicates that if the decomposition temperature never reaches 400 °C, and/or it is not allowed to soak for an hour or two at 400 °C or higher, that the Mg-nitrate does not fully decompose. In the XRD results, it is suggested that in samples not fully decomposed there are several phases present simultaneously: the nitrate, some apparently 'dehydrated phase' and MgO (not shown).

The digital X-ray radiographic images indicate that the higher atomic number material (hafnia) is uniformly dispersed when heated to higher temperatures. Digital radiographs indicate clearly that a sample decomposed at only 100 °C (Fig. 5a) does not have a homogeneous dispersion of hafnia. The sample is mounted upside down in the radiography instrument. The hafnia particles in this case clearly collected at the bottom of the sample. This suggests that in the absence of sufficient 'frothing' action, the denser particles settle due to gravity. A detailed study of the digital X-ray radiographic images at various resolutions of two samples decomposed at 425 °C (Fig. 5b and c) clearly showed hafnia to be uniformly dispersed. It is interesting to note that visual inspection

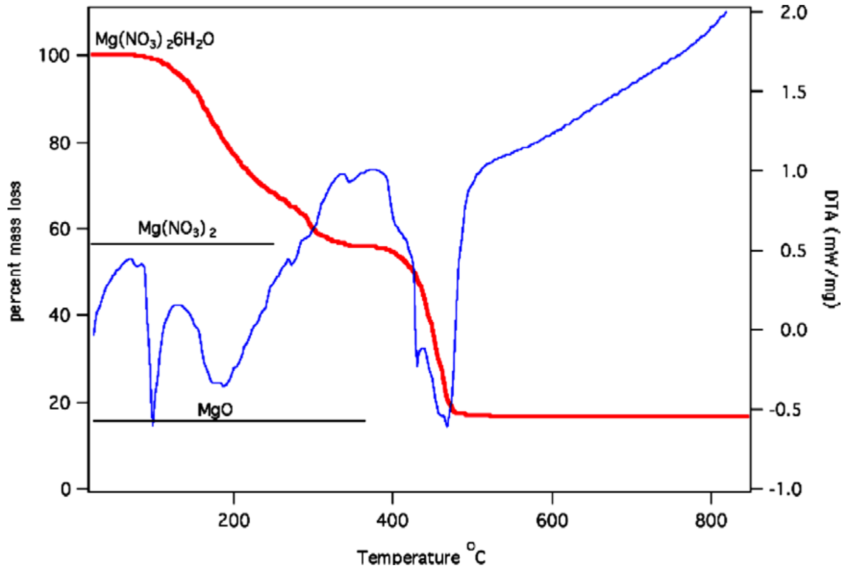

Fig. 3. *TGA/DSC*: The weight loss curve (starting upper left, red) is consistent with a two stage decomposition: first all water is lost, then all NO groups, leaving MgO. The DSC curve (starting lower left, blue) is consistent showing endotherms roughly corresponding to water and NO loss. Note: heating rate 10 °C/min, gas (N_2) flow rate 50 sccm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

