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Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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Summary

A testing program was carried out at the Pacific Northwest Laboratory (PNL) to demonstrate that commercial nuclear fuel grade UO_2 pellets can be fabricated from UO_3 powder produced by the modified direct denitration (MDD) process being evaluated by the Atomic Vapor Laser Isotope Separation Program (AVLIS) for metal product processing. Specific objectives were to receive UO_3 powder made by the AVLIS MDD process at Oak Ridge National Laboratory, reduce it to a sinterable UO_2 powder, fabricate high density light water reactor (LWR) fuel pellets, and characterize them for comparison to nuclear fuel grade pellets.

A previous study by Davis and Griffin (1992) established techniques for processing and evaluating thermally denitrated UO_3 powders. The evaluation was based on the behavior of the resulting UO_2 powder during pellet preparation and final pellet characterization. A significant conclusion of this study was that adding ammonium nitrate to the uranyl nitrate feed solution before denitration greatly improved sintering properties of the final UO_2 powder. The purpose of the current study was to optimize the processes used in the previous work for converting AVLIS MDD UO_3 powder to UO_2 powder and to use this powder to fabricate LWR fuel pellets with 96% theoretical density (TD) or higher. The only obvious difference in the MDD UO_3 used in the two studies is that the material used in the present study starts with uranyl nitrate having an ammonia/uranium ratio of 2.6 and the previous study started with a ratio of 2.0. Other properties were the same.

Experimental parameters that were varied during the reduction of MDD UO_3 powder to UO_2 were primarily the reducing atmosphere, the temperature at which the reduction took place, and the time in the reduction cycle that the reducing atmosphere was used. The four types of reduction processes were

Run ID	Heat-up Atm.	4-h Hold	Cool-down
Type 1	50% Ar - 50% H_2	50% Ar - 50% H_2	50% Ar - 50% H_2
Type 2	50% Ar - 50% H_2	50% Ar - 50% H_2	Ar
Type 3	Ar	50% Ar - 50% H_2	Ar
Type 4	Ar - 4% H_2	Ar - 4% H_2	Ar - 4% H_2

Maximum hold temperatures were varied from 500 to 1000°C. Reductions were carried out on 100-g batches of UO_3 powder spread in a thin layer in molybdenum trays. A 6-in.-diameter tube furnace was adapted for processing kg quantities of material, but the program was terminated before it could be tested. Pellet pressing was carried out in a 0.425-in.-diameter die at pressures necessary to achieve green densities of 5.0 g/cm^3 (46% TD). Sintering was carried out in Ar - 4% H_2 at 1700°C for 8 h.

A summary of the significant results that characterize the reduction of UO_3 powder to UO_2 and the subsequent pellet fabrication are listed in Table S.1. In addition to these results, ceramographic evaluation of selected pellets indicated acceptable microstructures. The final pellet density was used as the primary criteria in evaluating the reduction process. The pellet densities listed in Table S.1 were obtained using sterotex as a die lubricant. Using zinc stearate as a die lubricant increased the densities by approximately 0.5% TD both in this study and the previous study of Davis and Griffin. The target density of 96% TD was achieved over a wide range of reducing conditions. On the basis of density alone, it was not possible to select an optimum reduction process.

Table S.1. Summary of Reduction Sintering Results

Run ID	Type	Maximum Hold Temp (°C)	Tap Density (g/cm^3)	Surface Area (m^2/g)	Oxygen/ Metal Ratio	Sintered Density (% TD)
As-Received UO_3			1.18	7.42		
2	1	1000	1.67	7.01	2.15	96.5
3	1	900	1.47	12.91	2.15	95.8
4	1	800	1.48	7.72		94.5
5	2	800		11.57		95.6
6	3	800	1.65	1.97	2.03	93.6
8	4	800	1.40	15.12	2.07	95.6
9	1	600	1.37	13.10	2.10	95.6
10	3	600	1.45	5.51	2.05	95.3
11	4	600	1.43	5.93	2.04	95.1
12	3	600	1.44	4.84	2.08	96.0
13	3	800	1.51	2.07	2.02	92.5
14	3	800	1.63	2.27	2.10	89.0
15	3	600 (2 h) 800 (2 h)	1.46	6.24	2.05	96.5
16	3	700	1.64	3.09	2.06	94.6
17	3	600	1.45	6.38	2.08	96.1
18	4	600	1.43	8.86	2.11	95.9
19	4	600	1.41	5.24	2.04	96.0
20	4	600 (8 h)	1.37	4.74		93.5
21	4	600	1.44	6.12		95.1
22	3	600	1.46	5.29	2.11	96.0
24	3	550	1.46	7.53	2.13	

The UO_3 reduction process appeared to be controlled by the temperature that the UO_3 powder was heated to before being reduced. In Type 1, 2, and 4 reduction runs, the powder was exposed to the reducing gas during heatup, and this continued throughout the 4-h hold. In Type 3 runs, the powder was exposed to reduction gas only during the 4-h hold temperature. The Type 3 runs are therefore deemed best for consistent results. Reducing gases other than 50% Ar - 50% H_2 used in the type 3 runs could be used. A reduction temperature of 600°C was found to give adequate final densities, and lower temperatures offer the potential for further optimizing the powder properties.

The results obtained are of significant value for defining the direction of future work. Follow-on work should be directed towards lowering the reduction temperatures to the 500 to 600°C range and using safer and/or less expensive sweep gases, i.e., nitrogen instead of argon in noncombustible mixtures. The furnace set up to reduce larger batches of UO_3 will provide a closer simulation to commercial production and larger amounts of powder for parametric fabrication studies. Characterization of the UO_3 and UO_2 powders, as well as the sintered pellets, using differential thermal analysis/ thermogravimetric analysis (DTA/TGA), x-ray diffraction, electron microscopy and particle size analysis would lead to a better understanding (of the reduction process) and provide a firm basis for selecting a commercial reduction process. The impact of other process variables on the final pellet densities, such as the ammonia/uranium ratio in the MDD process and the die lubricant used in the pellet pressing, should also be studied.

The results of this study have demonstrated that

1. MDD-derived UO_3 powders can be reduced to sinterable UO_2 powder using reduction techniques that allow control of the final powder characteristics.

2. The resulting UO_2 powders can be processed/sintered using standard powder preparation and pellet fabrication techniques to yield pellets with densities greater than 96% TD.

3. Pellet microstructures appear similar to those of power reactor fuel, and because of the high final pellet densities, it is expected that they would remain stable during in-reactor operation.

Reference

Davis, N. C., and C. W. Griffin. 1992. *Pellet Fabrication Development Using Thermally Denitrated UO_2 Powder*. PNL-4305, 1982 and reissued as PNL-4305, 1992.

Acknowledgments

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1.0 Introduction

The Atomic Vapor Laser Isotope Separation Program (AVLIS) uses the modified direct denitration (MDD) process to produce UO_3, which will be subsequently used to fabricate commercial UO_2 fuel. A testing program was carried out at Pacific Northwest Laboratory (PNL)[a] to assist the AVLIS program in demonstrating that UO_3 produced by the MDD process can be reduced to UO_2 powder, which is suitable for fabricating high-density pellets.

The thermal denitration of uranyl nitrate followed by H_2 reduction typically results in UO_2 powder that is not easily fabricated into high-density UO_2 pellets (US AEC 1961). The oxide particles/aggregates tend to be hard, dense, and relatively large. Comminution can be used to produce a more active powder, but the improvement in powder sinterability is limited. The MDD process for converting uranyl nitrate to UO_3 was developed at Oak Ridge National Laboratory (ORNL) (Haas et al. 1981) to address this problem of sinterability. The MDD process adds NH_4NO_3 to the uranyl nitrate solution before the denitration step.

It has been shown in studies at PNL (Davis and Griffin 1992) that this MDD method of thermal denitration resulted in a UO_3 precursor that reduced to UO_2 powder with better sintering characteristics. This previous work sought to produce fast breeder reactor (FBR) fuel having densities in the range of 88 to 92% theoretical density (TD). The results indicated that UO_2 pellets with densities as high as 98% TD could be fabricated from powder obtained by reducing the MDD-derived UO_3 powders. The lower densities required for fast breeder reactor fuel pellets (88 to 92% TD) were achieved by adding pore formers to the UO_2 powder before pressing and sintering.

The purpose of the present study was to determine if the AVLIS-supplied MDD-derived UO_3 powder can be reduced to a UO_2 powder that can be sintered to densities required for commercial fuels. As a means for establishing the typical characteristics of commercial UO_2 fuel, a brief survey of current information was carried out, and a summary is included in Appendix A. Typical ranges for final pellet density are 94 to 96% TD (US DOE 1987). If final sintered pellets with densities as high or higher than 96% TD can be fabricated from the AVLIS supplied UO_3, then adding pore formers, as was done previously (Davis and Griffin 1992), can be used to reduce the densities and achieve the required density. Thus, final pellet density will be an important property in evaluating the suitability of the AVLIS UO_3 powder. The present study was considered to be only a scoping study, not a comprehensive study of related reduction parameters and the controlling mechanisms.

The MDD-derived, naturally-enriched UO_3 powder was provided by Oak Ridge National Laboratory (ORNL). The material had been prepared from a uranyl nitrate solution with NH_4NO_3

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

additions to give a NH_4^+/U ratio of 2.6. The previous study involved UO_3 prepared from a solution having a NH_4^+/U ratio equal to 2.0 (Davis and Griffin 1992). This was the only obvious difference in the powder prepared by ORNL and that used previously.

1.1 Previous Work

The previous study by Davis and Griffin (1992) at PNL to convert UO_3 powders to UO_2 demonstrated that the resulting UO_2 powders could be used to produce FBR low density fuel pellets. The UO_3 powder provided by ORNL for that study was produced with and without adding the NH_4NO_3 to the uranyl nitrate feed solution. The results of this earlier work at PNL indicated that adding NH_4NO_3 to the uranyl nitrate solution before denitration resulted in a UO_3 precursor that could be reduced to a sinterable UO_2 powder. This sinterable UO_2 powder yielded final UO_2 pellet densities as high as 98% TD. To produce low-density FBR fuel pellets (88 to 92% TD), pore formers were added to the UO_2 powder before pressing and sintering.

A significant conclusion of the PNL study was that the presence of the NH_4NO_3 in the thermal denitration feed solution greatly improved sintering properties of the final UO_2 powder. The other UO_3 processing conditions, such as the denitration temperatures (390 to 620°C) or the concentration of the feed solution, had little effect on the sinterability of the final UO_2 powder. However, the sinterability of the final UO_2 powder was greatly improved by adding ammonium nitrate to the feed solution before the thermal denitration. In this previous work, the NH_4^+/U ratio in the uranyl nitrate solution was maintained at 2.0 with little variation.

The study of Davis and Griffin established a process for evaluating the thermally denitrated UO_3 powders supplied by ORNL. This process involved the reduction of the powders, powder preparation, pellet pressing, sintering, and pellet characterization. The process for evaluating the UO_2 powder was based on the behavior of the powder during pellet preparation and the final pellet characterization. The process is summarized in Appendix B.

1.2 Experimental Procedure

The present study to evaluate the AVLIS supplied MDD-derived UO_3 powders is based on the previously developed process flow chart described in Appendix B. In the present case, 4 kg of UO_3 powder were received from ORNL to be evaluated. A detailed description of the material is included in Appendix C. The material was identified as KN-18-CP-1 and had been prepared from a uranyl nitrate solution having a NH_4^+/U ratio of 2.6. This increase in the NH_4^+/U ratio over the previous ratio of 2.0 was the only obvious difference between the present powder and that used previously (Davis and Griffin 1992). The total batch of calcined material was screened, and only the -25 mesh powder was included in the material sent to PNL. Tap density and surface area measurements were carried out at PNL to characterize the material as-received. The values of 1.18 g/cm^3 and 7.42 m^2/g are listed in Table 2.

Reduction of the UO_3 powder was carried out in a cold-wall refractory-metal furnace (resistance heated) that was considerably smaller than the furnace used in the previous study (1/6 the total volume). Figure 1 is a picture of the furnace used for both reducing the UO_3 and sintering the UO_2 pellets. The furnace can operate in a vacuum or in atmospheres with inert or reducing gases. Reducing gases also included the capability to use combustible hydrogen mixtures. The UO_3 powder was reduced by spreading it uniformly over the bottom of a 6- by 6- by 1-in.-high molybdenum tray. The tray inside the furnace in Figure 1 is the same as the tray used for UO_3 reduction. Only one tray of material was reduced at a time. For the initial 50-g batches of UO_3 spread uniformly across the tray, the resulting powder depth was approximately 0.2 in. The cover gas flow rate was nominally 20 standard cubic feet per hour (SCFH). After reduction, the resulting powders were characterized by measuring total weight loss, oxygen to metal ratio (O/M), tap density and surface area. Appendix D discusses the method used for determining the O/M.

Powder preparation and pellet pressing were carried out in a manner similar to that used previously. It is to be noted that the UO_2 powder from each reduction cycle was processed through the different preparation steps regardless of the observed quality. Powder quality varied depending on the reduction process, and this in turn affected the behavior during the powder preparation and pressing. The powder was preslugged, granulated, lubricant added, and then pressed into a 0.425-in. (1.080 cm) diameter green pellet. To the extent possible, semi-automatic hydraulic pressing was used to produce uniform commercial-type pellets. However, in some cases target densities for green processing could not be achieved, even with excessive pressure. Sintering was carried out at 1700°C for 8 h using the same furnace used in the current reduction process. The tray in front of the furnace in Figure 1 is a sintering tray with green (as-pressed) UO_2 pellets to be sintered. Centerless grinding was used to prepare the pellets for final evaluation. The typical type of green (as-pressed), as-sintered and after-centerless grinding are shown in Figure 2.

1.3 Experimental Results

The study was carried out in three different series of reduction runs. The first series of thirteen reduction runs was exploratory and used 50-g batches of UO_3 powder to establish the basic behavior of the as-received UO_3 material. The second series of nine runs repeated selected runs on larger 100-g batches of powder and extended the reduction parameters to other conditions to optimize the powder characteristics. The third set of four reduction runs was designed to determine effectiveness of using lower reduction temperature (below 600°C) to produce higher density UO_2 pellets.

