



Characterization of minor actinide mixed oxide fuel

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A B S T R A C T

The global nuclear energy partnership (GNEP) was created in order for ‘fuel-cycle supplier’ nations to provide assured supplies of nuclear fuel to ‘fuel-cycle customer’ nations. The customer nations would utilize the fuel for electricity generation and subsequently return it to the supplier nation after it is spent. This spent fuel would then be reprocessed by the supplier nation in order to recycle the actinide constituents, mainly uranium and plutonium, in advanced nuclear power reactors, and thus reduce waste volumes [1,2]. The International Atomic Energy Agency would control the nuclear materials. One of the thrust areas for the GNEP program is the development of these actinide bearing fuels for transmutation in a fast reactor.

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1. Introduction

In this day and age of high gas prices and global warming worries, research in alternative sources of energy such as nuclear power is seeing a boom, despite its lack of popularity [3]. Nuclear power is produced using an open fuel cycle, i.e. by burning enriched uranium fuel until it is spent, and then discarding it as waste, all around the world. This spent fuel still contains energy-rich fissionable material. The desire to reduce waste volumes in the US and increase the energy available out of the fuel has led to research on mixed oxide (MOX) fuels, particularly minor actinide MOX (MA-MOX) research.

Current studies involve characterization of precursor powder morphology effects in the areas of flowability and porosity in order to predict manufacturability. Pre-production pellets were characterized in order to determine impurity levels and locations prior to final production of pellets to be inserted into the ATR [4–6]. The fuel composition evaluated in this study were proposed by Hilton et al. [7] because little is known about irradiation performance of oxide fuels with high concentrations of Pu, Np and Am as actinide transmutation fuels. Some experiments with Np and Am have been performed in France and Japan, but these would be some of the first in the US [8,9]. The three compositions to be studied are: one MOX composition, $(U_{0.80}Pu_{0.20})O_{1.98}$ and two MA-MOX compositions with oxygen to metal ratios (O/M) of $(U_{0.75}Pu_{0.20}Am_{0.03}Np_{0.02})O_{1.98}$ and $(U_{0.75}Pu_{0.20}Am_{0.03}Np_{0.02})O_{1.95}$. This paper covers characterization of the precursor powders and investigation of pre-production pellets.

2. Experimental methods

2.1. Pellet fabrication

Pellet precursor actinide oxide powders were mixed and milled in order to blend the feed and recycled dry scrap powder oxide. The mixing and milling process was an intense operation designed to increase physical contact between the oxide particles, slightly reduce oxide particle size, and activate particle surfaces. Following the blend mixing/milling step, polyethylene glycol and synthetic motor oil were mixed the oxide feed powder as powder binder and die lubricant. This powder blend was then compressed into a right circular cylinder shape (pellets) by applying a uniform pressure of 150 MPa (die diameter of 0.6 cm) in order to reach a predetermined green density and size. Prior to sintering the pellets, a binder burnout cycle was performed during which the additives were evolved from the pellets. The fragile nature of the pellets prior to binder burnout necessitated careful handling of the pellets as well as quick turnaround between pellet pressing and binder burnout. The burnout cycle was conducted at ~ 450 °C for approximately 1 h.

The primary purposes of the sintering process were to increase the density of the oxide pellets to a target density of above 92%, fix the O/M ratio, and fuse and grow grains. For these pre-production pellets the density was increased from a green density of 57 wt% to 89 wt% for the MOX pellets (theoretical density of 11.05 g/cc) and 88 wt% for the MA-MOX pellets (theoretical density of 11.08 g/cc). After binder burnout the pellets were sintered via a rapid heat up cycle to 1750 °C for 4 h in an inert atmosphere of argon and humidified Ar-6% H_2 . Pellets were then selected out of each batch for metallography and microanalysis. Since these were pre-production pellets it was decided to perform metallography and microanalysis

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prior to O/M ratio adjustment due to time sensitivity. The remaining pellets underwent a stoichiometric adjustment at about 1500 °C in order to reduce the O/M ratio to that of the three desired compositions: one MOX composition of $(U_{0.80}Pu_{0.20})O_{1.98}$ and two

MA-MOX compositions of $(U_{0.75}Pu_{0.20}Am_{0.03}Np_{0.02})O_{1.98}$ and $(U_{0.75}Pu_{0.20}Am_{0.03}Np_{0.02})O_{1.95}$. The pellets characterized in this paper were pre-production MOX and MA-MOX pellets and were analyzed in order to optimize pellet processing techniques.