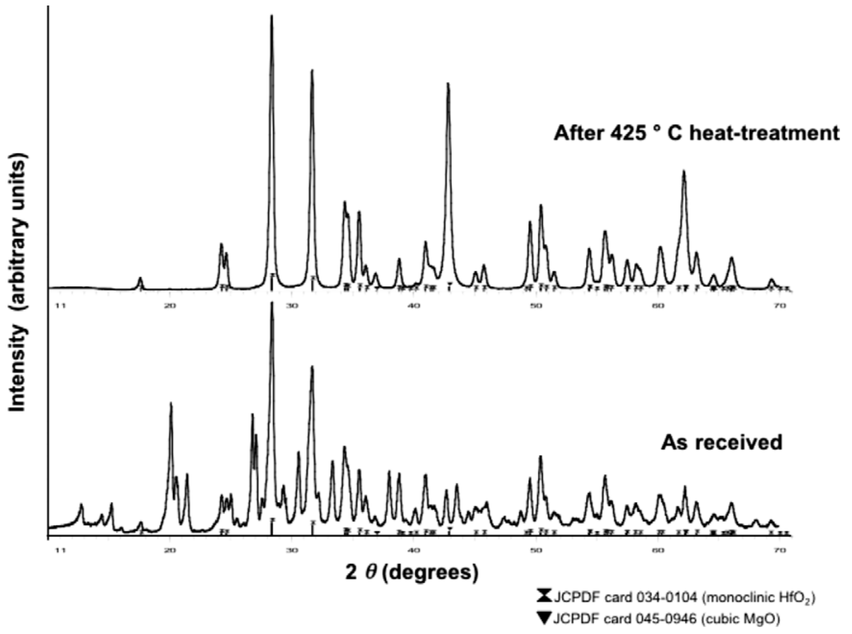

Fig. 4. *XRD:* Initially (lower panel) the peaks correspond to HfO_2 with a nearly standard powder intensity (JPPDF index) and magnesium nitrate hexahydrate, all unmarked (for clarity) peaks. After full decomposition at 425 °C (upper panel), the HfO_2 peaks are still present, all the magnesium nitrate hexahydrate peaks are gone, and MgO in nearly the standard isotropic peak ratios, is now the only Mg containing phase present.

does not indicate that the hafnia segregates. Indeed, visually, the high temperature ($T > 400$ °C) and low temperature ($T \sim 100$ °C) samples are identical.

Full reconstruction of the micro X-ray radiographs into a computed tomography data set of the W/Mn sample revealed that these larger (~500 μm diameter) and denser (~13 g/cm^3) particles were also well dispersed (Fig. 6), in agreement with visual inspection. This suggests that even very high-density actinides can be readily dispersed using this approach.

One interesting finding was the influence of the highest temperature on pore size distribution. Stopping the process at approximately 425 °C produced a sample with pores as large as 2 cm across (Fig. 1), whereas, as determined using confocal microscopy of several X-sections, the largest pores in samples produced at 500 °C were about two orders of magnitude smaller, the largest being of the order of 100 μm across. Also, the overall density of pellets produced at 500 °C is clearly far higher than those generated at 425 °C.

Chemical analysis was also used to explore dispersion. The most meaningful result from this technique was the finding that the Mg/Hf ratio was constant throughout samples generated at $T > 400$ °C. As noted earlier, two samples (six total) for chemical analysis were taken from the top, middle and bottom of the sample. The Mg/Hf ratio was measured to be virtually identical at each location.

Finally, it is interesting to reflect on potential caveats regarding the use of actinides dispersed in MgO as a nuclear fuel. The first question regards reprocessing. Can MgO be readily and selectively dissolved? Thermodynamically the answer is quite clear. In all acid solutions, and even in a weakly basic aqueous solution, thermodynamic calculations and experimental results confirm MgO is 100% soluble near room temperature [1]. In contrast, actinides are only soluble in strong acids. For example, uranium is virtually insoluble, and plutonium nearly so, for pH > 5, although UO_3 and PuO_2 are the stable phases in aqueous media. Moreover, studies of the kinetics of MgO dissolution show that the rates are reasonably high even for weak acid solutions [2–4]. Hence, the conclusion is selective dissolution of MgO to leave actinide (possibly partially oxidized) is practical.

A second issue is safety. Is it safe to operate a reactor in which the matrix material can be dissolved by accidental exposure to water? Clearly, this will be a function of the reactor design. This means, as with all nuclear reactors, engineering controls to prevent a criticality situation in an accident must be designed. Prevention of criticality will also be an issue in the engineering of the reprocessing protocol. One possible safety step: Make certain aqueous fluid in reactor system with a pH > 8.

In order for fuels of any new design to be considered viable positive answers to questions regarding (i) heat transfer, (ii) radiation stability, (iii) fission product thermodynamics in the composites, and (iv) kinetics of migration within the matrix must be documented. MgO matrices, perhaps with enhancements, appear to meet at least minimal requirements, although clearly additional work is needed.

Regarding the first point: MgO is known to have high thermal conductivity. In fact, because of this unique property of MgO, it was suggested that a mixed form of MgO and pyrochlore could be developed as an inert matrix fuel with high thermal conductivity [5,6]. Recent investigations also suggest that MgO based matrices have good thermal and radiation stability. The thermal stability and radiation stability of an HfO_2/MgO/HfO_2 tri-layer have been recently investigated by Usov et al. [7]. It was shown in Ref. [7] that the tri-layers are stable in terms of: (i) resistance to amorphization; (ii) resistance to compositional mixing and (iii) resistance to pronounced nucleation and growth of extended defects. We expect similar behaviors in the composite phases presented here.

