CONF-780545--10

HEDL-SA-1399-FP

FABRICATION OF ThO_2, UO_2, and PuO_2-UO_2 PELLETS

MASTER

by

D. E. Rasmussen, W. R. Jentzen, and R. B. McCord

Hanford Engineering Development Laboratory
Richland, Washington

operated by

Westinghouse Hanford Company

A paper for presentation at the 80th Annual Meeting and Exposition of the American Ceramic Society, May 10', 1978, Detroit, Michigan.

ABSTRACT

Fabrication of ThO pellets for EBR-II irradiation testing and fabrication of UO_2 and PuO_2-UO_2 pellets for United Kingdom Prototype Fast Reactor (PFR) irradiation testing is discussed. Effect of process parameters on density and microstructure of pellets fabricated by the cold press and sinter technique is reviewed.

This paper was prepared in connection with work performed for the U.S. Energy Research and Development Administration under Contract No. E (45-1)2170.

DISCLAIMER

INTRODUCTION AND BACKGROUND

The Hanford Engineering Development Laboratory (HEDL) fabricates mixed oxide fuel pellets and insulator fuel pellets for irradiation testing as part of the national breeder reactor development program. This presentation discusses the fabrication of depleted UO_2 insulator pellets, ThO_2 insulator pellets, and mixed oxide (PuO_2-UO_2) fuel pellets. The 92% TD ThO_2 pellets are for irradiation testing in EBR-II, which started in 1977 as part of the national program to investigate the irradiation behavior of proliferation-resistant fuel systems. The depleted UO_2 insulators and PuO_2-UO_2 fuel are for irradiation testing in the Prototype Fast Reactor (PFR) in the United Kingdom, which starts in 1978. Experimental fuel for PFR will be steady-state irradiated and then returned to the U. S. for safety transient irradiation testing. About 26 kg of the required 125 kg of PuO_2-UO_2 fuel has been fabricated to date. Fabrication history will be reviewed briefly. Fuel made to date is 92% TD solid pellets, although other designs are anticipated including annular pellets and solid pellets of slightly lower density (90% TD).

DEPLETED UO_2 INSULATOR PELLET FABRICATION

Safety Considerations

Because of the concern for radiological control and potential risk of handling heavy metal elements, all depleted UO_2 and natural UO_2 operations at HEDL are conducted inside open-face hoods with negative atmosphere flow away from the operator. Air monitoring equipment continuously analyses the condition of the room atmosphere.

Raw Material

Depleted UO_2 used at HEDL is derived from the ammonium diuranate (ADU) process as applied to the depleted by-product of the Oak Ridge gaseous diffusion ^{235}U enrichment process. The depleted UO_2 powder is dark olive drab in color and is of a very fine particle size as seen in the electron micrographs in Figure 1 and the size distribution curve in Figure 2. Physical properties of depleted UO_2 powder are summarized in Table 1.

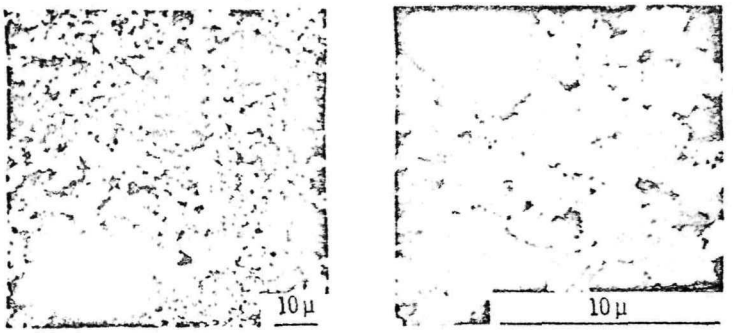

Figure 1. Scanning Electron Micrograph of As-Received Depleted UO_2 Powder

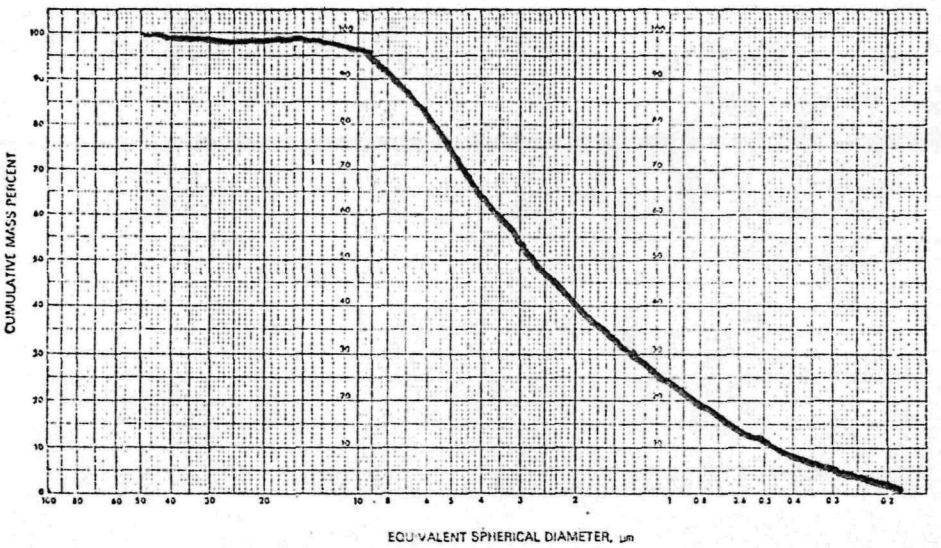

Figure 2. Particle Size Distribution of Depleted UO_2 Powder

Table 1. Properties of Depleted UO_2 Powder

U Metal Content	87.5 wt %
^{235}U in U	0.224 wt %
Average Particle Size	0.3 μm
Surface Area	3.3 m^2/g
Total Impurities	<1460 ppm
Melting Point	2800°C
Theoretical Density	10.96 g/cc