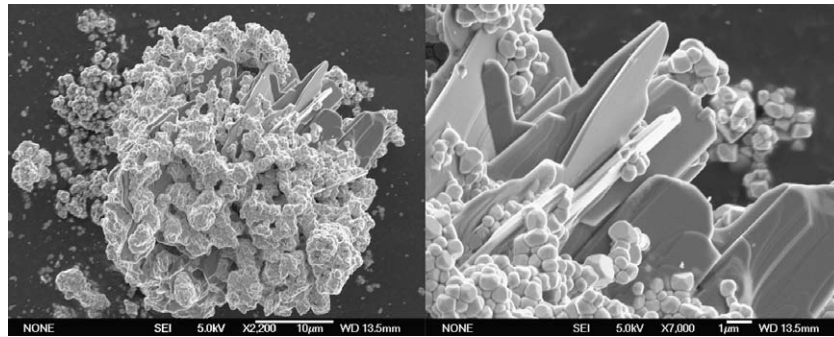


Fig. 1. Representative NpO_2 precursor powder particle morphology (secondary electron images (SEI), FEG-SEM).

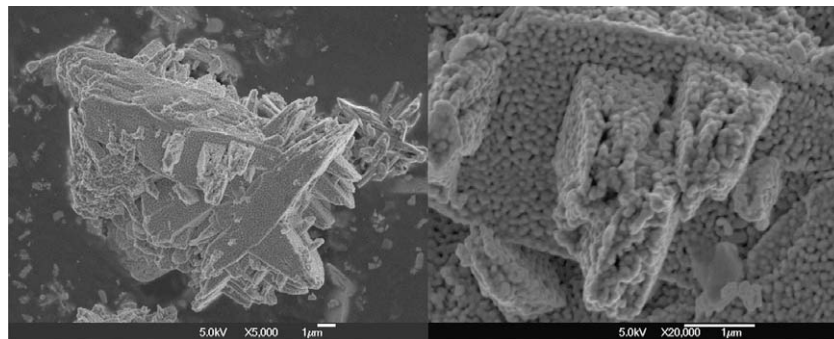


Fig. 2. Representative AmO_2 precursor powder particle morphology (SEI, FEG-SEM).

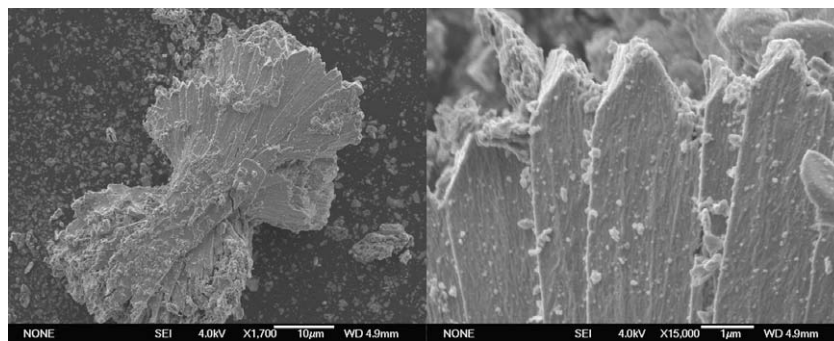


Fig. 3. Representative PuO_2 precursor powder particle morphology (SEI, FEG-SEM).

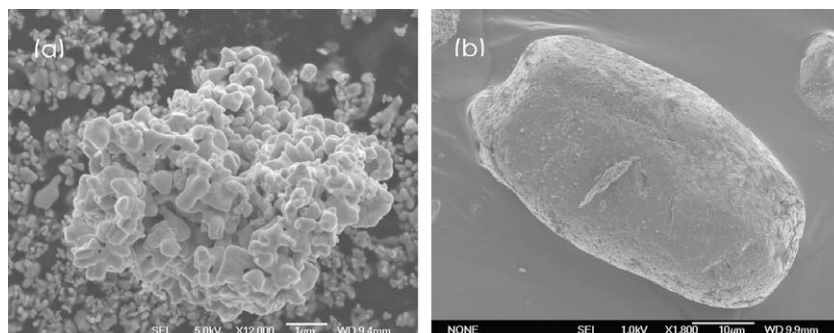


Fig. 4. (a) Representative DUO_2 precursor powder particle morphology, (b) Representative $HEUO_2$ precursor powder particle morphology (secondary electron images, FEG-SEM).

