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Report on Characterization and Processing of MDD Powder

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SUMMARY

Uranium oxide powers most civilian nuclear reactors worldwide. A large infrastructure based on a well-established technology is in place to support this strategic component of the energy industry. Because uranium oxide fuels are used so ubiquitously, it is expected that ceramic fuel pellets will continue to be used. A better understanding of the properties of the starting materials, the processing methods used to fabricate fuel pellets and how the properties of pellets change in service, are important aspects being studied via experiments, models and simulations. A close integration of these approaches is essential if we are to find new ways to optimize both the fuel composition and structure for the purpose of improving performance, *e.g.*, designed microstructures, reducing process losses, *e.g.* by net shape sintering, and enabling reprocessing of used fuel; *e.g.*, incorporation of transuranics.

Ceramic oxide fuel pellets are typically cold pressed and sintered from a powder feedstock. Consequently, a complete understanding of pellet fabrication requires a thorough knowledge of the process from powder synthesis through quality control and acceptance. In this study, uranium oxide powder synthesized by Modified Direct Denitration (MDD) is evaluated. Use of powders synthesized by novel, simplified approaches such as MDD are both a challenge and an opportunity. The MDD synthesis process offers an opportunity to simplify the fabrication process potentially reducing process losses. MDD also provides a simple path to incorporate transuranics from used fuel reprocessing with minimal handling. The challenge is to demonstrate and ultimately prove the reliability and reproducibility of simplified processing with the performance of fuel pellets experiencing in-pile service.

This report summarizes a processing study of uranium oxide pellets made from MDD uranium oxide.

CONTENTS

ACRONYMS

EBS	Ethylene Bis Stearamide
MDD	Modified Direct Denitration
O/M	Oxygen to Metal ratio
ORNL	Oak Ridge National Laboratory
SEM	Secondary Electron Microscopy
SPEX	Manufacturer of SPEX brand high-energy mill
STA	Simultaneous Thermal Analysis
TGA	Thermogravimetric Analysis
UHP	Ultra High Purity

1. Introduction

Ceramic oxide nuclear fuel pellets are by far the most common fuel used by the nuclear energy industry in the US and abroad. The manufacturing of ceramic oxide pellets, which relies exclusively on cold pressing and sintering techniques, has been identified as an area where improvements in processing can be anticipated. Simplified processing will lead to reductions in processing losses and may lead to new methods that allow improved fuel pellet performance due to better dimensional control and minimization of defects. In this study, uranium oxide synthesized by MDD (Modified Direct Denitration) is processed.

It is well known that ceramics are path dependent meaning that the microstructure and; therefore, the properties of the ceramic depend on details of how the pellet was fabricated. In other words, one must know more than that a powder was milled prior to pressing, one must also know if the milling was by a high energy mill or a ball mill, how long it was milled, with what type and, how much media, in what size container, etc. Since numerous processing steps are necessary for pellet manufacture, each with its own set of variables, a tremendous number of possible processing paths open up creating an enormous field of research.

It is also understood that the properties of a ceramic are dependent on its chemical composition and macro and micro-scale structure. While the mechanical properties of fuel pellets are generally given less emphasis than thermochemical properties, fuel rod failure is of great concern to the nuclear energy industry. These failures can often be traced to fuel cladding interactions due to fracture of the ceramic or undesired dimensional changes of the ceramic in pile. Ceramics will fail at the location where the largest flaw exists in an imposed stress field. A defect may be a pore, impurity, crack, or even a single large grain. Therefore, control over both the composition and structure is vital to maintaining desired material properties. Increasing our scientific understanding of the fabrication process allows us to better control the structure of the pellet with regards to grain size, grain boundaries and the distribution and structure of pores.