1.3.1 First Series of Reduction Runs

The first series of thirteen reduction runs involved four different thermal and gas-composition sequences that are described in Table 1. These different sequences will be referred to as run types. Because the furnace used to reduce the UO_3 was considerably smaller than the one used previously (Davis and Griffin 1992), some concern was expressed that heating the UO_3 powders to the reduction temperature in Ar could result in excessive oxidation of the heating elements. For this reason, the UO_3

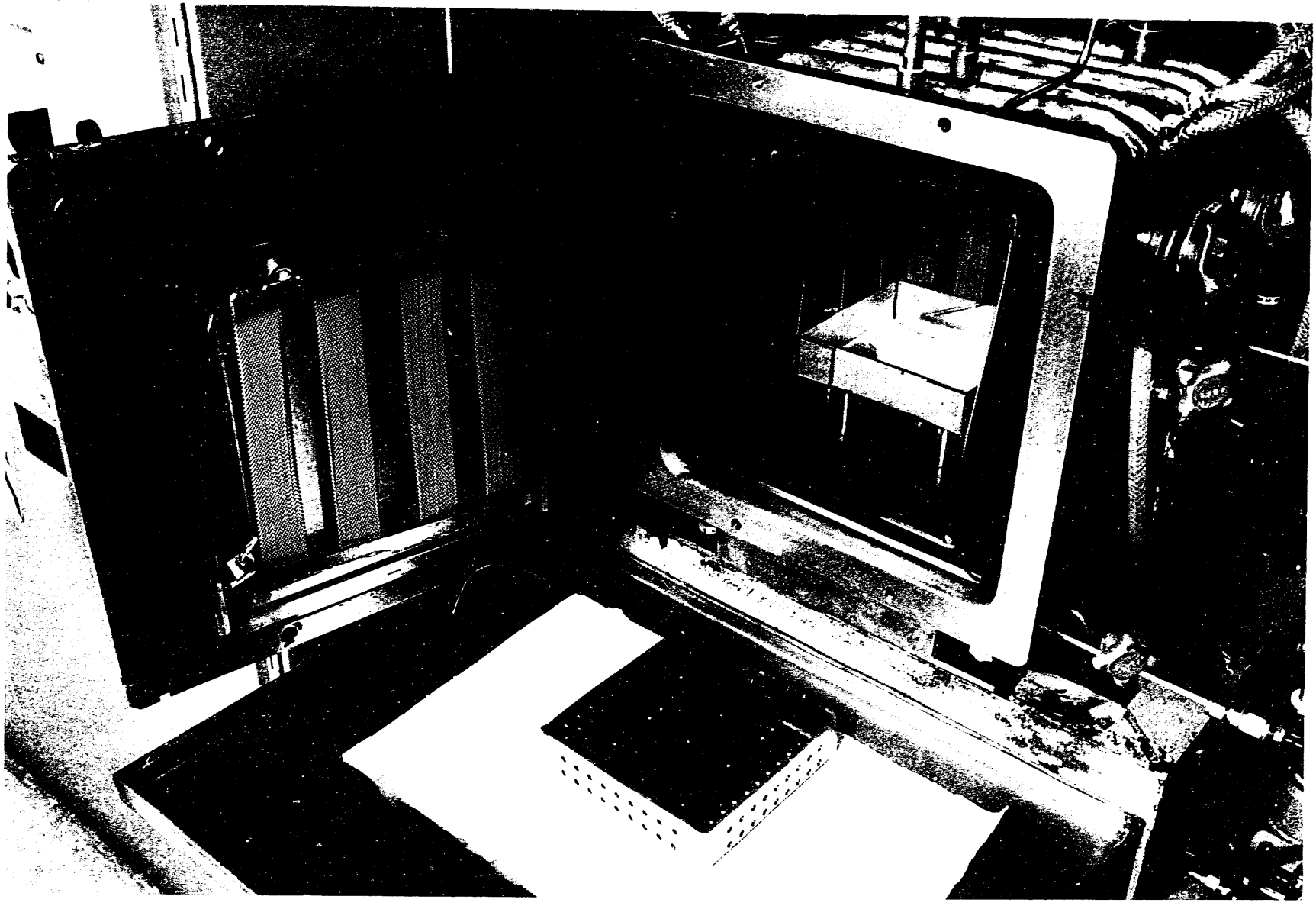

Figure 1. Furnace Used for the Reduction/Sintering Processes With Sintering Tray and Green Pellets

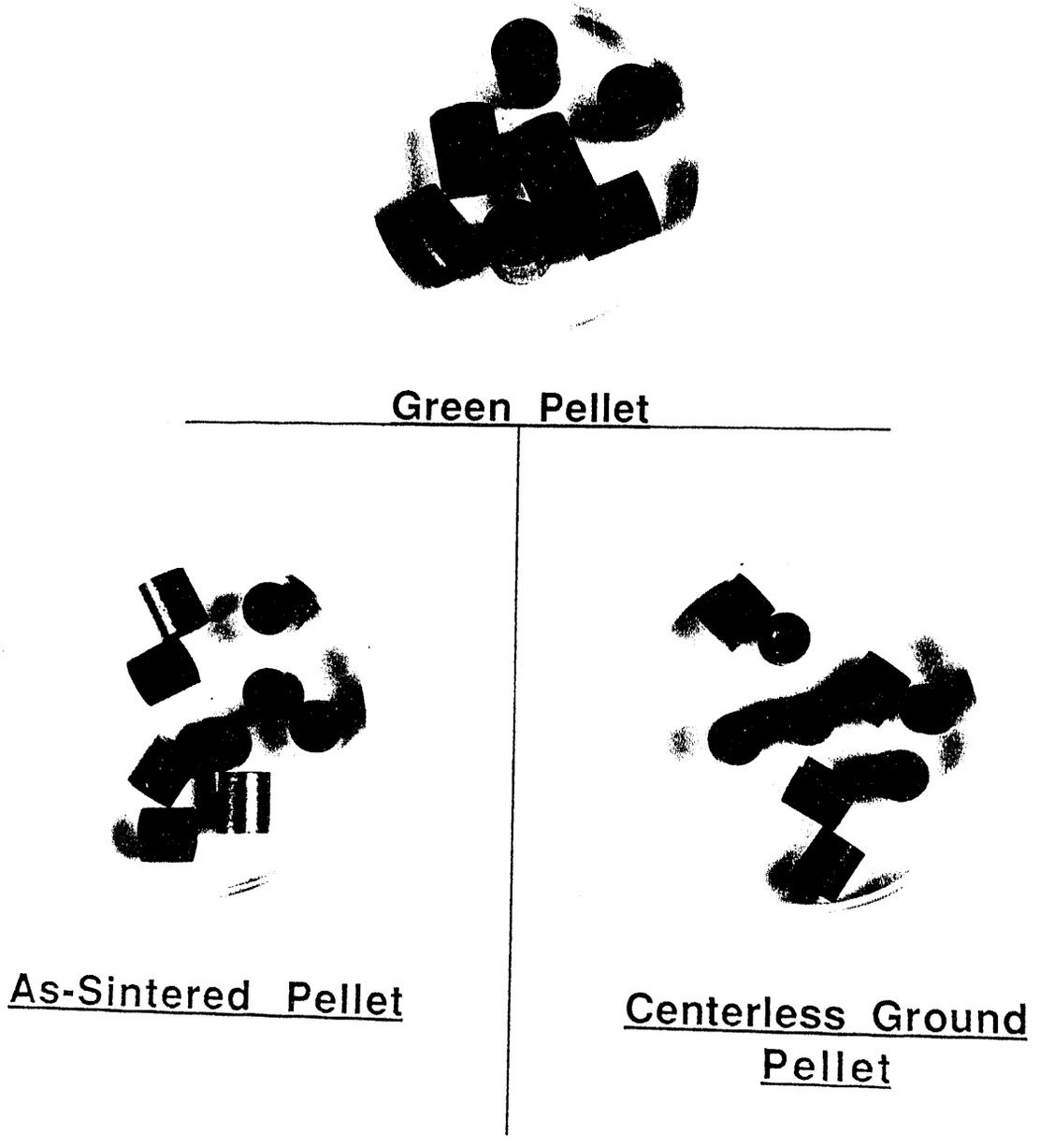

Figure 2. As-Pressed "Green," As-Sintered, and Centerless-Ground Sintered Pellets. The green pellets are 0.425-inch Diameter.

Table 1. Gas Compositions Used in the Four Types of UO_3 Reduction Runs

Run ID	Heatup	Maximum Temperature	Cooldown
Type 1	50% Ar - 50% H_2	50% Ar - 50% H_2	50% Ar - 50% H_2
Type 2	50% Ar - 50% H_2	50% Ar - 50% H_2	Ar
Type 3	Ar	50% Ar - 50% H_2	Ar
Type 4	Ar - 4% H_2	Ar - 4% H_2	Ar - 4% H_2

batch sizes were kept small (50 g), and for the initial runs, a reducing atmosphere was used during the heatup (run Types 1 and 2). Run Types 1, 2, and 3 had the same temperature sequencing as the previous study of Davis and Griffin, i.e., a 300°C/h heatup, a 4-h hold at maximum temperature, and 300°C/h cooldown. The cover gases used in Type 1, 2, and 3 runs varied for the different temperature sequencing and involved Ar and 50% Ar - 50% H_2. The Type 1 run with the entire cycle being carried out in 50% Ar - 50% H_2 was considered to be the safest in terms of furnace operation. The Type 3 run is the standard reduction run that was used in the previous study (Davis and Griffin 1992).

In addition to Type 1, 2, and 3 runs, two reduction runs were carried out in a quartz tube using an Ar - 4% H_2 flow gas bubbled through 0°C water. Heatup and cooldown were carried out in about 1-1/2 h with 6 h at maximum temperature. These will be referred to as Type 4 runs. These were carried out in the same furnace and in the same manner as the thermal anneals used for determining O/M (see Appendix D). Because of the smaller size of this furnace, batch sizes of the UO_3 powder were limited to less than 10 g.

Table 2 is a description of the first series of reduction runs and the resulting powder characterizations. The first run was a Type 1 run to 800°C. "Burnback," or spontaneous oxidation of the powder, was observed after run 1 when the furnace was opened and the powder was exposed to ambient air. The furnace was always opened after it had been cooled overnight, and the temperature was on the order of 20°C. Whether burnback occurred is noted in Table 2 under the column "Burnback" by a Y (yes) or N (no).

In run 2, the maximum temperature was increased to 1000°C to try to produce a more stable powder that would not burn back when exposed to air. Burnback did not occur after run 2. Since burnback did not occur after a maximum temperature of 1000°C, the temperature was reduced to 900°C where again no burnback occurred. Run 4 repeated run 1 to confirm that burnback did occur for a maximum temperature of 800°C. To confirm the observations made after run 1, burnback did occur for run 4.

As a possible solution to burnback, run 5 was changed from a Type 1 to a Type 2 run to 800°C. The change from Type 1 to Type 2 meant that cooldown was carried out in Ar. This modification to the reduction cycle was not successful, and burnback again was observed. At this point, it was decided

Table 2. Summary of the First Series of UO_3 Reduction Runs

Run ID	Type Run	Max. Temp. (°C)	RT Cond.	Burn-Back	Wt Loss (%)	Tap Density (g/cm^3)	Sfc Area (m^2/g)	O/M
As Received						1.18	7.42	
1	1	800	N	Y		1.49		2.37
2	1	1000	N	N	6.6	1.67	7.01	2.15
3	1	900	N	N	7.6	1.47	12.91	2.15
4	1	800	N	Y	6.4	1.48	7.72	--
5	2	800	N	Y	6.8	1.66	11.57	--
6	3	800	Y	N	8.2	1.65	1.97	2.03
7	4	800	N/A	N	7.9			2.00
8	1	800	Y	N	7.5	1.40	15.12	2.07
9	1	600	Y	N	6.9	1.37	13.10	2.10
10	3	600	Y	N	7.7	1.45	5.5	2.05
11	4	600	N/A	N	7.9	1.43	5.93	2.04
12	3	600	N	N	7.8	1.56	4.84	2.08
13	3	800	N	N	7.8	1.51	2.07	2.02

that the previously used heatup in Ar (Davis and Griffin 1992) may be necessary to produce a powder that would not burn back, even though it may result in some oxidation of the furnace elements.

In run 6, two changes were made. First, the run was changed from a Type 2 to a Type 3 run to 800°C, meaning that both heatup and cooldown were done in Ar. Second, an additional step was added to the procedure. Before opening the furnace, the powder was subjected to a 1-h purge of Ar bubbled through room temperature water. Whether this conditioning was used is listed under "RT Cond" and indicated by a Y (yes) or N (no). The powder in run 6 did not burn back. Run 10 was similar to run 6 in that the same conditions were used, except the maximum temperature was dropped to 600°C. Again burnback was not observed, even though it was expected that burnback would be even more favored than in run 6. Because two changes were made in these runs (6 and 10), it cannot be ascertained whether the RT conditioning or the Type 3 run was responsible for preventing the burn-back. Alternatively, preventing burnback could have been an interrelated phenomena due to some combination of the two conditions.

The effectiveness of the room temperature (RT) conditioning with water in preventing burnback was verified in run 8 (a Type 1 run to 800°C). That is, run 8 was a repeat of runs 1 and 4 with only

RT conditioning added. Burnback was not observed after run 8, indicating that RT conditioning did contribute to preventing burnback. In run 9, the temperature was dropped further, to 600°C, in a Type 1 run with RT conditioning. As discussed above, this was expected to be even more likely to burn back than the 800°C run. Burnback was not observed, and therefore we conclude that RT conditioning was effective in preventing burnback.

Alternatively, the effectiveness of a Type 3 run versus a Type 1 run in preventing burnback was checked by repeating runs 1, 4, and 5, except with a change to a Type 3 run in run 13 with no RT conditioning. No burnback was observed. Run 12 was a Type 3 run to the lower temperature of 600°C, and in this case also, no burnback was observed. Runs 12 and 13 indicate the effectiveness of a Type 3 run in producing UO_2 powder that does not burn back when exposed to air. Thus, it can be concluded that the heatup in Ar, characteristic of a Type 3 run, is an important factor in achieving stable UO_2 powder.

The Type 4 runs were carried out in a different reduction furnace and provided a means of determining the effectiveness of low H_2 concentrations together with the addition of water vapor. These Type 4 runs were carried out to 800°C (run 7) and 600°C (run 11) and resulted in stable UO_2 powder. Whether adding water vapor was critical in the reduction was not determined. However, these runs did show that the reduction of UO_3 powders could be achieved in a noncombustible H_2 gas mixture.

Characteristics of the UO_2 Powder

Table 2 includes the measured tap densities, surface areas, and O/Ms for the resulting UO_2 powders. Type 1 runs to 600, 800, and 900°C where burnback did not occur resulted in the highest surface areas. The Type 2 run to 800°C, which did burn back, also had a very high surface area. This suggests that Type 1 and 2 runs tend to result in higher surface area UO_2 powders than Type 3 and 4 runs. Such an observation would be consistent with the tendency of the UO_2 produced in Type 1 and 2 runs to burn back when exposed to air since higher surface areas would be expected to result in surface reaction and reoxidation. The reason for these high surface areas for type 1 and 2 powders could be related to the temperature at which the reduction occurs. For the Type 1 and 2 runs, reduction probably starts at a temperature considerably before 600°C. For a Type 3 run, this reduction is delayed until H_2 is introduced at 600 to 800°C. For a Type 4 run, the lower concentration of H_2 during the heatup cycle may limit the rate of reduction and hence result in the reduction occurring primarily during the hold time at maximum temperature. At this point, it is difficult to determine whether 1) the high surface area is due to a reduction at low temperature or 2) heating UO_3 to high temperatures before reduction results in a precursor that has a lower surface area and produces a lower surface area UO_2 powder.