2.2. Pellet metallography and microanalysis

The pellets were mounted in Epon Resin 815 C thermosetting epoxy mixed with diethylenetriamine as the catalyst/hardener. The 3.175 cm mounts were rough ground in a Buehler Beta Vector automatic grinder/polisher using sequential SiC grits of 320, 400, 600 and finally 15 μm (600 soft). The first stage of polishing was done on a Buehler Beta Vector with a trident cloth charged with 6 μm diamond paste. The polishing was completed in 8–10 min using 375–700 g of force and a speed of approximately 100 RPM. Final polishing was accomplished with a Buehler Vibromet 2 vibra-

tory polisher with 1 μm diamond paste on a Metcloth media for approximately 2 h. Metallographic analysis and imaging was performed using a Leica DMIRM microscope with SPOT diagnostics camera and software.

The metallographic mounts were carbon coated in an EMITECH K950 evaporator for electron probe microanalysis (EPMA) with a JEOL 8200. Background corrected element distribution maps were collected for plutonium (Pu), uranium (U), tungsten (W), calcium (Ca), oxygen (O), and carbon (C). The distribution maps were set up to characterize $1280 \times 1280 \mu$ areas with a resolution of 256×256 steps at 5 μm intervals with a 5 μm beam diameter.

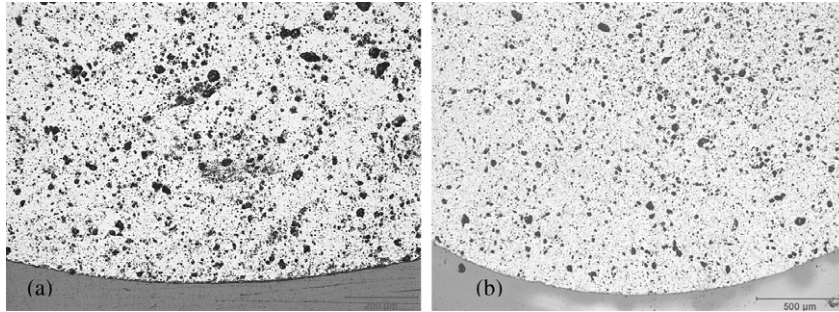


Fig. 5. Optical micrographs of (a) MOX and (b) MA-MOX pellets mounted in the radial direction (magnification of 100 \times).