MDD powder synthesis provides a possible path for improving our control over the composition and microstructure of fuel pellets. This report documents developments in the processing of uranium oxide pellets from MDD powder feedstock synthesized at ORNL. This report follows on initial work described in the report titled “Report on Receipt, Characterization and Processing of Direct Nitridation Feedstock” prepared last year. In that report, initial processing results of pellets made from MDD UO_3 powder are presented. In summary, that report found that direct pressing of the as synthesized trioxide uranium oxide powder resulted in very low sintered densities such that pre-treatment of the powder would be required. A second report entitled “Report on Feedstock Characteristics Produced by Standard and Advanced Methods”, also submitted last year, focused on characterization of not only pure uranium oxide powders made by the MDD process but also compared various compositions with powders made by conventional powder solid solution processing. These compositions included 95 at% uranium oxide with 5 at% cerium oxide, 80% uranium oxide with 20 at% cerium oxide and 70 at% uranium oxide with 30 at% cerium oxide. In this report, two MDD synthesized powder feedstocks, uranium oxide and 95 at% uranium oxide with 5 at% cerium oxide have been studied further. Several powder conditioning steps have been explored as well as various sintering conditions in order to achieve high density pellets.

2. Powder Characterization

MDD powders were converted from uranium trioxide to uranium dioxide by heat treatment in a reducing atmosphere. Powder was heated to 650˚C or 850˚C for 1 hour under argon 6% hydrogen. It is known from previous studies that at 850˚C, the powder will fully reduce to $UO_{2.00}$ within an hour. At 650˚C, full reduction is not expected. It is known that oxygen defects in

partially reduced powders enhance diffusion rates therefore increasing the driving force for sintering. Further, due to the lower temperature, less coarsening of the powder is expected. It is known from sintering theory that finer powders have a higher driving force for sintering; therefore, the lower reducing temperature is expected to result in a more active powder.

All powders were milled in a zirconia jar in a SPEX mill for either 15 min or 45 min. In some cases, ethylene bis stearamide (EBS) was added at a concentration of either 0.25 wt% or 0.6 wt% as a pressing aid to increase green density. Table I lists the average particles size of powders characterized in this study before and after milling. As seen in the table, milling reduced the average particle size as expected. Contrary to expectations, no significant difference was seen in the particle size of powders reduced at different temperatures.

Particle size distribution was measured with a Horiba LA-950 laser light scattering instrument. This instrument determines a particle size distribution, utilizing Mei and Fraunhofer scattering theory. Samples were prepared for analysis by preparing a dilute slurry of powder in ethylene glycol, and then adding a small amount of the slurry to a reservoir of ethylene glycol to achieve a satisfactory transmittance of light. The sample was then subjected to sonication and analyzed. Sonication continued in incremental steps until the particle size results did not change.

Table I Particle size of powders before and after milling

Composition	Reducing Temperature	Avg Particle Size before milling	Avg particle size after milling
UO_2	650C	3.5	1.3
UO_2	850C	3.2	1.3
95/5 U/Ce	650C	3.5	1.5
95/5 U/Ce	850C	4.2	1.2

3. Powder Conditioning and Pellet Preparation

Pellets were pressed using a 5.70 mm diameter punch and die set lubricated with a thin coating of oil. The powder was uni-axially pressed into pellets using pressures ranging from 75 to 200 MPa in a manual hydraulic press.

Table II shows the green density of pellets pressed from both MDD powders as a function of powder conditioning variables. All of these pellets were pressed at 75 MPa consolidating pressure. As seen, powders pressed without lubricant or milling resulted in pellets with low green densities (<40% of theoretical). By adding the powder conditioning steps of milling, sieving and pressing aid significantly increased the green density obtained. The different reducing temperature seemed to have no effect on green density.

Table III shows the green density of pellets pressed at a higher consolidating pressure of 200 MPa. As seen, the green density of the pellets is significantly increased. The effect of pressing aid is also seen where, contrary to expectations, more pressing aid results in a lower green density.

Table II Green density of pellets pressed from various powders with the processing conditions shown.