The results of this series of 13 reduction runs can be summarized by the following:

1. Type 1 reduction runs using 50% Ar - 50% H_2 sweep gas with maximum temperatures of 900°C and 1000°C did not burn back when exposed to room temperature air. For a maximum

temperature of 800°C, burnback was observed to occur for a Type 1 run when exposed to air at room temperature unless it had been conditioned at room temperature using Ar bubbled through water.

2. Adding an Ar cooldown to a Type 1 reduction run (Type 2) at 800°C did not prevent burnback, indicating additional stabilization is necessary.

3. Adding an Ar heatup and cooldown to a Type 1 reduction run (Type 3) eliminated burnback at 800°C and resulted in reduction runs with no burnback for maximum temperatures as low as 600°C.

4. Reduction in the noncombustible gas mixture of Ar - 4% H_2 equilibrated with 0°C water appears to be an effective means for reducing UO_3 to UO_2. Adding water vapor to the sweep gas in a Type 4 run was derived from the success of the O/M measurement technique in reducing UO_3 to stoichiometric UO_2 (see Appendix D). Whether the addition of water vapor contributes directly to this reduction has not been determined.

From this first series of reduction runs, it was concluded that UO_2 powders produced by Type 1 and 2 reductions have higher surface areas than powders produced using the same maximum reduction temperatures in Type 3 and 4 runs. Stable UO_2 powders can be produced at temperatures as low as 600°C by either Type 3, Type 4 or Type 1 and 2 runs with RT conditioning. This stabilization is achieved by either reducing the surface area (Type 3 and 4 runs) or by deactivating the surface using a layer of adsorbed water (RT conditioning).

Powder Processing/Pressing

The powders produced in the reduction runs in Table 2 were used to fabricate a series of UO_2 pellets for the first sintering tests. For run 1, it appeared that the amount of oxidation during burnback made the powder too difficult to process, and for run 7, the quantity of powder was too small. In other cases, the color of the powder, the hardness of the granules during granulation, or the pressure required in forming were indicators of the ability to make good quality pellets. The following observations were made:

1. The burned-back powder tended to be very dark, extremely soft, and when granulated, the slugged powder would smear back to powder fines. Excessive pressures were required to slug and in turn press green pellets. This is probably related to the high surface areas of the powders.

2. The higher temperature (800°C) Type 3 reductions (run 6 and 13) produced powder that was brownish-orange in color with dense particles that were difficult to press. The low surface areas suggest such a behavior. These powders resulted in low-density green pellets with little physical integrity.

3. The preferred powder appeared greenish-brown. It could be processed to target slug densities of approximately 4.3 g/m^3 with reasonably low pressures (20 Kpsi), granulated to feed material

with approximately 80% of the granules in the -20 + 100 mesh range, and pressed into green pellets with consistent density, slightly above 5.0 g/cm^3.

The densities of the preslugged and green pellets are listed in Table 3. Sterotex,[a] a conventional organic lubricant additive, was used (0.3 wt%) in the granulated feed for all these pellet samples.

Pellet Sintering/Grinding/Evaluation

Sintering was carried out in the same cold-wall refractory-metal furnace (resistance heated) used for the reduction process. The green pellets were placed in molybdenum sintering trays and sintered to 1700°C using the same sintering cycle reported previously (Davis and Griffin 1992). The sintering cycle involved heating at 150°C/h to 450°C and at 300°C/h to 1700°C, holding for 8-h at 1700°C, and then cooling at 400°C/h. Sintering was carried out in a flowing atmosphere of 50% Ar - 50% H_2. After sintering, all the pellets were centerless ground using a diamond wheel to provide a uniform finish for inspection and accurate dimensional measurements. Pellet evaluation included geometric and immersion density, visual inspection, and microstructural examination. A complete compilation of all the densities with the slugging and final pressing pressures is given in Appendix E.

Table 3 lists the final sintered densities along with the slugging and green densities. The green and final density values are averages over several pellets, and the actual values are given in Appendix E. The green densities were determined by geometric measurements and calculation, while the final sintered density values were made by water immersion. When the final sintered densities are compared with the reduction parameters in Table 2, the following observations are made:

1. The very highest density was found for run 2 with 96.5% TD. This is somewhat surprising since run 2 was a Type 1 reduction at the highest temperature of 1000°C. High temperatures are typically expected to lower the surface area and sinterability. However, since both Type 1 and Type 2 reductions have access to H_2 at the beginning of the cycle, reduction can start at a very low temperature. The low-temperature reduction produced extremely small particles with a high surface area that remained high even after heating to 1000°C. The high maximum temperature of 1000°C caused some pre-sintering of the particles, reducing to 7.01 m^2/g the surface area, which may have been as high as 12 to 15 m^2/g at a lower temperature before heating to 1000°C. See, for instance, the other Type 1 and Type 2 reductions that were made at lower temperatures, such as 3, 5, 8, 9. Perhaps the other reason run 2 produced the highest sintered density was that the UO_2 powder pressed to the highest green density—5.6 g/cm^3.

2. Comments similar to those in (1) could be made about run 3. Although the maximum temperature was only 900°C, it was a Type 1 reduction, and the final surface area was quite high—12.9 m^2/g. The final density of 95.8 g/cm^3 was slightly less than run 1 and can probably be related to the somewhat lower green density.

(a) Sterotex is a powdered vegetable stearine produced by Capital City Products Company, Columbus, Ohio.

Table 3. Summary of UO_2 Powder Preparation/Pressing/Sintering Results

Run ID	Type Run	Max. Temp. (°C)	Sfc Area (m^2/g)	Slug Density (g/cm^3)	Green Density (g/cm^3)	Sintered Density (g/cm^3)	Sintered Density (%TD)
2	1	1000	7.0	4.10	5.60	10.58	96.5
3	1	900	12.9	4.05	5.05	10.49	95.8
4	1	800	7.7	3.95	4.73	10.35	94.5
5	2	800	11.6	3.60	4.62	10.45	95.6
6	3	800	2.0	4.25	5.36	10.29	93.6
8	1	800	15.1	4.0	4.72	10.49	95.6
9	1	600	13.1	3.8	4.81	10.45	95.6
10	3	600	5.5	4.43	4.93	10.48	95.3
11	4	600	5.9	4.40	5.05	10.43	95.1
12	3	600	4.8	4.30	5.10	10.52	96.0
13	3	800	2.1	4.30	5.31	10.13	92.5

3. The next two runs (4 and 5) should probably have been scrapped and not processed. Similar to run 1, which was not processed, runs 4 and 5 had burned back on exposure to air. However, it is interesting to note that the resulting powders could only be pressed to extremely low green densities of 4.6 to 4.7 g/m^3, perhaps due to the oxidation of the powder. In spite of this low green density, the samples remained intact during the large amount of shrinkage that occurred during sintering. Although the sintered pellets were dimensionally non-uniform, the high surface area allowed the powders to sinter to a high density.

4. Type 3 reductions to 800°C (runs 6 and 13) produced a powder that sintered poorly and resulted in the lowest final densities. These lower densities reflect the difficulties encountered in pressing the powder in the previous section. The relatively low surface areas of the powder would also be expected to cause it to be less sinterable. This observation is not consistent with the previous study by Davis and Griffin (1992) that found very little change in behavior between Type 3 runs to 800°C versus 600°C.

5. Type 3 reduction to 600°C resulted in good final densities in agreement with the previous study (Davis and Griffin 1992). The surface areas range from 4.8 to 5.5 m^2/g, and this appears to be high enough to give good sintering behavior, but low enough to be pressible to a reasonable green density.

6. Reduction in Ar - 4% H_2 (run 11) produced relatively high-density pellets. The ability to achieve good UO_2 powders reduced in non-combustible gas mixtures is a significant safety consideration that should be studied further.

From the final pellet densities, it can be concluded that UO_2 pellets with densities in the range from 95 to 96% TD densities can be produced using a variety of reduction conditions. Thus, it would appear

that choosing an optimum reduction technique cannot be based solely on the final densities. However, some reduction techniques can be ruled out, such as those producing burned-back powder that did not press well (runs 4 and 5) or the Type 3 runs to 800°C that resulted in low density pellets.

One of the considerations in choosing a reduction technique is whether it has the possibility of being scaled up to larger batches. A Type 3 reduction cycle provides for more control of the temperature at which the reduction occurs. For Type 1, 2, and 4 runs where reduction can occur during the heatup cycle, the amount/rate of reduction occurring as the temperature increases will depend on the communication of the powder with the H_2 and thus be strongly dependent on the batch size. For a Type 3 run, most of the reduction is delayed until the H_2 is introduced at the maximum temperature. The surface areas produced in the Type 3 runs to 600°C were 4.8, and 5.5 m^2/g. This reflects the consistency of the reduction process for a Type 3 reduction run. From this, we conclude that although Types 1 and 2 runs were useful in the exploratory runs, the associated unknowns rule them out of further consideration as viable processes for larger scale tests. Type 4 runs are considered of interest because of safety considerations since Ar - 4% H_2 is a noncombustible gas mixture.

Microstructural Characterization

Microstructural characterization was performed for sintered pellets fabricated from UO_2 reduced in runs 10, 11, and 12. Figures 3, 4, and 5 include an overview and a more detailed microstructure for each of these pellets. The porosity is fairly uniformly distributed and has dimensions as large as 100 μm. This porosity may be directly attributable to the pressing lubricant, sterotex. In Figure 4(a) from run 11, the porosity appears to be distributed along lines perpendicular to the pressing direction, suggesting a relationship with the pressing of the green pellet. Two different grain sizes appear to be present: the large grains being about 20 μm and the smaller or subgrain structure having grain sizes less than 1 μm. This bimodal grain size may reflect an inhomogeneity in the UO_2 powder. This inhomogeneity could result from the reduction process or the original calcining to produce UO_3.

The microstructure shows that specimens from runs 10 and 12 contained inclusions of relatively hard material. In Figure 5(b) (run 12), the large pore just left of center and the smaller pore above it contain a "grayish" inclusion. {The typical size and shape of the particles can be seen more clearly in the upper left hand region of Figures 8(b) and 9(b) that are presented later in this report.} The amount of material in these inclusions was not determined quantitatively, but it would appear that it was significantly less then 1%. It was ascertained that the material was not an artifact of the polishing and grinding and that the material was alumina (Al_2O_3). Because it occurred in pellets made from powder reduced in runs 10 and 12 and not in that from run 11, it was deduced that the alumina was associated with the furnace used to perform the Type 1, 2, and 3 reduction runs. Inspection of the furnace indicated the presence of white finely dispersed powder that had resulted from a previous use of alumina powder in the furnace.