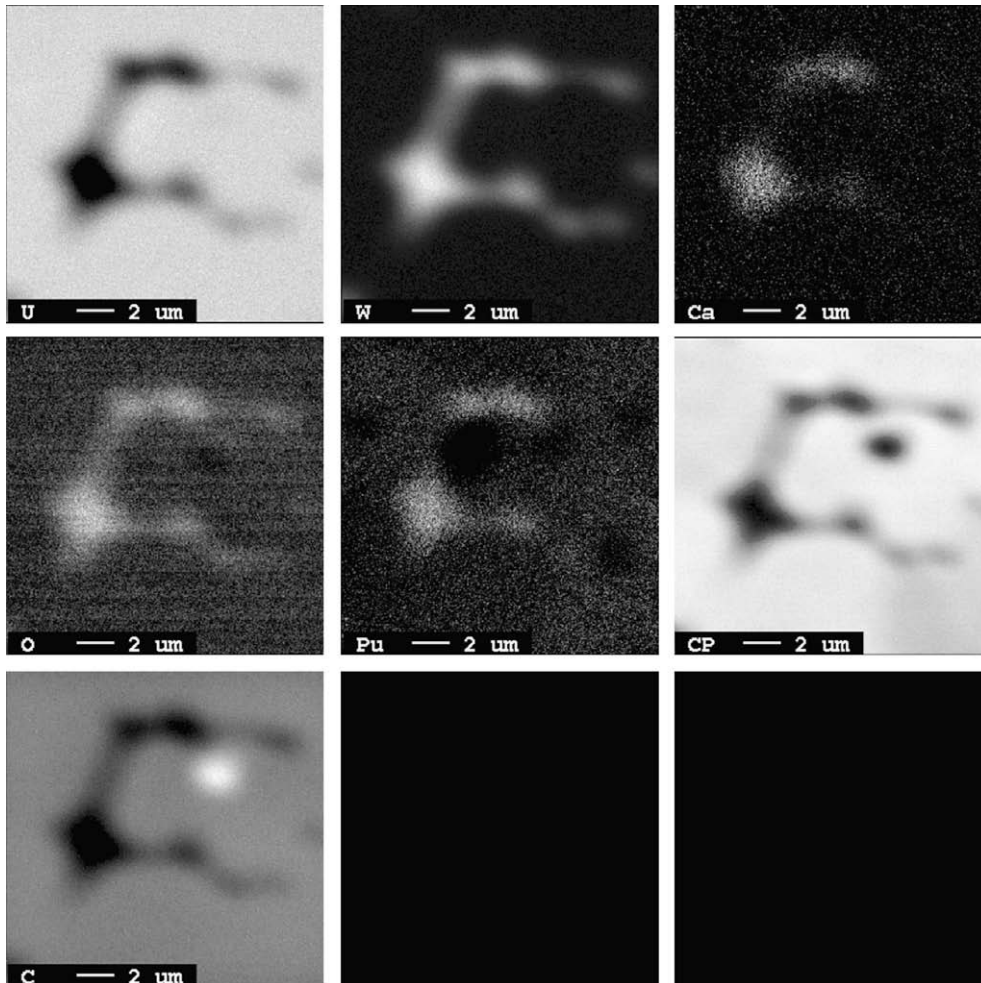


Fig. 6. Element distribution maps for U, W, Ca, O, Pu, C, and a backscatter electron image for a MOX pellet at a grain boundary region.