Composition	Reducing Temperature	Pressing aid	Milling time	Green density (% theoretical)
UO_2 (A)	650C	N	0 min	37.4%
UO_2 (B)	850C	N	0 min	37.6%
UO_2 (C)	650C	0.6%	15 min	50.4%
UO_2 (D)	850C	0.6%	15 min	50.9%
95/5 U/Ce	650C	N	0 min	38.5%
95/5 U/Ce	850C	N	0 min	39.1%
95/5 U/Ce	650C	0.6%	45 min	54.3%
95/5 U/Ce	850C	0.6%	45 min	54.9%

Table III Green density of pellets pressed from various powders with the processing conditions shown.					
Composition	Reducing Temperature	Pressing aid	Milling time	Compaction pressure	Green density (% theoretical)
UO_2	650C	0.25%	15 min	200 MPa	58.3%
UO_2	650C	0.6%	15 min	200 MPa	52.5%
95/5 U/Ce	650C	0.25%	15 min	250 MPa	61.0%
95/5 U/Ce	650C	0.6%	45 min	250 MPa	56.9%

4. Sintering

Sintering was performed in either a tube furnace or a Netzsch dilatometer (DIL 402C). In both cases, all fixturing was alumina. Both furnaces have computer controlled atmosphere systems that allow precise mixing of gettered argon (10^{-16} ppm O_2), UHP argon (~5 ppm O_2), argon with 1000 ppm O_2, or argon with 500ppm H_2. This system allows sintering under a wide range of conditions.

In the initial screening, pellets pressed at the lowest consolidating pressure (75MPa) were sintered under various atmospheres. Although the green density of the pellets was relatively low, the initial screening was intended to look for trends in sintering behavior to identify atmospheric conditions where sintering rates were enhanced. In Figure 1, the sintering behavior of four of the uranium oxide powders identified as A, B, C and D are plotted. All were sintered under the same conditions, namely a constant heating rate of 20˚C/min to 1550˚C and held for 4 hours. The atmosphere was constant with a flow rate of 40 ccm (cubic centimeters per minute) of argon containing 1000 ppm O_2 and 460 ccm of gettered argon resulting in a total oxygen concentration of about 80 ppm O_2. It can be seen that the powders that have not been milled and contain no pressing aid (ethylene bis(stearamide)) (EBS) shrink considerably more than those without. This is not an indication of enhanced sintering but a function of the much lower green density. The more important features are the onset of sintering and the slope of the curve which indicates the