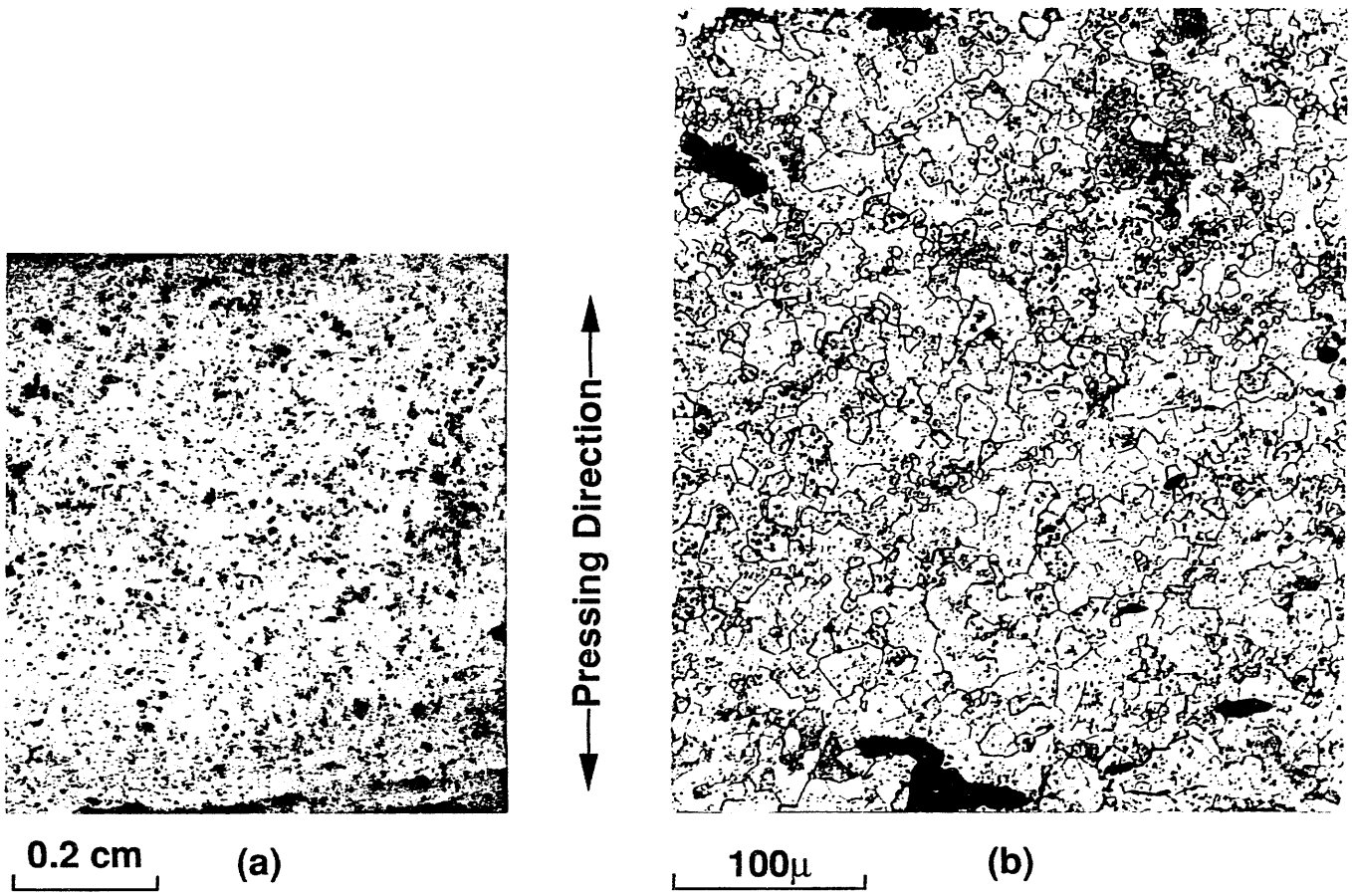

Figure 3. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 10

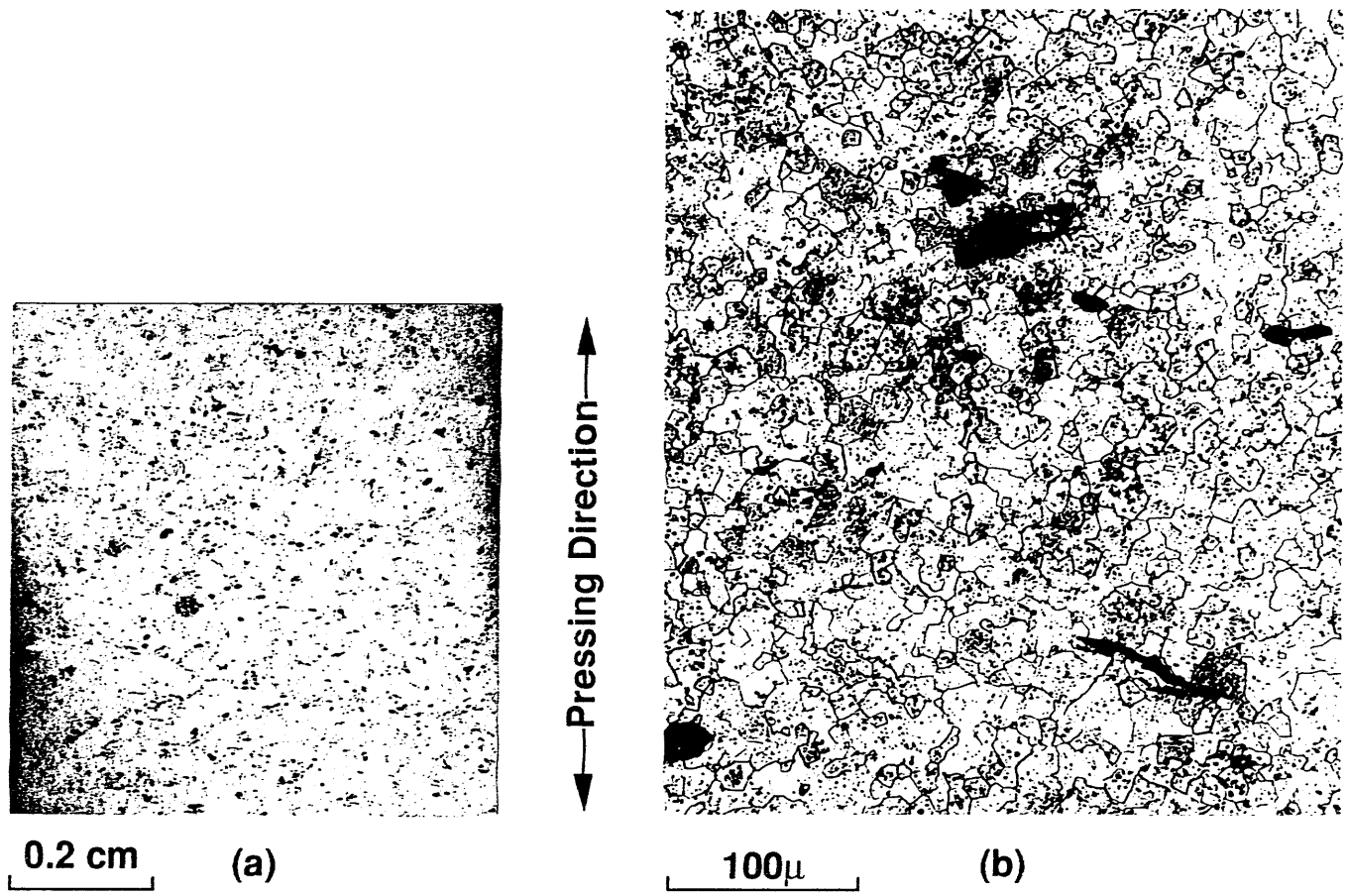

Figure 4. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 11

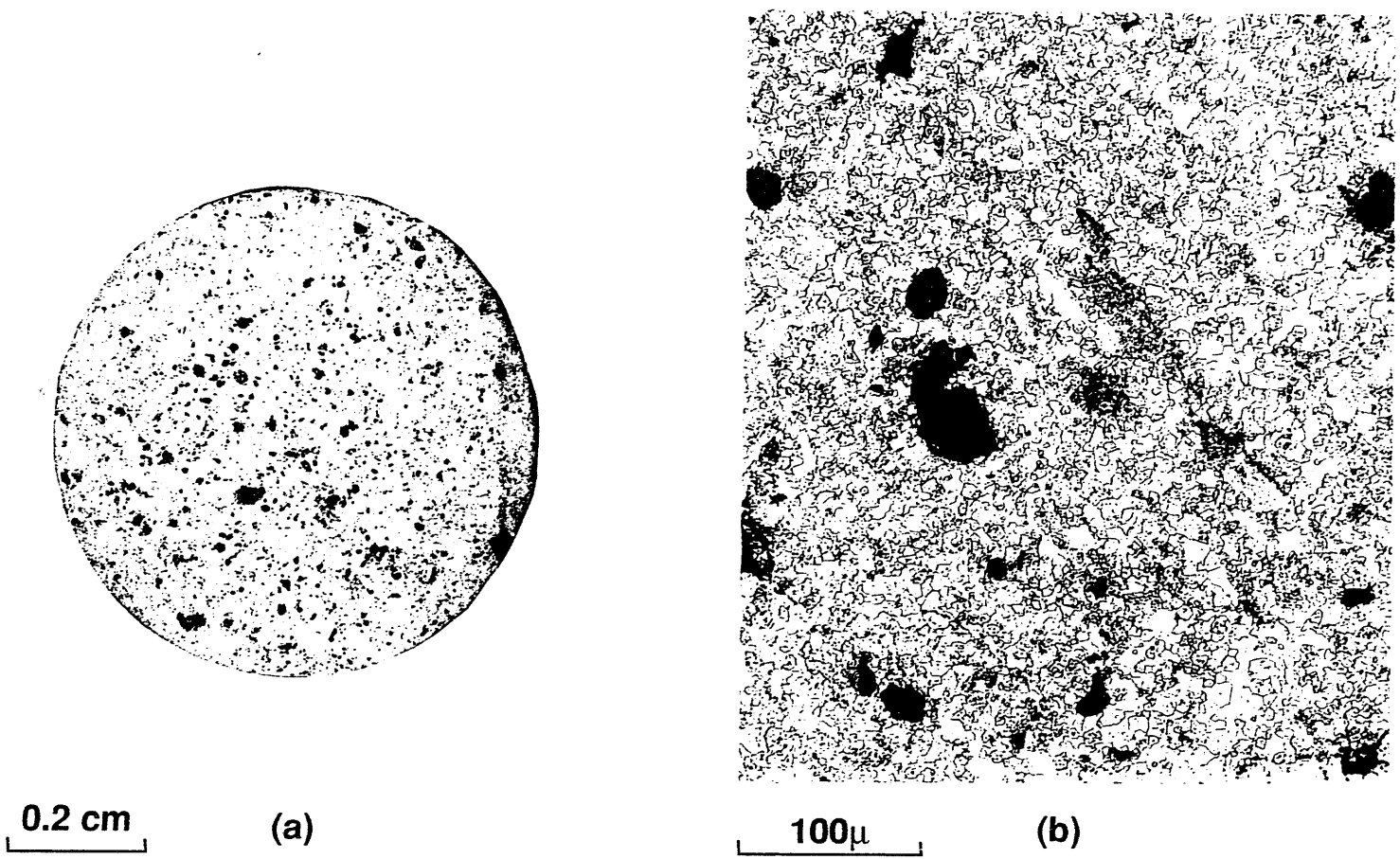

Figure 5. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 12

1.3.2 Second Series of Reduction Runs

The objective of the second series of reduction runs was to prepare larger batches of UO_2 powder and to extend the data base on the Type 3 and 4 reductions. These larger 100-g batches of powder provided sufficient material to study the effect of pressing parameters on the final sintered density. The parameters describing the second series of reduction runs are listed in Table 4. As discussed above, no Type 1 and 2 reduction runs were included in the matrix because of the difficulty of controlling reduction rates as the batch size varies. Heatup/cooldown rates for the reduction runs were as used previously for a Type 3 run so that only the conditions to be specified are those during the maximum temperature portion of the cycle.

Type 4 runs were included in the second series of reduction runs because of the safety considerations associated with Ar - 4% H_2, which is a noncombustible gas mixture. A modified Type 4 run was used and referred to as a Type 4R. Similar to the description in Table 1, Ar - 4% H_2 was used throughout the run. Type 4R runs differed from the previous Type 4 runs in that the Type 4R runs were carried out in the same furnace as the Type 1 through 3 runs and used the same heating cycles with the same gas (Ar - 4% H_2) in all three cycles. No moisture was added to the Ar - 4% H_2 in the Type 4R runs.

Runs 19 to 22 were carried out with the UO_3 powder contained in a covered tray to reduce the alumina contamination that was identified in the microstructures of the first series of reduction runs. Run 20 differed from run 19 in that the powder was held at the maximum temperature for 8 h rather than 4 h to effect more complete reduction. In runs 21 and 22, the cover was modified to permit better communication between the furnace sweep gas and the powder.

Table 4. Summary of Second Series of UO_3 Reduction Runs

Run ID	Type Run	Max. Temp. (°C)	Tap Density (g/cm^3)	O/M	Sfc Area (m^2/g)
14	3	800	1.63	2.10	2.27
15	3	600 (2 h) 800 (2 h)	1.46	2.05	6.24
16	3	700	1.64	2.06	3.09
17	3	600	1.45	2.08	6.38
18	4R	600	1.43	2.11	8.86
19	4R[(a)]	600	1.41	2.04	5.24
20	4R[(a)]	600 (8 h)	1.37	--	4.74
21	4R[(a)]	600	1.44	--	6.12
22	3[(a)]	600	1.46	2.11	5.29

(a) Indicates the pan containing the powder was covered.

Reduced UO_2 Powders

Table 4 lists the resulting UO_2 powder characteristics from the second series of reduction runs. The surface areas for the two Type 3 runs to 600°C (runs 17 and 22) are 6.38 and 5.28 m^2/g which is consistent with 4.8 to 5.5 m^2/g found in the first series. Increasing the reduction temperature to 700 and 800°C reduced the surface areas to 3.09 and 2.27 m^2/g, respectively. The 2.27 m^2/g is in good agreement with the values of 1.97 and 2.07 m^2/g found in the first series. Run 15 with the initial 2-h hold at 600°C and the subsequent increase to 800°C for 2 h gave a surface area of 6.24 m^2/g, which is in the range of the surface areas for a 4-h hold at 600°C. The good agreement of the surface areas of the reduced powders in the second series with the first series further confirms the ability to control the reduction process in a Type 3 run.

The surface areas for the Type 4R runs range from 4.7 to 8.9 m^2/g. This broad range may reflect the difficulty in controlling the rate of reduction in a Type 4 run. This is particularly true because the tray cover interferes with the accessibility of the sweep gas to the powder bed.

As expected, the tap densities for powders reduced at 700 and 800°C (run 14 and 16) are both higher than the tap densities for the other reduction runs. The higher tap densities are consistent with the lower surface areas.

Powder Processing/Pressing/Sintering

The resulting UO_2 powders from the second series of reduction runs were preslugged, granulated, sieved, and processed like the first series. Pellets were pressed using either sterotex or zinc stearate as a die lubricant. Zinc stearate had been used as a lubricant in the study by Davis and Griffin (1992) and may have been responsible for the higher densities achieved in that study. Two different types of pellets were pressed: one using 0.3 wt% sterotex as a binder and one using 0.3 wt% zinc stearate. The pellets were sintered to 1700°C using the previous sintering parameters. The average densities of the sintered pellets are given in Table 5. A more complete tabulation of the slugging and pressing parameters as well as the densities for the individual pellets are listed in Appendix E.

In general, pellets pressed with zinc stearate resulted in consistently higher final densities than those pressed with sterotex. For pellets pressed with zinc stearate, most of the UO_2 powder from the reduction runs in the second series resulted in final pellet densities in the range of 96 to 97% TD.

In agreement with the results from the first series of reduction runs, the powder obtained by reducing UO_3 at 800°C in a Type 3 reduction run resulted in the lowest sintered densities. Dropping the maximum temperature from 800 to 700°C (run 16) raised the densities somewhat, but these densities are still lower than the other densities. As indicated above, this drop in densities for a Type 3 run when the temperature is raised from 600°C to 700 and 800°C is not consistent with the results of the previous study (Davis and Griffin 1992), and future studies should address this apparent discrepancy.

Table 5. Final Densities for the Second Series of Reduction Runs

Run ID	Type Run	Max. Temp. (°C)	Average Sintered Density (TD) Sterotex	Average Sintered Density (TD) Zinc Stearate
14	3	800	89	91.5
15	3	600 (2 h) 800 (2 h)	96.5	96.8
16	3	700	94.6	95.5
17	3	600	96.1	96.6
18	4	600	95.9	96.5
19	4[(a)]	600	96.0	96.2
20	4[(a)]	600 (8 h)	93.5	94.9
21	4[(a)]	600	95.1	96.3
22	3[(a)]	600	96.0	96.8

(a) Indicates the pan containing the powder was covered.

The effect of attempting to reduce the alumina impurities by covering the pan during reduction can be determined by comparing final pellet densities from similar reduction runs for the uncovered (run 16) versus the covered (run 22) case. The final densities are essentially the same, and there is no obvious reduction of densities for run 16 that could be attributed to higher concentration of alumina inclusions. The lower densities in run 20 probably reflect the lower surface areas of the powder after the longer hold time at 800°C, but there is an uncertainty associated with the method used in covering the powder tray. The effect of the cover in restricting the H_2 containing sweep gas from communicating with the powder surface may not have been constant during the test series.

From final pellet densities in the second series of reductions, it can be concluded that the AVLIS supplied MDD-derived UO_3 powder can be used to produce high-density (96 to 97% TD) UO_2 pellets.