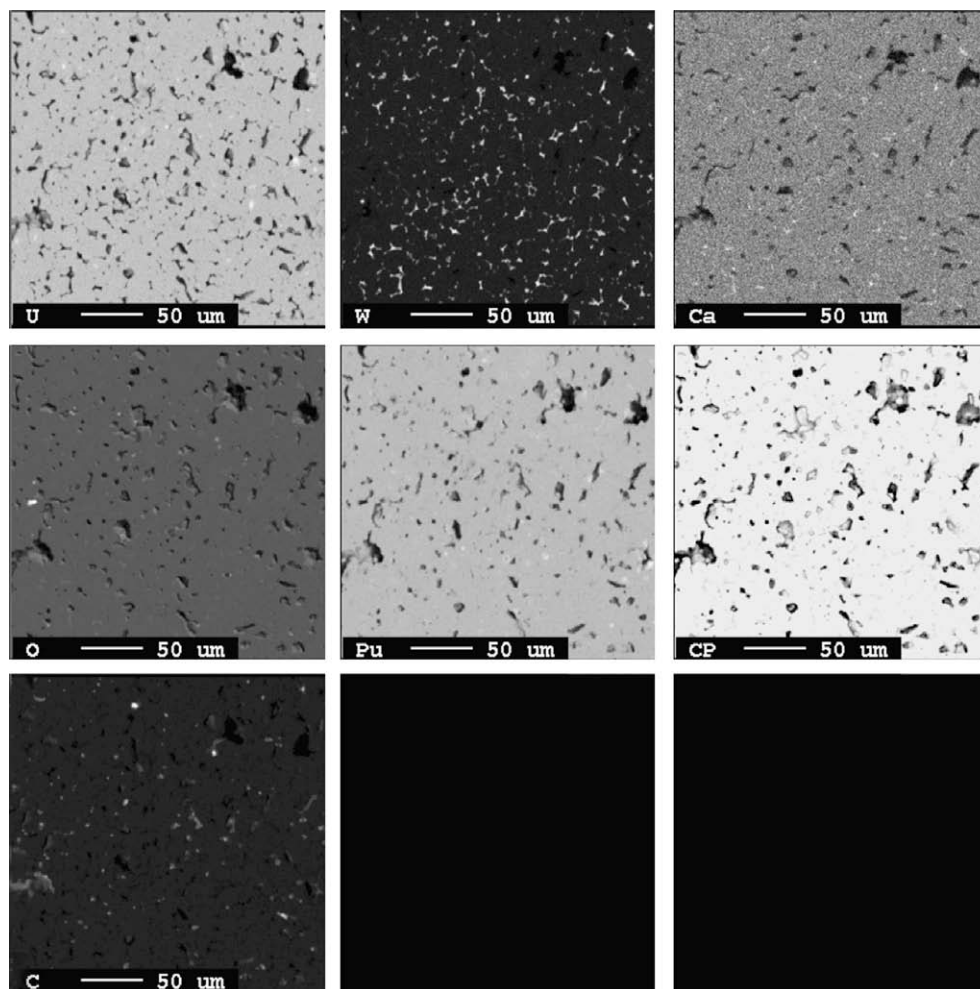


Fig. 7. Large area element distribution maps for U, W, Ca, O, Pu, C, and a backscatter electron image for a MOX pellet.

The relative quantitative precision for this analysis is 10% at an expected concentration level of 0.5 wt%.

3. Results and discussion

3.1. Powder characterization

Powder samples for DUO_2 , highly enriched uranium oxide (HEUO_2), AmO_2 , NpO_2 , and PuO_2 received from France, Sweden, and the United States were mounted on carbon tape. They were then characterized using a field emission gun scanning electron microscope (FEG-SEM) for particle morphology, particle size, and particle size distribution. Representative secondary electron images of the actinide precursor powders can be seen in Figs. 1–4. Excluding the HEUO_2 the powder morphology indicated low flowability and high grain porosity. The average particle size for each oxide was between 5 and 10 μm . The particle size distribution within each oxide ranged from 1 to 60 μm .

3.2. Pellet metallography and microanalysis

Optical micrographs of MOX and MA-MOX pellets, respectively, can be seen in Fig. 5. Overall the pellet porosity was homogeneously distributed, only minor cracking was observed. Large areas of impurities as seen by optically visible inclusions were not readily observed. The average percent porosity measured in the longitudinal direction of the MOX pellets was $15 \pm 5\%$.

Pre-production MOX pellets were characterized using an EPMA in order to determine impurity levels and location.¹ Initial wave dispersive spectroscopy analysis taken of a representative area of a pellet indicated that the impurities in the pellet consisted of W, Ca, and C. Element distribution maps of U, W, Ca, O, Pu, and C at a grain boundary in that pellet and a backscatter electron image of the same area are shown in Fig. 6. The element distribution maps of a lower magnification area in the same MOX pellet are shown in Fig. 7. The EPMA analysis revealed elevated quantities of W, which exceeded the fuel specification (the specifications are proprietary). The W was attributed to the volatilization of the W in the furnace heating elements and subsequent diffusion of W into the pellets. Improvement of the inert atmosphere in the furnace during sintering is expected to limit the diffusion of W into the pellets. Due to the furnace configuration the heating element material can not be changed. Calcium and C impurities found in minimal quantities – mainly in the grain boundaries, were attributed to the fuel processing steps, mainly during the milling operations. Further work on production MOX and MA-MOX microanalysis will be discussed in future papers [10,11].

4. Conclusions

The precursor powders consisted of very small particles with morphologies that varied from simple spheroids to complicated

¹ Pre-production MA-MOX pellets were not analyzed using WDS or EPMA.

crystals or a mixture of both. The average particle size for each oxide was between 5 and 10 μm although the particle size distribution ranged between 1 and 60 μm . Pellet metallography indicated homogeneous porosity throughout the pellets with minimal or no cracking. The average percent porosity was around $15 \pm 5\%$ for the MOX pellets.

Analysis of pre-production pellets indicated high levels of W, which was determined to have been caused by interaction between the heating elements and the atmosphere. Low levels of Ca and C were noted and attributed to the processing techniques. Production pellets will be analyzed for Ca, C, and W as well as Pu and U for the MOX pellets. For the MA-MOX pellets Am and Np will also be analyzed.

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