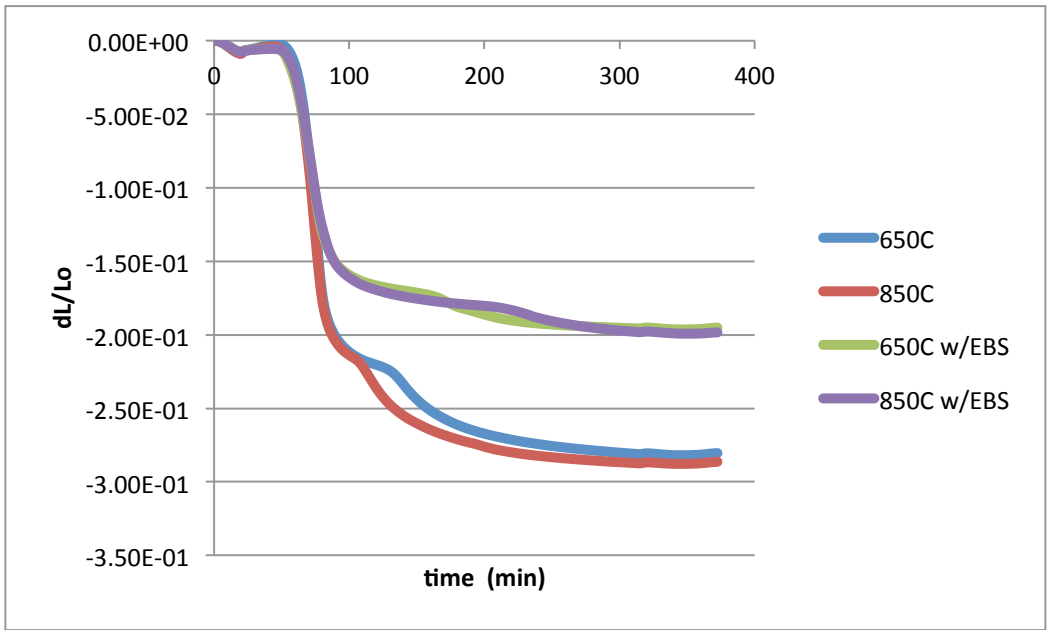

Figure 1 Dilatometry showing sintering shrinkage of pellets prepared with MDD powders.

sintering rate. As seen, all of the powders started sintering at the same time (and temperature). Similarly, the initial sintering rate is the same. It is only during the soak at temperature that some differences are observed. These differences are minor relative to the initial sintering behavior as indicated by the sintered densities of these samples shown in Table IV.

Table IV Sintered density of pellets pressed from various powders with the processing conditions shown.

Composition	Reducing Temperature	Pressing aid	Milling time	Sintered density (% theoretical)
UO_2 (A)	650C	N	0 min	84.6%
UO_2 (B)	850C	N	0 min	82.2%
UO_2 (C)	650C	0.6%	15 min	89.6 %
UO_2 (D)	850C	0.6%	15 min	89.0%

As with the pure uranium oxide powders, pellets pressed from the 95/5 uranium oxide/cerium oxide powder reduced at 650˚C showed a minor enhancement in sintering relative to those reduced at 850˚C. This is seen in Figure 2. The pellets reduced at 650˚C sintered to about 2% higher density than those reduced at 850˚C although the sintering rates and profiles show all the same features. This demonstrates that the powders are slightly more active when reduced at a lower temperature as expected.