Microstructural Characterization

Microstructural characterization of sintered pellets fabricated from UO_2 reduced in runs 15, 17, 18, and 22 and pressed using zinc stearate was carried out. Figures 6, 7, 8, and 9 include 1) overall microstructures to determine porosity distribution and 2) higher magnification microstructures to examine grain size distribution. The porosity in this series of pellets appears to be finer and more elongated than the previous series, and the overall microstructure has a "swirled appearance," probably resulting from the flow of particles during pressing. The microstructure associated with pellets pressed using zinc stearate can be compared to the previous pellets (Figures 3 through 5) using sterotex. The pellets pressed with sterotex tended toward a larger more random porosity consistent with the lower density than those pressed with zinc stearate. As in the previous series of pellets, two different grain sizes

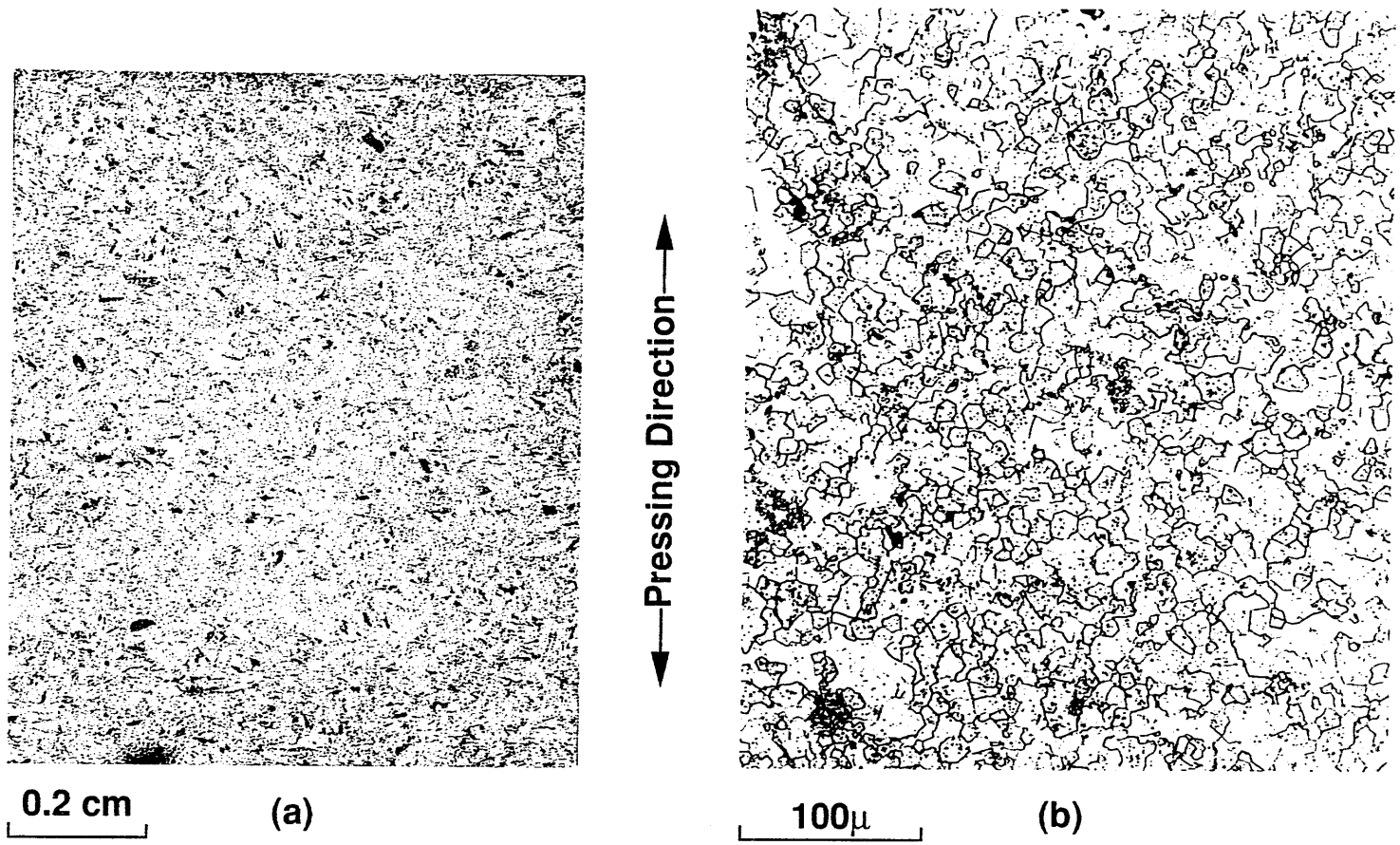

Figure 6. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 15

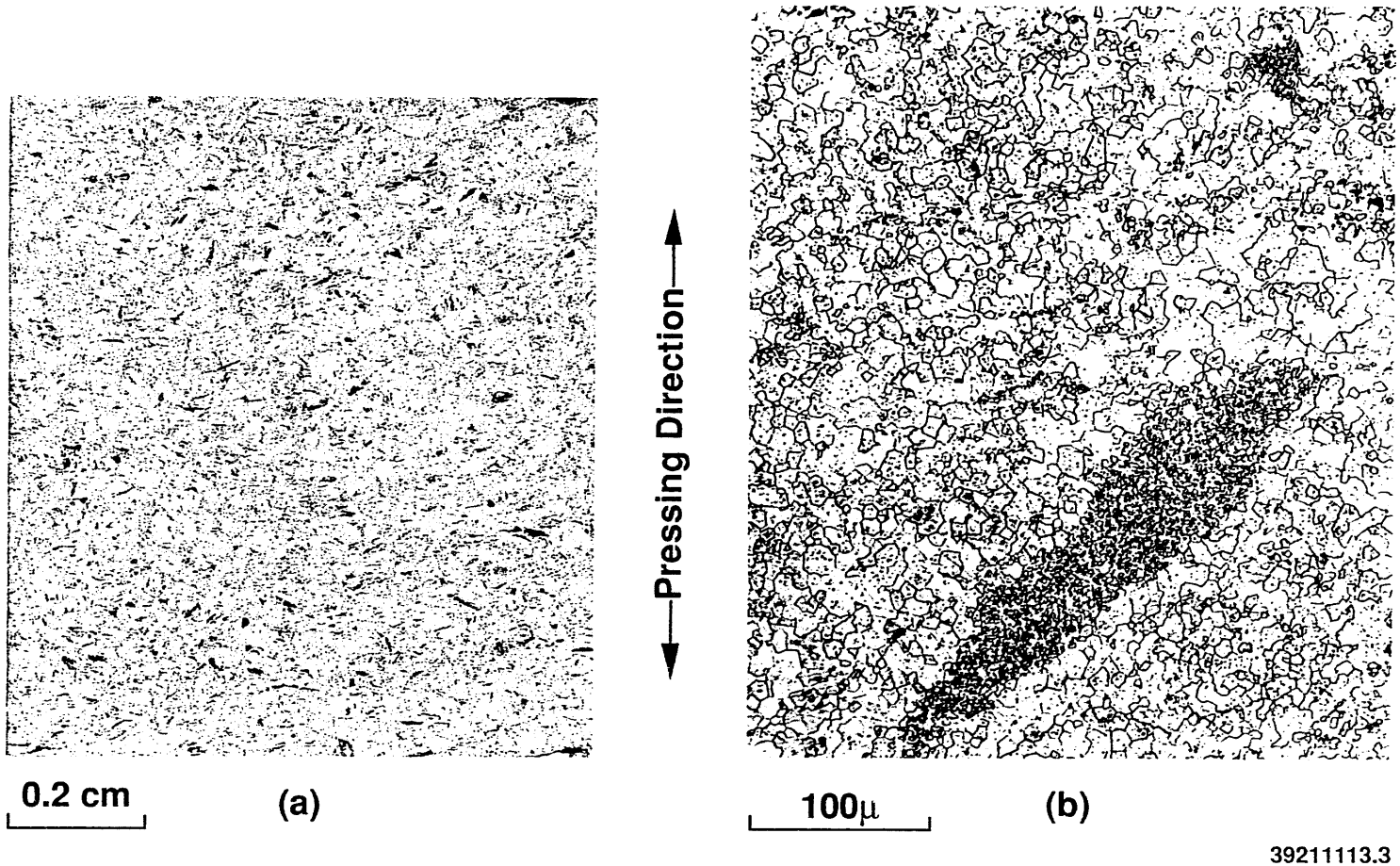

Figure 7. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 17

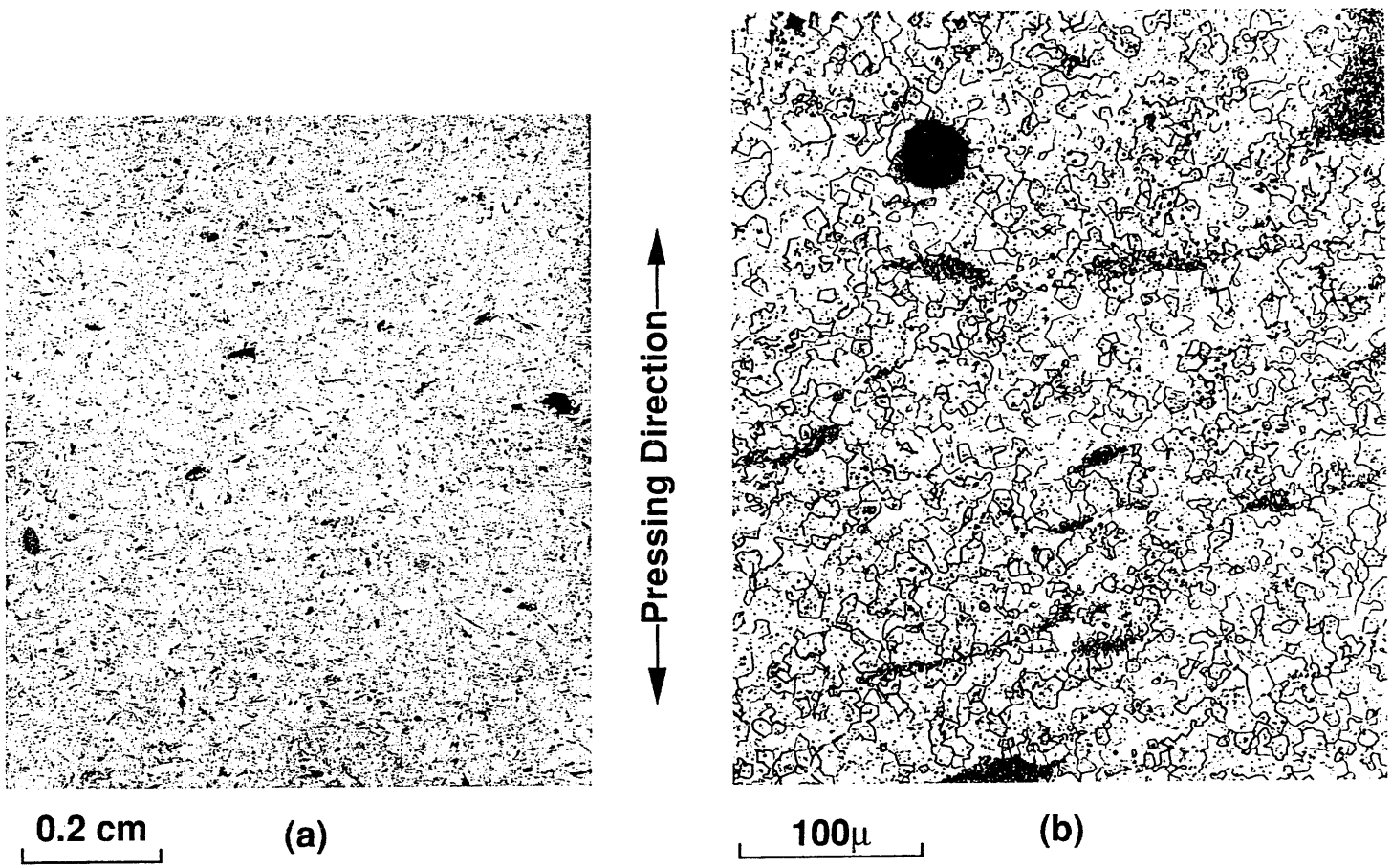

Figure 8. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 18

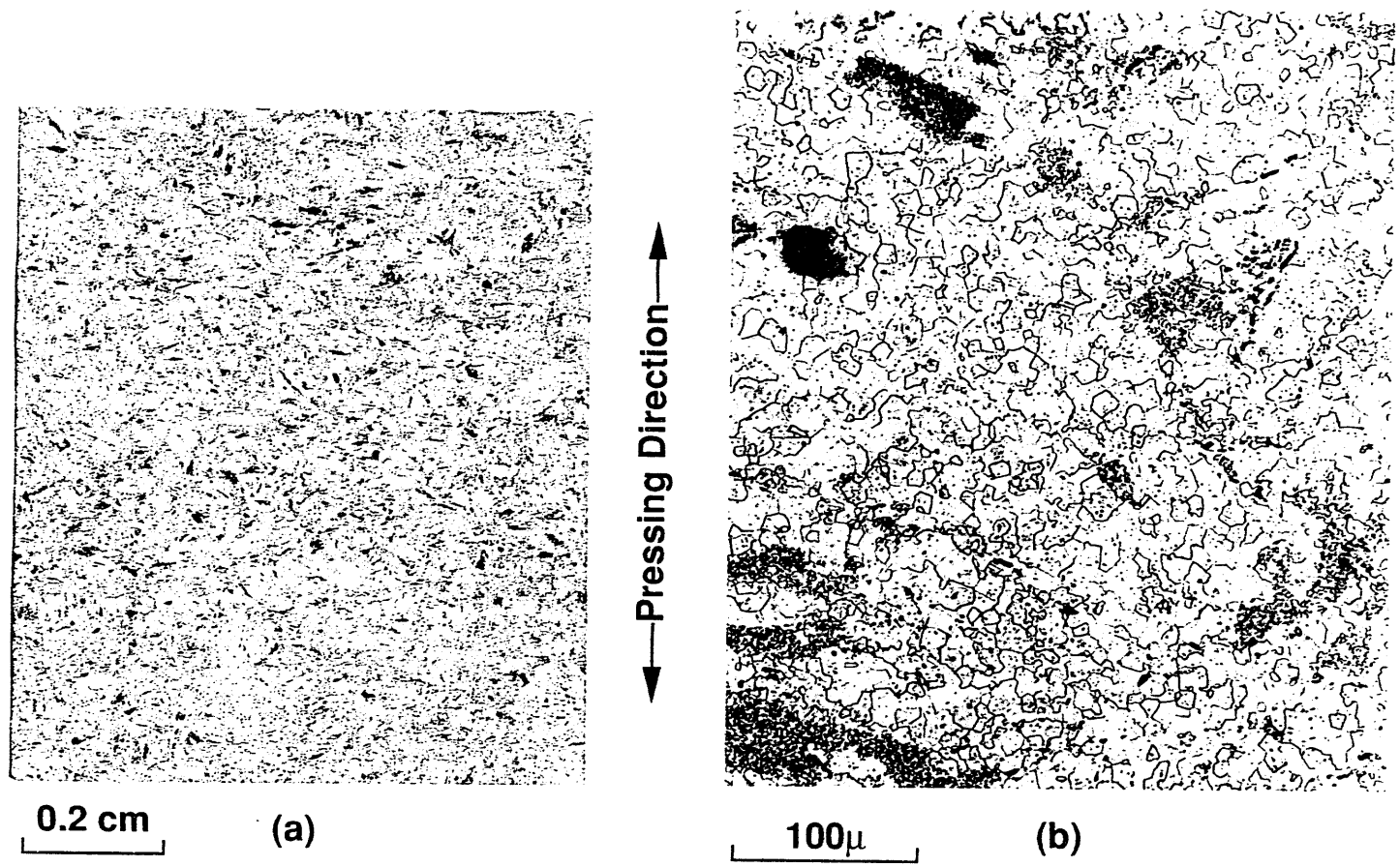

Figure 9. Microstructure of a Sintered Pellet Prepared Using Powder from Reduction Run 22

appear to exist: large grains about 20 μm and a smaller or subgrain structure with grain sizes less than 1 μm. This bimodal grain size may reflect the inhomogeneity in the UO_2 powder resulting either from the reduction process or from the inhomogeneity of the original precursor from the calcining step to produce UO_3.

The inclusions previously found in the microstructure and attributed to finely dispersed alumina (Al_2O_3) powder were observed to also be in the microstructures of the second series of pellets. Figures 8(b) and 9(b) include one of these inclusions in the upper left hand quadrant. To minimize this type of contamination, a cover was placed on the molybdenum tray containing the UO_3 powder, and run 22 was one of the reduction runs carried out with a cover. Obviously {Figure 6(b)} the cover was not effective in eliminating the contamination, and the dispersive action of the vacuum pumpdown and backfill procedures carried the alumina under the cover. Extensive cleanup or rebuilding the furnace may be necessary to eliminate the alumina inclusions.