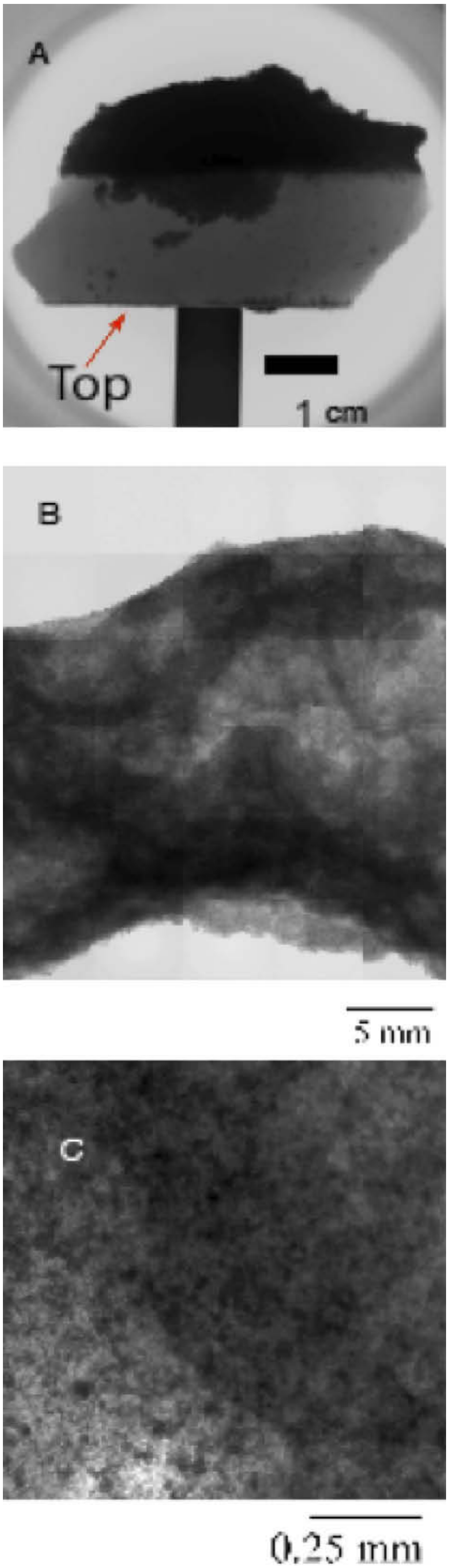

Fig. 5. *Digital X-ray radiographic test of HfO in MgO homogeneity*: (A) Digital radiography reveals what visual inspection of a HfO/MgO sample does not. A low temperature decomposition process (100 °C) left the HfO_2 particles (dark area) segregated at the bottom. (B) Digital radiography reveals no evidence of large scale segregation of HfO_2 particles in samples created by decomposition at $T > 400$ °C. Variations in apparent density are not top-bottom. These apparent density variations reflect the distribution of void volume. (C) Close up inspection of any part of the samples produced at $T > 400$ °C reveals well dispersed HfO_2 in MgO.