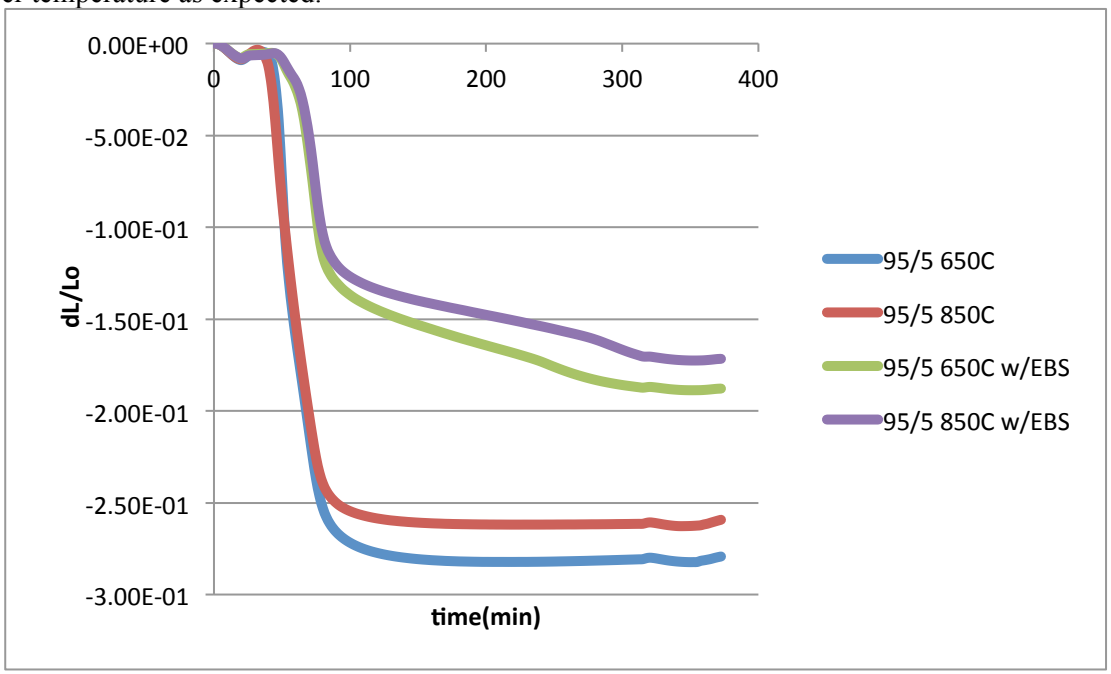

Figure 2 Dilatometery showing sintering shrinkage of pellets made from MDD powders.

Figure 3 shows the sintering behavior of pellets pressed from the same powder uranium oxide containing 0.6 wt% EBS that were milled and sieved. All pellets were sintered to a temperature of 1550˚C for 4 hours at a sintering rate of 20˚C/min but under different atmospheres. As seen in the figure, almost no effect is seen by sintering under different atmospheres despite the fact that the partial pressure of oxygen ranged from about 100 ppm to 10^{-16} ppm O_2. A slight increase in sintering behavior is seen when the pellet is sintered under an atmosphere with a constant pO2 of about 80 ppm O_2.

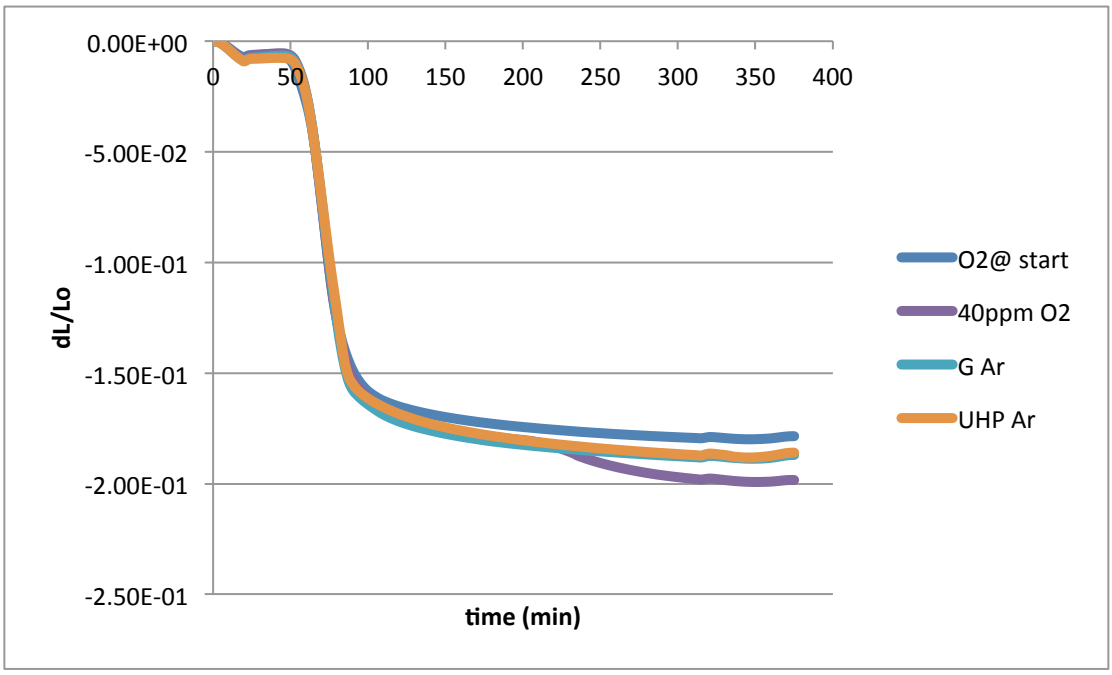

Figure 3 Dilatometery showing sintering shrinkage of pellets made from MDD powders.