The effect of reduced alumina impurities on the fuel-pellet densities can be determined by comparing densities from similar reduction runs for the uncovered (run 16) versus the covered (run 22) case. It is expected that the total alumina in the run 22 pellet was less than that in the run 16 pellet. The final densities are essentially the same, and no obvious reduction of densities appears for run 16 that could be attributed to a higher concentration of alumina inclusions.

1.3.3 Third Series of Reduction Runs

The purpose of the third series of reduction runs was to determine if lowering the reduction temperature of a Type 3 run to a temperature below 600°C would improve the powder's sinterability and result in a higher density final pellet. A Type 3 or Type 4 reduction run of 4 h at 600°C has been found to yield a good sinterable powder. Increasing the temperature to 800°C (run 6, 13, and 14) resulted in powder that gave lower density sintered pellets. Even powder reduced at 700°C did not result in final sintered densities as high as the powder reduced at 600°C. This suggests that even lower reduction temperatures (less than 600°C) may result in powders that sinter to higher densities than those reduced at 600°C. To determine if a lower temperature would produce as good or better powder, four additional reduction runs (runs 23 through 26) on UO_3 powder were carried out. All the runs used were Type 3 runs, where heatup and cooldown were carried out in Ar. The reduction parameters and a description of the resulting powder are summarized in Table 6. Run 23 to 500°C resulted in a powder that burned back or oxidized when the furnace was opened, exposing the powder to air. Run 24 to 550°C did not burn back. In runs 25 and 26, the powder was initially reduced at 550°C and then subsequently heated to higher temperatures. These runs resulted in powders that burned back upon exposure to air. The final heat treatment at 800°C in runs 25 and 26 was introduced to stabilize the powder, but apparently this was not the effect since burnback occurred in both cases.

The successful reduction in run 24, without burnback, indicates that stable powder UO_2 can be made at temperatures lower than 600°C. The UO_2 powder from run 24 was characterized with the following results: tap density, 1.46 g/cm^3; surface area, 7.53 m^2/g; and O/M, 2.13. Comparing these

Table 6. Summary of Third Series of UO_3 Reduction Runs

Run ID	Max. Temp. (°C)	Powder Condition
23	500	Burned Back
24	550	Good Appearance
25	550 (2 h)	
	800 (2 h)	Burned Back
26	550 (4 h)	
	800 (2 h)	Burned Back

characteristics to those for the Type 3 runs at 600°C indicates a similar tap density, but a higher surface area and O/M. The higher surface area suggests a more sinterable powder, but the higher O/M indicates that reduction was not as complete. The higher surface area is as expected and is consistent with the purpose of the series that was to use the lower reduction temperature to produce UO_2 powders that could possibly be sintered to higher densities. Green pellets were prepared from the powder reduced in run 24, but the experimental work was terminated before the pellets could be sintered. Therefore, we were not able to determine if the lower reduction temperature resulted in higher final pellet densities.

1.4 Discussion of Results

Table 7 is an overall compilation of the UO_2 powder characteristics and the final sintered densities using sterotex and zinc stearate as lubricants. Pellets pressed using zinc stearate tended to give higher densities than sterotex, and, in general, pellets pressed with sterotex had densities greater than 95% TD, and pellets pressed using zinc stearate had densities greater than 96% TD. The higher densities achieved using zinc stearate may be related to the differences observed in the microstructures. The pellets pressed with sterotex tended toward larger more random porosity than those pressed with zinc stearate.

The final pellet densities indicate that the target density of 96% TD can be achieved using several different reduction cycles. Runs 15, 17, 18, 19, 21, and 22 all had densities greater than 96% TD for pellets pressed with zinc stearate. Furthermore, the fact that using zinc stearate resulted in densities about 1% higher than sterotex in the second series of pellets suggests that the powder in the first series with pellet densities greater than 95% TD would have probably resulted in pellet densities greater than 96% TD if zinc stearate had been used as a lubricant. This implies that the majority of the reduction processes used could produce pellets with densities greater than 96% TD. Taken one step further, if density is used as the primary selection parameter, the present study did not lead to an optimum set of reduction parameters. Thus other criteria must enter into the selection, such as how well the reduction process could be applied to larger batches or continuous operation.

Table 7. Summary of UO_3 Reduction Runs and UO_2 Sintering

Run ID	Type Run	Max. Temp. (°C)	Tap Density (g/cm^3)	Sfc Area (m^2/g)	O/M	Average Sintered Density Sterotex (% TD)	Average Sintered Density Zn St. (% TD)
As-Received			1.18	7.42			
2	1	1000	1.67	7.01	2.15	96.5	
3	1	900	1.47	12.91	2.15	95.8	
4	1	800	1.48	7.72		94.5	
5	2	800		11.57		95.6	
6	3	800	1.65	1.97	2.03	93.6	
8	4	800	1.40	15.12	2.07	95.6	
9	1	600	1.37	13.10	2.10	95.6	
10	3	600	1.45	5.51	2.05	95.3	
11	4	600	1.43	5.93	2.04	95.1	
12	3	600	1.44	4.84	2.08	96.0	
13	3	800	1.51	2.07	2.02	92.5	
14	3	800	1.63	2.27	2.10	89	91.5
15	3	600 (2 h) 800 (2 h)	1.46	6.24	2.05	96.5	96.8
16	3	700	1.64	3.09	2.06	94.6	95.5
17	3	600	1.45	6.38	2.08	96.1	96.6
18	4	600	1.43	8.86	2.11	95.9	96.5
19	4(a)	600	1.41	5.24	2.04	96.0	96.2
20	4(a)	600 (8 h)	1.37	4.74		93.5	94.9
21	4(a)	600	1.44	6.12		95.1	96.3
22	3(a)	600	1.46	5.29	2.11	96.0	96.8
24	3(a)	550	1.46	7.53	2.13		

(a) Indicates the pan containing the powder was covered.

The present study did identify some reduction parameters that did not lead to stable and/or sinterable powder. The UO_2 powder obtained by reducing UO_3 at 800°C in a Type 3 reduction run resulted in the lowest sintered densities, 93.6 and 92.5% TD for runs 6 and 13 in the first series and 89 and 91.5% TD for run 14 in the second series. Dropping the temperature from 800 to 700°C (run 16) raised the densities to 94.6 and 95.5% TD; however, these densities are still somewhat lower than obtained when powders are reduced at lower temperatures. These results are not consistent with the previous study (Davis and Griffin 1992) where reductions from 600 to 800°C did not seem to affect the final density. This remains an unresolved issue.

The resulting microstructures for the final sintered pellets were shown in Figures 3 through 5 for pellets pressed using sterotex and in Figures 6 through 9 using zinc stearate. Appendix A lists the typical characteristics for UO_2 commercial fuel. Typical grain sizes for commercial fuels range from 5 to 15 μm. The porosity requirements are that the pore morphology leads to minimal in-reactor densification (e.g., <0.5% TD). To establish that the porosity is stable would require such testing as a resinter test or irradiation test. Alternatively, a qualitative assessment can be based on the pore morphology and the previous observation (Freshley et al. 1976) that densification is minimized if only a small quantity of pores with diameters less than 1 μm exist. The occurrence of the bimodal grain size (20 and 1 μm) is important only if the smaller, less than 1-μm grains contribute to in-reactor densification. Such densification can be expected to occur if an appreciable amount of porosity associated with these smaller grains that can be closed by in-reactor densification exists. Because of the high densities (>96% TD) of the current fuel pellets, it is expected that very little densification can be achieved by resintering or in-reactor densification. However, further study will be required to establish the stability of the current microstructures.

Surface areas are often associated with a powder's activity or its ability to sinter. In Table 7, surface areas ranged from 1.97 to 15.12 m^2/g. The lowest surface areas were found for runs 6, 13, and 14 (1.97, 2.07, and 2.27 m^2/g). These powders were produced by Type 3 runs to 800°C and have in common that they resulted in the lowest density sintered pellets. The highest surface areas were for runs 3, 5, 8, and 9, and they all resulted in sterotex densities greater than 95% TD, which within experimental error are as high as those for any other powder. These runs have in common that they are not Type 3 runs, and hence, the heatup was done in a H_2 containing sweep gas so that reductions started during the heatup. Therefore, the reduction of UO_3 to UO_2 is expected to occur at lower temperatures. The highest sintered density pellets resulted from powders with intermediate surface areas, such as run 15 with a surface area of 6.24 m^2/g, that produced one pellet with a sintered density for zinc stearate of 97% TD (average density of 96.8% TD). This illustrates the importance of powder characteristics other than surface area in determining the final densities.

The preceding discussion points out that sintering is a complex process dependent on a wide variety of parameters. A partial list includes

- surface area
- powder morphology, which in turn is dependent on the powder precursor (UO_3)
- chemical purity since many impurities can enhance or inhibit sintering
- particle size distribution
- green density

- stoichiometry
- sintering temperature, time, and heating rates

In commercial practice, most of these variables are addressed in the powder specifications that have been developed to meet a specific objective. Because of funding and time constraints, this study was limited to determining whether the MDD-derived UO_3 powder supplied by AVLIS could be fabricated into commercial grade pellets on a laboratory scale. To meet this goal with minimum resources, addressing a wide variety of parameters was not considered, and a sintering test with pellet evaluation was the major objective.

1.5 Comparison to Previous Results

The results of the present study can be compared to the earlier study of Davis and Griffin (1992). The previous study included a variety of starting UO_3 powders that had been calcined both at ORNL and National Lead of Ohio. In this follow up study, it was determined that additions of NH_4NO_3 to the uranyl nitrate feed solution improved the sinterability of the UO_2 powder and resulted in higher density UO_2 pellets. Thus, an important parameter in preparing sinterable UO_2 powders from UO_3 is the presence of NH_4^+/U. For the study by Davis and Griffin, the nominal NH_4^+/U ratio was 2.0, whereas in the current study, this ratio was 2.6. This difference in ratio may play an important role in the differences found between the present and previous studies.

Another difference in the method of denitration is in the tube temperature of the calcining kiln. The current UO_3 powder was prepared using a tube temperature of 600°C. Previously, the tube temperatures ranged from 390 to 620°C, but most of the reductions were done at temperatures near 500°C. Thus, the current UO_3 powders represent tube temperatures at the upper limit of the previous denitrations.

The present as-received UO_3 powder had a surface area of 7.42 m^2/g and a tap density of 1.18 g/cm^3 compared to UO_3 powders in the previous study that had surface areas in the range from 8.1 to 11.5 m^2/g and tap densities from 0.77 to 0.97 g/cm^3. It would appear that the present powder had a lower surface area and a higher tap density, suggesting that it may not be as active (with respect to sintering) as the previous powder.

The characteristics of the resulting UO_2 powders can also be compared. The most meaningful comparison of the present and previous results is to compare reduced UO_2 powder using similar reduction parameters, i.e., to compare only the present Type 3 reductions to 600°C (i.e., runs 10, 12, 17, and 22) with the previous powder that was also reduced by the nominal reduction method. These UO_2 powders for the present study had surface areas in the range of 4.84 to 6.38 m^2/g, tap densities from 1.44 to 1.46 g/cm^3, and O/Ms from 2.04 to 2.08. If the powders reduced at the higher temperatures in Davis and Griffin are deleted from the ranges of powder characteristics, the surface areas are from 6.91 to 11.91 m^2/g, and the tap densities range from 0.84 to 1.26 g/cm^3 with O/Ms in the range from

2.13 to 2.26. This comparison indicates that the present UO_2 powders have lower surface areas, higher tap densities, and lower O/Ms than those in the previous study of Davis and Griffin.

The lower O/Ms in the present study compared to the previous study may reflect the period of time the powder is exposed to air between the reduction and the O/M measurement. It was observed in the present study that the O/M of the powder increased with increasing time when exposed to an air atmosphere. All the O/Ms listed in the present study were measured shortly after reduction. The exposure times for the previous powders are not known.

The final sintered densities for the present study can also be compared with the previous study. Again comparing only current powder lots reduced in Type 3 runs to 600°C, we have the present density range of 95.3 to 96.1% TD compared to the previous density range for UO_2 (NH_4^+/U ratio equal 2.0) of 97.2 to 98.1% TD. It is to be noted that the lowest densities for the present study were pressed using sterotex rather than zinc stearate. Considering only present densities using zinc stearate gives a range of 96.6 to 96.8 g/cm^3. Thus, for the Type 3, 600°C reduction, the present powder is not yielding pellets as dense as obtained in the previous study. This would be consistent with the higher tap densities and lower surface areas found for both the UO_3 and UO_2 powders in the current study.

In the previous study (Davis and Griffin 1992) considerable attention was given to a pellet pressing problem that developed during the later stages of the study. This problem was an end-defect on the pressed green pellets that occurred as a shallow, surface flake, scale or blister, and was not a typical endcap usually associated with higher pressures. One way to prevent the end-defect was to use the hold-down feature of the hydraulic press during pellet ejection and thus restrain the pellet during ejection. Such a solution was not considered appropriate for extension to production situations. Alternatively, it was recommended that a change in powder morphology be made by reducing the sub-micron particles (reflected in a lower tap density), which would improve powder packing (less pressure to obtain green density). By adjusting the parameters in the calcining kiln, several UO_3 powder lots containing uniform agglomerates and a minimum quantity of sub-micron fines were processed. This revised processing produced UO_2 powders that could be pressed without the end-defect. It is significant that the end-defect seen previously was not observed in the present work. It appeared as if the current powder morphology was different, with the current powder having a lower surface area and higher tap density. Controlling the physical properties of the powder is an important consideration both in processing and in final density.

1.6 Recommendations for Further Work

The present study was designed to determine if the MDD-derived UO_3 powder supplied by AVLIS could be reduced to UO_2 that could then be fabricated into commercial grade fuel pellets on a laboratory scale. By properly choosing the reduction parameters and by using previously developed methods of powder preparation, pellet pressing, and sintering, pellets with densities as high as 97% TD can be fabricated. However, pellets with densities greater than the original goal density of 96% TD were obtained for a wide range of reduction conditions. The study did not result in a specific "best"

method for producing sinterable UO_2 powder, and thus other criteria must enter into the selection process, such as whether the reduction process can be applied to larger batches or to continuous operation.

Because of the inherent controllability of the Type 3 reduction process, as compared to other processes considered in this study, it is the most suitable for scale-up to larger batches or to continuous operation. The current study confirmed the results of the previous study in that a Type 3 reduction to 600°C gave good, sinterable UO_2 powder. At the later stages of the present study, the Type 3 reduction process was extended to temperatures less than 600°C. This appeared to produce stable powder in some cases, but burnback was a problem. As shown earlier, burnback can sometimes be solved by deactivating the surface using "RT conditioning." Whether these lower temperatures would result in higher final densities was not established because the final sintering was not carried out.