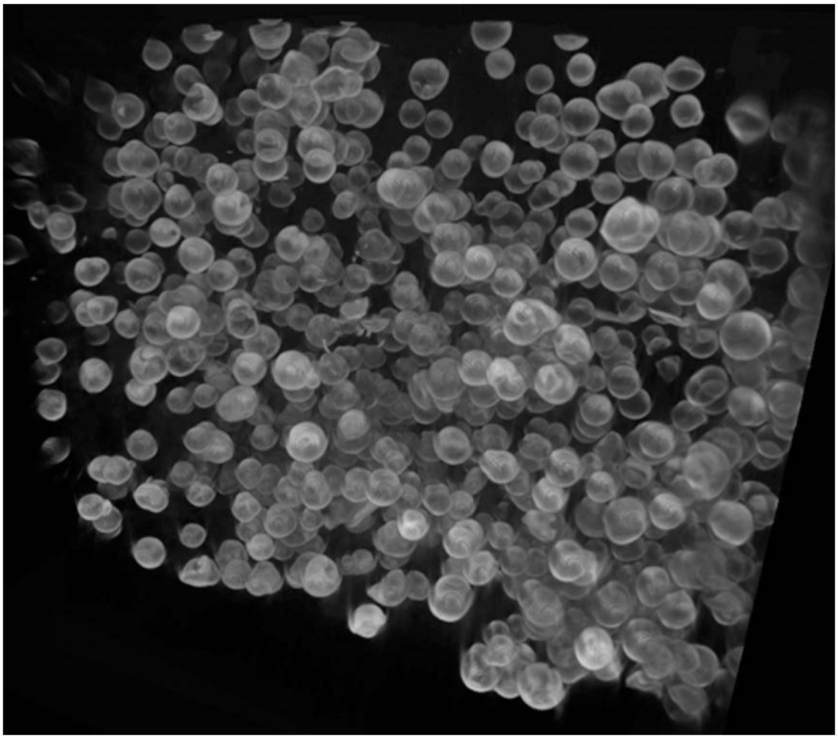

Fig. 6. 3-D micro X-ray computed tomographic image of W/Mn in MgO reveals that the W/Mn particles (~500 μm diameter) are well dispersed in the MgO (not visible) matrix. Field of view is approximately 1 cm.

In terms of thermodynamic stability, the viability of MgO is not clear. Strictly from consideration of relative thermodynamic stability, many FPs would prefer to reside in the actinide phase, not in the MgO phase. However, consideration of kinetic and metastable structures appear to mitigate against the driving forces of thermodynamics. Computations suggest some of the fission products may form complexes that will precipitate in MgO. For example, our DFT calculations indicate that for Cs in MgO, oxide precipitate Cs_2O can form at high burn-up conditions [8]. The DFT results show that the precipitation tendency is greatly reduced in oxides with larger cation sizes. Computations also suggest that the interface between the actinide and matrix could act as a metastable getter, preventing diffusion of FPs back into the actinide phase. At the fuel/inert matrix interface, density functional theory (DFT) based first-principles calculations [8,9] indicate that fission products with large atomic sizes such as Xe and Cs are strongly bound at actinide MgO interfaces. For fission product with relatively smaller atomic size, such as Sr, the interfacial segregation is weaker. Moreover, from previous experimental studies [7], it does not appear that a new phase of compound will form at the fuel/inert matrix interface.

There may be FPs for which neither precipitation nor surface gettering is effective. In such cases, the separation method presented here will require modification (e.g. removal of the surface of the actinides particles, post matrix dissolution, by physical or mechanical processing) to effect a clean separation. It may also be that the participates within the MgO matrix do not readily dissolve and required another form of separation. Significant experimental work is required to address these issues.

Other issues have not yet been addressed in the literature in any significant fashion. For example, it is not clear that void spaces are altogether a negative. If sufficient void space is available (>27%) there should be a percolation path available for most gas to escape. It may also be that void/MgO interfaces are also good gettering locations for FPs. The impact of voids on thermal conductivity is probably no worse than a factor of two, according to standard percolation theory [10]. The effect of void space on initial actinide loading may also be significant. Indeed, even assuming a trimodal distribution of actinide particles without any matrix particle loading is limited to about 90%. With matrix and 'percolation limit' void concentration, an upper limit target of 50% by volume fuel is reasonable.

4. Summary

A simple method for creating a surrogate to a nuclear fuel with all the basic requirements for safe separation of FP and actinides was developed. Specifically, hafnia particles or W (shell)/Mo (core) and magnesium nitrate hexahydrate were physically mixed and heated in a simple beaker, without agitation during heating, to 425 °C. Analysis with micro X-ray radiography and tomography, and X-ray diffraction clearly showed this produced a solid 'ceramic' of MgO in which micrometer and sub-millimeter scale surrogate fuel particles were homogeneously dispersed. Visual inspection shows it is highly porous, with many void spaces approximately a centimeter across. Other techniques, particularly TGA/DSC suggest that the mechanism of dispersion was the creation of an internal agitation of the mixture due to the generation of water and NO during the nitrate decomposition. Separation of the MgO and 'fuel' particles can readily be achieved as the former, and not the latter, is soluble in weak acid. Several questions about the process must be addressed in future work to really assess the value of this technology for advanced fuel technology. Can complex shapes be readily created? What is the best pore structure, and can it be achieved? Can the technology be 'generalized', that is can matrices other than MgO be produced?

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