Some of the pellets made from the MDD powders were cross sectioned, polished and characterized by SEM. Due to the relatively low density of the pellets (~89%) significant porosity was expected; however, as seen in Figures 4 and 5, porosity was highly irregular. The non-uniform porosity is an indication of poor powder filling of the die cavity and limited powder rearrangement during pressing. The result was unexpected. The processing steps of milling, addition of pressing aid and sieving are specifically intended to minimize these types of defects. Ultimately, it is believed that the morphology of the powder is a significant contributor to the difficulties in processing the powder. A representative morphology is shown in Figure 6 which is shown to be agglomerated and angular, aspects that make particle packing non-uniform.

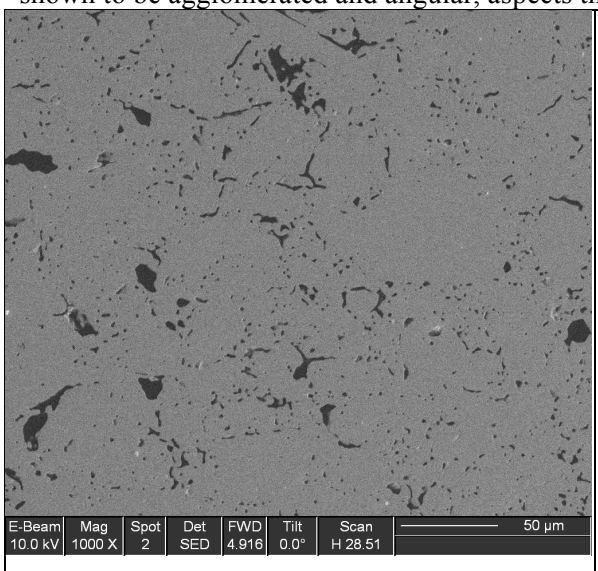

Figure 4 Pellet prepared from MDD UO_2 powder reduced at 650˚C with 0.6wt% EBS sintered at 1550˚C for 4 hrs.

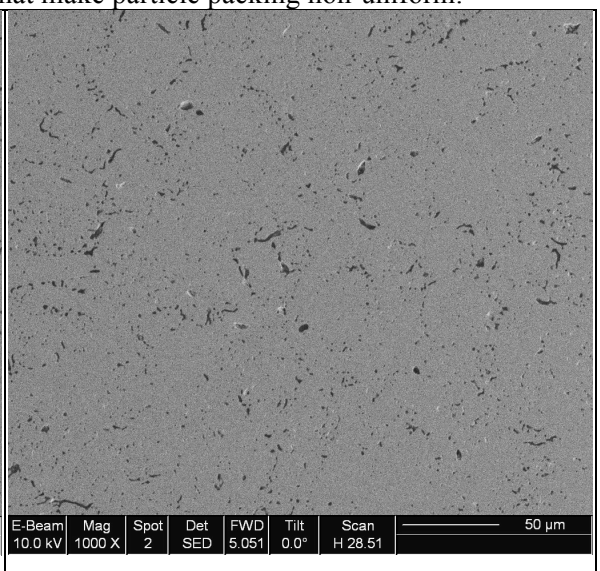

Figure 5 Pellet prepared from MDD 95/5 UO_2/CeO_2 powder reduced at 650˚C with 0.6wt% EBS sintered at 1550˚C for 4 hrs.

Guided by the data collected, a final set of samples were prepared using the best conditions identified. The lower concentration of pressing aid (0.25% EBS), milling for 15 minutes and sieving. Pressing was performed at 200 MPa. Sintering was accomplished with a slow initial ramp rate (2˚/min to 500˚C) to ensure burnout followed by a 10˚/min ramp to 1650˚C held for 4 hours. The atmosphere was UHP argon until the soak temperature was reached at which point additional oxygen was introduced (1 ccm of pure oxygen in 1000 ccm of argon). Several pellets were made under these conditions with densities averaging 92% of theoretical. The microstructure of a pellet prepared under these conditions is seen in Figure 7.