A noncombustible mixture of Ar - 4% H_2 was found be a viable sweep gas for reducing UO_3 to a stable UO_2 powder. Adding water vapor to Ar - 4% H_2 in runs 7 and 11 appeared to be an effective means for facilitating reduction. Whether water vapor plays an important role in the reduction process was not established. These results of the present study could be important if a noncombustible gas mixture offered advantages for safety considerations.

The present reduction study was directed solely at producing sinterable powder with the final sintered pellet density being the means for evaluating the process. Although such a process is a direct approach to the problem, it does not lead to a thorough understanding of the processes controlling the reduction. Characterizing the reduction process using measurements such as the differential thermal analysis/thermal gravimetric analysis (DTA/TGA) can be particularly useful in determining the underlying processes and in establishing future directions. More extensive characterization of the powders using measurements such as particle size analysis, phase identification (x-ray) or scanning electron microscopy (SEM) should also be useful.

Basic tests that would support the qualification of these pellets for commercial nuclear fuel were not carried out. These include data such as impurity analyses of the final pellets and indicators of the stability in a radiation environment such as resinter testing. Ultimately, actual irradiation testing would be required for qualification as commercial power reactor fuel.

If the results of the laboratory study are to support the commercial production of UO_2 fuel pellets, it is necessary to demonstrate that laboratory processes can be scaled up to commercial quantities of material. In preparation for scaling up to powder batches as large as 1000 g, a larger furnace was identified for use. Figure 10 is a picture of this furnace and the stainless steel retort that was designed and fabricated to use in reducing UO_3. The volume available for powder reduction was 6 in. in diameter over a uniform hot zone 12 in. in length. It was planned that the initial operation would be carried out using noncombustible mixtures of H_2.

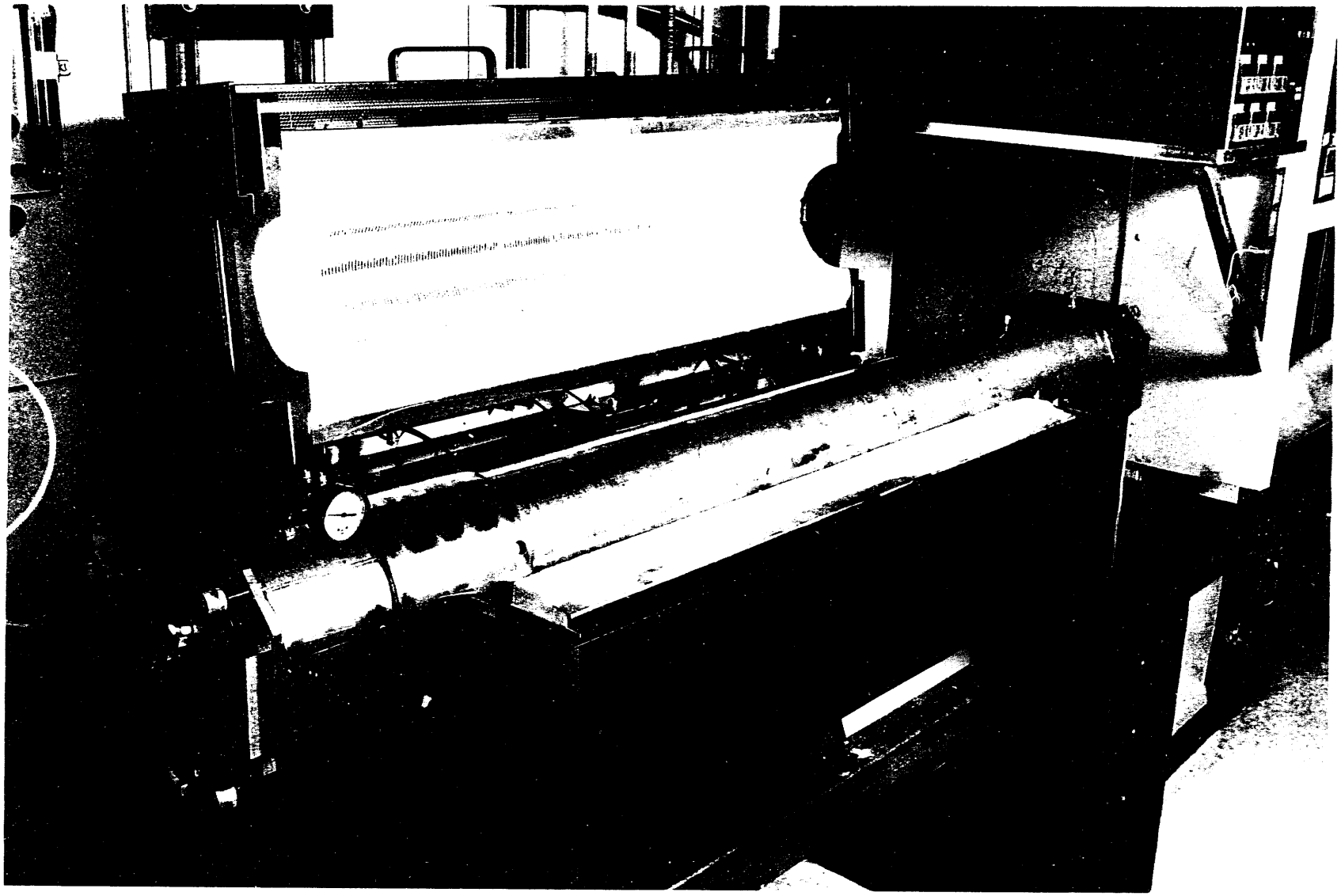

Figure 10. Furnace and Associated Retort for the Reduction of Large Batches of UO_3 Powder

Only one type of UO_3 powder was provided by ORNL for evaluation. The ability to achieve sintered densities greater than 96% TD for a number of different reduction parameters suggests that the reduction of UO_3 to UO_2 may not be the critical process in developing a powder that will sinter to high densities. The critical process may be the initial calcination process to produce UO_3. The UO_3 powder provided by ORNL for this study had been calcined from a uranyl nitrate solution to which NH_4NO_3 had been added to give a NH_4^+/U ratio of 2.6. In the previous study (Davis and Griffin 1992), this NH_4^+/U ratio had been 2.0. The comparison of the present results with those from the previous study suggest that higher densities may be achieved by going to an NH_4^+/U ratio of 2.0. However, the present study did not observe any problems with pressing defects in the green pellets, and this may also be attributable to the higher NH_4^+/U ratio. In addition to a lower NH_4^+/U ratio, the previous study tended to have lower calcining temperatures. To clearly define the effect of the NH_4^+/U ratio on final pellet density, a study involving only a change in the NH_4^+/U ratio should be carried out.

2.0 Conclusions

The "AVLIS Modified Direct Denitration: UO_3 Powder Evaluation" study at PNL demonstrated that AVLIS-enriched uranium converted to UO_3 can be used to prepare UO_2 pellets having densities in the range required for commercial power reactor fuel. Specifically, the program has demonstrated that

1. MDD-derived UO_3 powders can be reduced to sinterable UO_2 powder using reduction techniques that allow control of the final powder characteristics.

2. The resulting UO_2 powders can be processed/sintered using standard powder preparation and pellet fabrication techniques to yield pellets with densities greater than 96% TD.

3. Pellet microstructures appear similar to those of power reactor fuel, and because of the high final pellet densities, it is expected that they would remain stable during in-reactor operation.

4. The results of the present study confirm the results of a similar study carried out in 1982 (Davis and Griffin 1992).

The laboratory processes were selected on the basis that they could be scaled up to standard commercial fuel processing. However, larger scale testing may be required to establish techniques compatible with commercial fuel fabrication techniques.

3.0 References

Davis, N. C. and C. W. Griffin. 1992. *Pellet Fabrication Development Using Thermally Denitrated UO_2 Powder*, PNL-4305, 1982 and reissued as PNL-4305, 1992, Pacific Northwest Laboratory, Richland, Washington.

Freshley, M. D., D. W. Brite, J. L. Daniel, and P. E. Hart. 1976. "Irradiation-Induced Densification of UO_2 Pellet Fuel," *J. Nuclear Materials*, 62:138-166.

Haas, P. A., R. D. Arthur, and W. B. Stines. 1981. *Development of Thermal Denitration To Prepare Uranium Oxide and Mixed Oxide for Nuclear Fuel Fabrication.* ORNL-5735, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

U.S. Atomic Energy Commission (US AEC). 1961. *Uranium Dioxide Properties and Nuclear Applications*, J. Belle ed., Naval Reactors, Division of Reactor Development.

U.S. Department of Energy (US DOE). 1987. *Characteristics of Spent Fuel, High-Level Waste, and Other Radioactive Wastes Which May Require Long-Term Isolation*, Volume 3 of 6, DOE/RW-0184. Office of Civilian Radioactive Waste Management, Washington, D.C.

Appendix A

Typical Characteristics of Commercial UO_2 Fuel Pellets

Appendix A

Typical Characteristics of Commercial UO_2 Fuel Pellets

Current commercial UO_2 pellets are produced according to specifications agreed to between the vendor and the buyer. Specifications for sintered UO_2 pellets, as listed in the American Society for Testing and Materials (ASTM) C776-89, are $\geq$87.7 weight percent uranium on a dry weight basis, oxygen-to-uranium ratio of 1.99 to 2.02, impurity limits as listed in Table A.1, and equivalent boron content (EBC) of ≤ 4 μg/g. It also states in C776-89 that pellet dimensions, initial density, grain size, and pore morphology shall be specified by the buyer. Typical ranges for these buyer-specified parameters are initial density of 94 to 96% of theoretical density (10.31 to 10.53 g/cm^3), grain size of 5 to 15 μm, and a pore morphology that leads to minimal in-reactor densification (e.g., <0.5% TD) (US DOE 1987). A stable pore morphology largely consists of minimizing the quantity of pores of diameter less than 1 μm (Freshley et al. 1976). Burnup of commercial fuel is currently limited by regulation to 60 to 62 MWd/kgM peak rod-average. Fuel pellet characteristics, other than initial ^{235}U enrichment level, have not been particularly impacted by the desire to increase burnup levels; the principal impact has been on cladding and operating limits. One design change for the fuel pellet is to add Gd_2O_3 as a burnable poison.

References

U.S. Department of Energy (DOE). 1987. *Characteristics of Spent Fuel, High-Level Waste, and Other Radioactive Wastes Which May Require Long-Term Isolation*, Volume 3 of 6, DOE/RW-0184. Office of Civilian Radioactive Waste Management, Washington, D.C.

Freshley, M. D., D. W. Brite, J. L. Daniel, and P. E. Hart. 1976. "Irradiation-Induced Densification of UO_2 Pellet Fuel," *J. Nuclear Materials*, 62:138-166.

Table A.1. ASTM C776-89 Limits on Impurities in Sintered UO_2 Pellets

Impurity	Maximum Concentration (wppm)
Total Impurities	1500
Aluminum	250
Carbon	100
Calcium and Magnesium	200
Chlorine	25
Chromium	250
Cobalt	100
Fluorine	15
Hydrogen	2
Iron	500
Nickel	250
Nitrogen	75
Silicon	250
Thorium	10

Appendix B

Summary of Process Flow Chart

Appendix B

Summary of Process Flow Chart

The present study to demonstrate the viability of reducing UO_3 to UO_2 and producing high density UO_2 pellets was based on the previous process used by Davis and Griffin (1992). Figure B.1 is the flow chart taken from the earlier studies.

UO_3 Powder Preparation/Receipt of UO_3

The UO_3 powder lots were supplied by Oak Ridge National Laboratory (ORNL) and included powder produced by the thermal denitration of uranyl nitrate produced with and without additions of NH_4NO_3 to the feed solution. The test matrix included samples from the ORNL laboratory rotary kiln and from a larger scale rotary kiln at National lead of Ohio. Upon receipt at Pacific Northwest Laboratory (PNL), the bulk density and surface area of the as-received UO_3 were determined before reduction to UO_2 and subsequent processing.

Calcination/Reduction to UO_2

The as-received UO_3 powder was calcined/reduced in a batch furnace to remove residual moisture and volatile material not removed in the initial calcine at ORNL and to reduce the UO_3 to UO_2. Because moisture and volatile material are removed during this reduction process, both calcination and reduction are occurring at this time. However, to avoid confusion with the initial calcination that was carried out at ORNL, the conversion of the as-received UO_3 powder to UO_2 is referred to as "reduction." This reduction process was not considered to be a reference process for a commercial process because a continuous calcine/reduction furnace would be preferred over a batch-type laboratory process. The furnace was a cold-wall refractory-metal furnace (resistance heated) normally used for high-temperature sintering. The nominal reduction process involved heating the powder in flowing Ar to 600°C at a heating rate of 300°C/h. At 600°C, 50% Ar - 50% H_2 was introduced and the temperature was held constant for 4 h. After 4 h, the cover gas was changed to Ar, and the furnace was cooled at a rate of 300°C/h. To reduce the possibility of powder oxidation, the Ar flow was continued overnight until the powder had stabilized and cooled to room temperature before opening the furnace to air.

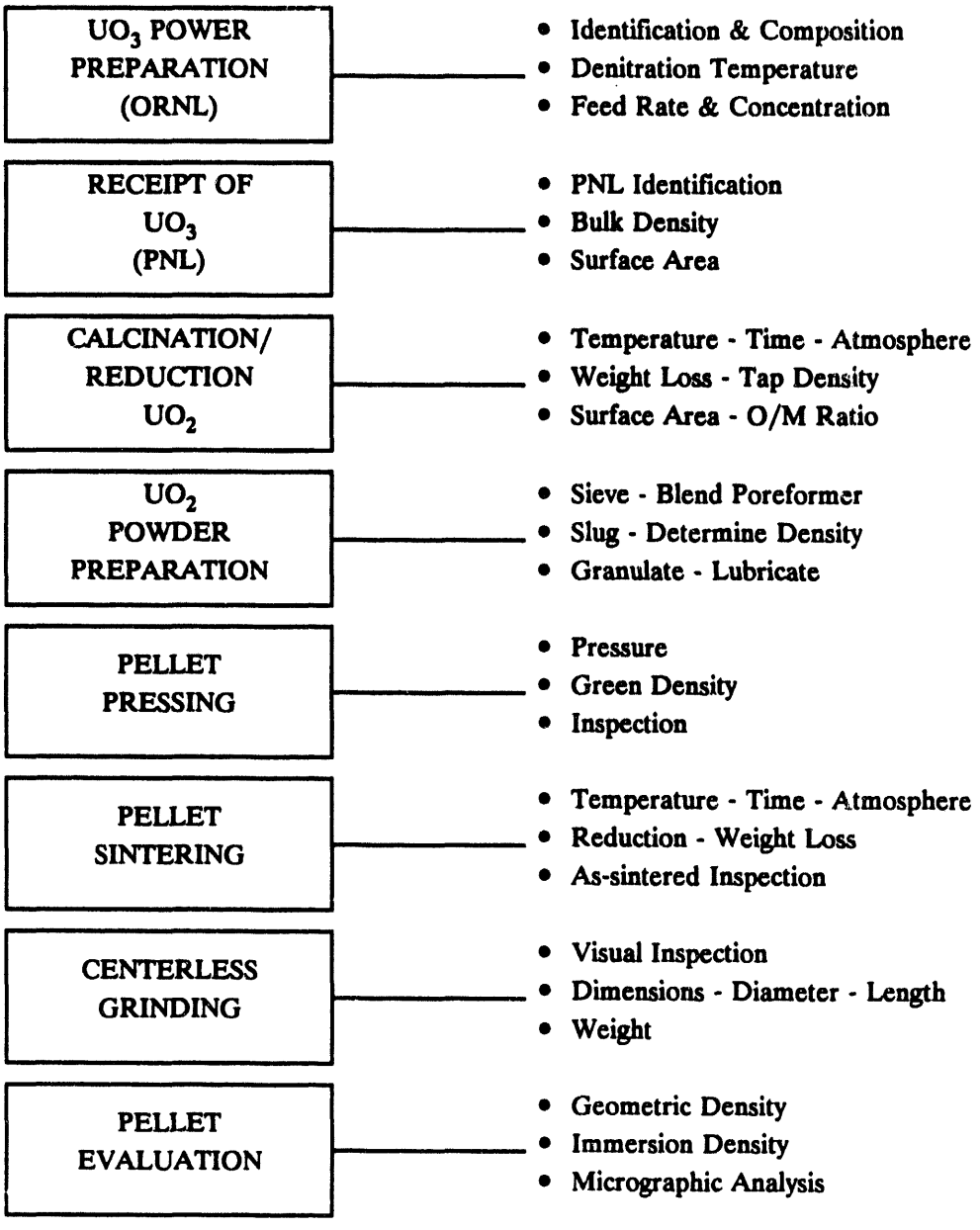

Figure B.1. Process Flow Chart with Evaluation Procedure

UO_2 Powder Preparation/Pressing

After reduction, the resulting UO_2 powder consisted of fine fluffy particles that required pressures as high as 25 Kpsi to obtain slug densities on the order of 4.3 g/cm^3. The slugs were granulated to pass through a 20-mesh screen. In the standard procedure, 0.3 wt% zinc stearate was blended with the granulated UO_2 to provide lubrication for pellet pressing. To obtain the lower fast breeder reactor fuel

(FBR) densities {88 to 92% theoretical density (TD)} pore formers were added to reduce pellet density. An automatic double action hydraulic press was used to press 0.425-in. (1.080 cm) diameter pellets using pressures in the range from 40 to 50 Kpsi. The green pellets were labeled, measured, weighed, and inspected visually before sintering.

Pellet Sintering/Grinding/Evaluation

The green pellets were placed in molybdenum sintering trays and sintered in a cold-wall refractory-metal furnace (resistance heated) similar to the one used above for the reduction cycle. The sintering cycle involved heating at 150°C/h to 450°C, at 300°C/h to 1700°C, holding for 8-h at 1700°C, and cooling at 400°C/h. The atmosphere was 50% Ar - 50% H_2 flowing at 20 standard cubic feet per second (SCFH) for the entire cycle. After sintering, all the pellets were centerless ground using a diamond wheel to provide a uniform finish for inspection and to allow accurate dimensional measurements. Pellet evaluation included geometric and immersion density, visual inspection, and final microstructural examination.

Reference

Davis, N. C., and C. W. Griffin. 1992. *Pellet Fabrication Development Using Thermally Denitrated UO_2 Powder*, PNL-4305, 1982 and reissued as PNL-4305, 1992, Pacific Northwest Laboratory, Richland, Washington.

Appendix C

Calciner Operating Parameters and Characteristics of the AVLIS-Supplied MDD-Derived UO_3

Appendix C

Calciner Operating Parameters and Characteristics of the AVLIS-Supplied MDD-Derived UO_3

Calciner Operating Parameters

- Modified Direct Denitration (MDD)
- Uranyl Nitrate Solution
  - NH_4NO_3/U: 2.6
  - Uranium concentration: 500 g/L
  - Acidity near neutral: 0.05 molar H^+ from HNO_3
  - Feed rate: 21 to 25 cc/min
- Calciner Tube Operation
  - Tube size: 4 in. ID
  - Furnace temperature: 600°C
  - Centerline temperature: 500 to 525°C
  - Air purge (outlet): 1/2 SCFM
  - Tube rotation: 10 rpm
  - Tube inclination: 3 degrees to the horizontal

Powder Characterization

- Phase Determination
  - Major constituent: $UO_3 * 0.8\ H_2O$
  - Intermediate constituent: UO_3 tetragonal
  - Minor constituent: UO_3 hexagonal
- H_20 Content: 0.52 wt%
- Nitrate (NO_3): 1.0 wt%
- Surface Area: 6.49 m^2/g
- Density: 6.00 g/cm^3
- Particle Size Analysis
  - 100% 29.85 μm or less
  - 90% less than 12.4 μm
  - 50% less than 3.93 μm
  - 10% less than 0.95 μm
- Sieve Analysis
  - 100% -25 mesh (710 μm)
  - 42.3% +60 mesh (250 μm)
  - 25.7% +140 mesh (105 μm)
  - 13.0% +230 mesh (62 μm)
  - 11.9% +400 mesh (38μm)
  - 7.1% -400 mesh

- Wt loss to 1000°C (U_3O_8): 7.8 wt%

- Major Impurities

Impurity	wppm
Fe	185
C	61
S	< 100
Na	60
Th	46
Cu	30
Zn	24
Ca	22
Al	19
Cr	19
K	20
Ni	14
Mg	14

Appendix D

Oxygen to Metal Ratio (O/M) Measurements

Appendix D

Oxygen to Metal Ratio (O/M) Measurements

The O/M of the powders was determined using the method described by McNeilly and Chikalla (1971). This technique is based on determining the weight loss (change) that occurs when the nonstoichiometric oxide is heated at 800°C for 6 h in an atmosphere in which the oxygen potential is maintained at approximately -101 Kcal/mole. The weight loss is equivalent to the amount of oxygen lost in the transition to stoichiometry. The oxygen potential can be approximated by equilibrating the specimen in Ar - 4% H_2 bubbled over 0°C water. The powder specimen was placed in an alumina tray, and the reduction was carried out in a heated quartz tube. The O/M of each powder batch was determined after the reduction to UO_2. The O/M of UO_2+x was determined from the following formula for x:

$$x = 270.03[W_i/W_f - 1]/16$$

where W_i and W_f are the initial and final weights of the powder before and after 6 h at 800°C.

Reference

McNeilly, C. E., and T. D. Chikalla. 1971. "Determination of Oxygen/Metal Ratios for Uranium, Plutonium, and (U,Pu) Mixed Oxides," *J. Nucl. Mater.* 39, 77-83.

Appendix E

Compilation of the Pressing Pressures and Resulting Densities for the Powder Slugging, Green Pellet Fabrication, and After Final Sintering

Table E.1. Slugging Pressure and Density Versus Sintered Density Using Sterotex as a Die Lubricant

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)(%T.D.)	Geometric (g/cm^3)(%T.D.)
2-10	1000	21.0	4.1	35.4	5.08	10.48 (95.6)	10.48 (95.6)
2-11				35.4	4.90	10.45 (95.4)	10.44 (95.3)
2-25				49.6	5.80	10.59 (96.6)	10.58 (96.5)
2-26				49.6	5.40	10.56 (96.4)	10.58 (96.5)
3-12	900	21.0	4.05	35.4	5.03	10.46 (95.4)	10.49 (95.7)
3-13				35.4	4.90	10.59 (96.6)	10.51 (95.9)
3-31				49.6	5.06	10.54 (96.2)	10.55 (96.3)
3-32				49.6	5.11	10.54 (96.2)	10.58 (96.5)
4-50	800	23.0	3.98	35.4	4.80	10.34 (94.6)	10.42 (95.1)
4-51				21.0	3.90	9.91 (90.4)	9.84 (89.9)
4-52				35.4	4.70	10.32 (94.2)	10.35 (94.4)
4-54				35.4	4.80	10.40 (94.9)	10.35 (94.4)
5-1	800	21.0	3.60	21.0	4.10	10.39 (94.8)	10.44 (95.3)
5-3				35.4	4.56	10.52 (96.0)	10.35 (94.5)
5-4				49.6	4.70	10.49 (95.7)	10.55 (96.2)
5-5				49.6	4.70	10.51 (95.9)	--

Table E.1. (contd)

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)(%T.D.)	Geometric (g/cm^3)(%T.D.)
6-14	800	10.6	4.25	35.4	5.60	10.35 (94.5)	10.36 (94.5)
6-17				39.6	5.15	10.30 (93.9)	10.26 (93.6)
6-33				32.6	5.50	10.34 (94.3)	10.32 (94.2)
6-34				28.3	5.20	10.03 (91.5)	10.23 (91.5)
8-6	800	28.3	4.00	35.4	4.40	10.41 (95.0)	10.43 (95.1)
8-7				35.4	4.45	10.43 (95.2)	10.42 (95.1)
8-18				49.6	5.00	10.52 (96.0)	10.55 (96.3)
8-21				49.6	5.03	10.52 (96.0)	10.55 (96.3)
9-8	600	28.3	3.8	35.4	4.60	10.44 (95.3)	10.43 (95.2)
9-22				49.6	4.90	10.53 (96.1)	10.45 (95.4)
9-23				49.6	4.90	10.47 (95.5)	10.49 (95.7)
9-24				49.6	4.84	10.45 (95.3)	10.49 (95.7)
10-35	600	22.7	4.45	42.5	4.98	10.47 (95.5)	10.47 (95.5)
10-36				39.6	4.92	10.44 (95.3)	10.43 (95.2)
10-38				43.9	4.80	10.44 (95.2)	10.47 (95.5)
10-40				43.9	5.00	10.44 (95.3)	10.53 (96.1)

Table E.1. (contd)

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)(%T.D.)	Geometric (g/cm^3)(%T.D.)
11-41	600	19.8	4.40	35.4	5.00	10.39 (94.8)	10.35 (94.8)
11-42				35.4	5.00	10.43 (95.2)	10.44 (95.3)
11-43				35.4	5.10	10.46 (95.4)	10.46 (95.4)
12-44	600	17.0	4.30	35.4	5.10	10.50 (95.8)	10.51 (95.9)
12-45				35.4	5.00	10.53 (96.0)	10.49 (95.7)
12-48				35.4	5.10	10.50 (95.8)	10.49 (95.7)
12-49				35.4	5.20	10.54 (96.2)	10.57 (96.4)
13-55	800	21.0	4.33	24.8	5.15	10.09 (92.1)	10.12 (92.3)
13-56				24.8	5.14	10.02 (91.4)	10.03 (91.5)
13-57				39.8	5.56	10.25 (93.5)	10.24 (93.4)
13-59				35.4	5.39	10.20 (93.0)	10.16 (92.7)
14-64	800	15.6	4.80	35.4	5.44	9.96 (91.0)	--
14-65				35.4	5.54	9.68 (88.3)	--
14-66				35.4	5.52	9.80 (89.5)	--

Table E.1. (contd)

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)(%T.D.)	Geometric (g/cm^3)(%T.D.)
15-26	800/600	17.0	4.33	46.7	5.29	10.58 (96.5)	--
15-27				46.7	5.30	10.57 (96.4)	--
15-28				46.7	5.31	10.56 (96.4)	--
16-38	700	14.2	4.39	46.7	5.70	10.38 (94.7)	--
16-37				46.7	5.60	10.39 (94.8)	--
16-40				46.7	5.50	10.34 (94.4)	--
17-14	600	17.0	4.30	46.7	5.24	10.53 (96.1)	--
17-15				46.7	5.32	10.53 (96.1)	--
17-16				46.7	5.34	10.54 (96.2)	--
18-2	600	17.0	4.10	51.0	4.90	10.45 (95.4)	--
18-3				46.7	5.20	10.51 (95.9)	--
18-4				46.7	5.18	10.55 (96.3)	--
19-49	600	17.0	4.25	39.6	5.13	10.48 (95.6)	--
19-50				42.5	5.22	10.53 (96.1)	--
19-51				43.9	5.26	10.55 (96.3)	--
20-61	600	22.7	4.39	49.6	5.24	10.21 (93.2)	--
20-62				49.6	5.20	10.26 (93.6)	--
20-63				49.6	5.20	10.29 (93.9)	--

Table E.1. (contd)

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)(%T.D.)	Geometric (g/cm^3)(%T.D.)
21-72	600	21.0	4.25	49.6	5.10	10.47 (95.5)	--
21-73					5.12	10.40 (94.9)	--
21-74					5.15	10.43 (95.1)	--
22-84	600	21.0	4.35	49.6	5.18	10.53 (96.0)	--
22-85				49.6	5.19	10.52 (96.0)	--
22-86				49.6	5.12	10.53 (96.0)	--

Table E.2. Slugging Pressure and Density Versus Sintered Density Using Zinc Stearate as a Die Lubricant

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)(%T.D.)	Geometric (g/cm^3)(%T.D.)
14-67	800	15.6	4.80	35.4	5.50	10.04 (91.6)	–
14-68				35.4	5.46	10.05 (91.7)	–
14-69				35.4	5.60	10.01 (91.4)	–
15-32	800/600	17.0	4.33	46.7	5.29	10.63 (97.0)	–
15-33				46.7	5.29	10.60 (96.7)	–
15-34				46.7	5.32	10.59 (96.6)	–
16-44	700	14.2	4.39	39.6	5.42	10.47 (95.7)	–
16-45				39.6	5.49	10.45 (95.3)	–
16-46				39.6	5.46	10.47 (95.6)	–
17-20	600	17.0	4.30	46.7	5.34	10.60 (96.7)	–
17-21				46.7	5.34	10.58 (96.6)	–
17-22				46.7	5.35	10.60 (96.7)	–
18-7	600	17.0	4.10	46.7	5.20	10.61 (96.8)	–
18-8				46.7	5.22	10.59 (96.7)	–
18-9				46.7	5.25	10.56 (96.3)	–

Table E.2. (contd)

Batch-Pellet Number	Reduction Temperature (°C)	Slugging		Green		Sintered Density	
		Pressure (Kpsi)	Density (g/cm^3)	Pressure (Kpsi)	Density (g/cm^3)	Immersion (g/cm^3)	Geometric (g/cm^3)(%T.D.)
19-55	600	17.0	4.25	46.7	5.35	10.54 (96.2)	–
19-56				46.7	5.37	10.51 (95.9)	–
19-57				46.7	5.38	10.52 (96.0)	–
20-66	600	22.7	4.39	49.6	5.27	10.40 (94.9)	–
20-67				49.6	5.28	10.40 (94.9)	–
20-68				49.6	5.26	10.40 (94.9)	–
21-78	600	21.0	4.25	49.6	5.18	10.51 (95.9)	–
21-79				49.6	5.13	10.58 (96.5)	–
21-80				49.6	5.12	10.57 (96.4)	–
22-90	600	21.0	4.35	49.6	5.21	10.59 (96.7)	–
22-91				49.6	5.20	10.61 (96.8)	–
22-92				49.6	5.21	10.61 (96.8)	–

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