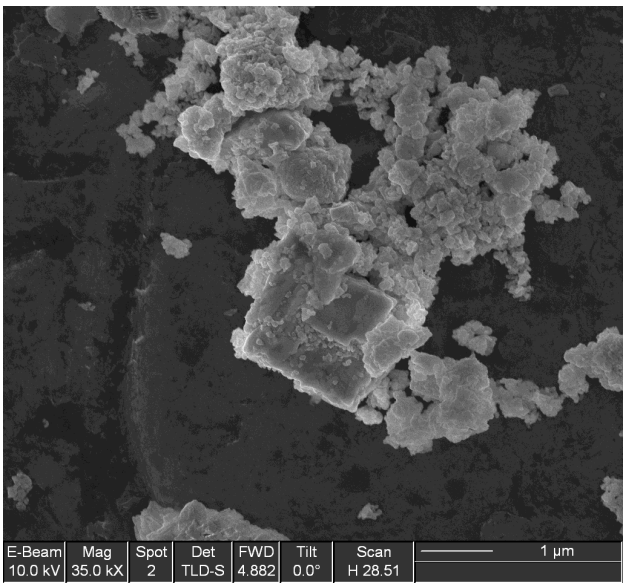

Figure 6 SEM of MDD uranium oxide powder after reduction at 650˚C.

5. Conclusions

Uranium oxide powder synthesized by the MDD method was characterized and processed following traditional cold press and sinter approaches. Previous work demonstrated the need to reduce the as-received uranium trioxide prior to processing. Powders were either partially or fully reduced before processing. It was found that milling sieving and adding a pressing aid resulted in pellets with high green density. The green density was comparable to or exceeded that of commercial powder.

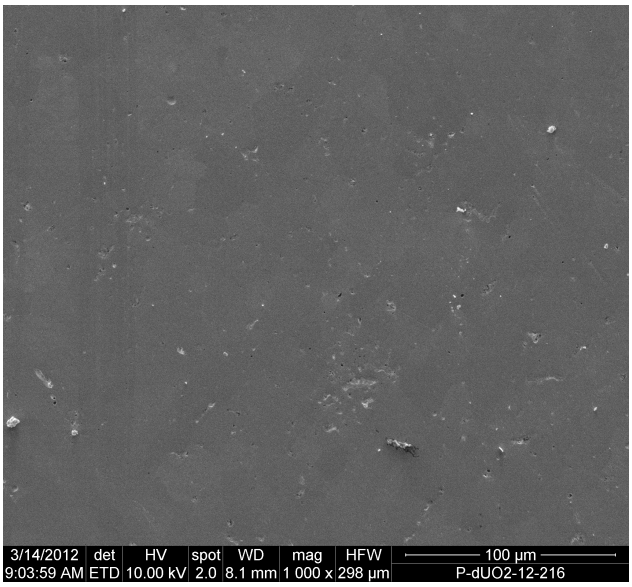

Figure 7 SEM image of cross section of pellet made from MDD uranium oxide powder.

Pellets were sintered under a wide variety of furnace atmospheres, heating rates and temperatures. The maximum sintered density obtainable was 92% of theoretical. This is significantly less than the 96% obtainable for a commercial powder and less than the 95% density typically specified for reactor designs. It is believed that a contributing factor to the low density is poor powder morphology and flow characteristics. It is anticipated that additional development work in the MDD synthesis process would benefit downstream processing.

6. References

E Luther “Report on Receipt, Characterization and Processing of Direct Nitridation Feedstock”, LA-UR 11-01737, 2011.

E Luther, “Report on Feedstock Characteristics Produced by Standard and Advanced Methods”, LA-UR 11-04839, 2011.