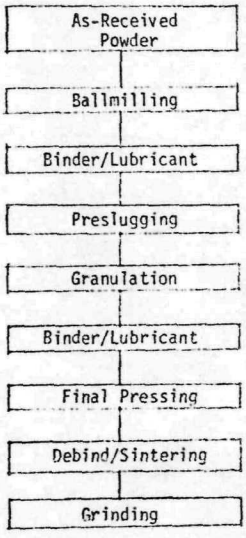

FIGURE 3. Depleted UO_2 Pellet Fabrication Process Flowsheet

Process Description

The first step is to ballmill 1 kg increments of depleted UO_2 for 10 hours in a rubber-lined ball jar containing a ratio of 8 pounds of tungsten carbide balls per one pound of UO_2. After milling, the depleted UO_2 is screened through a U. S. 325-mesh sieve to break up the particles. After screening, 0.1-0.5 weight percent (usually 0.1 w/o) Sterotex is added by dry mechanical mixing to serve as a binder lubricant.

The powder/binder mixture is compacted at low pressure (~10,000-20,000 psi) in a half-inch diameter die to achieve the desired "preslug" pellet density. The preslug pellets are granulated by hand through a 20-mesh screen. Minus 70-mesh particles are preslugged again so that the final powder contains less than 10% minus 70-mesh fines. Preslugging and granulation produce a consistent, free-flowing feed powder for the final pressing operation.

Another 0.1-0.6 weight percent (usually 0.2 w/o) Sterotex binder/lubricant is added to the granulated powder by dry mechanical mixing prior to final compaction at 20,000-70,000 psi to achieve the desired final "green" (unsintered) pellet density. Depleted UO_2 batch size is limited to 3.7 kg increments because of the sintering furnace capacity. Pellets are sintered at 1600°C for four hours in a ceramic muffle furnace.

Furnace atmosphere consists of 8 cfh of Ar-4% H_2, with all atmosphere flowing through a 0°C ice bath bubbler. Heating rate is 200°C/hour and cooling rate is 300°C/hour. The slow heating rate provides sufficient time for organic binder removal during the heat-up cycle. Depleted UO_2 pellets are generally sintered to a specification density of 95 $\pm$ 2.0% of theoretical. Pellets are centerless ground to specification diameter. An outline of the process unit operations is shown in Figure 3.

Process Parameter Effects

A number of process parameters have a direct influence on depleted UO_2 pellet fabricability and final pellet properties. The effects of the major parameters are discussed below.

Ballmilling. The depleted UO_2 was ballmilled to reduce particle size and increase surface area per unit weight. Pellet sinterability was thus improved, raising sintered pellet density from 92 to 95% of theoretical density.

Binder Lubricant. An organic binder such as Sterotex improves the compaction behavior of UO_2 powder and improves the pellet ejection behavior during pressing. For a given powder, too little binder results in poor particle-particle lubrication and compaction characteristics, resulting in low densities and green pellet strength. Too much binder/lubricant can cause poor compaction and loss of pellet density due to the pore-forming capability of the binder. Hence, binder acts as a density-controlling agent in two ways; first, increasing green pellet density by improved powder compression in the die, and secondly, as a pore-former to decrease density. For high-density depleted UO_2 insulator pellet fabrication, we are using the former property for improved compaction.

Compaction Pressures. Once basic starting powder particle size distribution and binder/lubricant concentration are established, variations in pressing pressures can be used to control pellet densities. Preslugging is kept at a low pressure for depleted UO_2 to allow easy granulation prior to final pressing and easy compaction to high green densities at final pressing. If the preslug pellets were pressed at high pressures, it would be more difficult to achieve the high densities specified. This effect is also used for mixed oxide fuel fabrication[1-6]. Therefore, for depleted UO_2, the preslugging pressure is low, which provides a feed with good flowability for consistent die-fill and low density to provide easy granulation and good final pressing characteristics. Increasing final pressing pressure can, within practical limits, increase green pellet density and sintered pellet density as seen in Figures 4 and 5.

Particle Granulation. Granulation of the half-inch preslug pellets affects final pressing characteristics of the depleted UO_2 powder. Reduction of the minus 70-mesh fines to less than 10% of the batch size increased the depleted UO_2 final green pellet density and increased the sintered pellet density. This is attributed to the subtle effect of particle size distribution on compaction behavior of depleted UO_2.

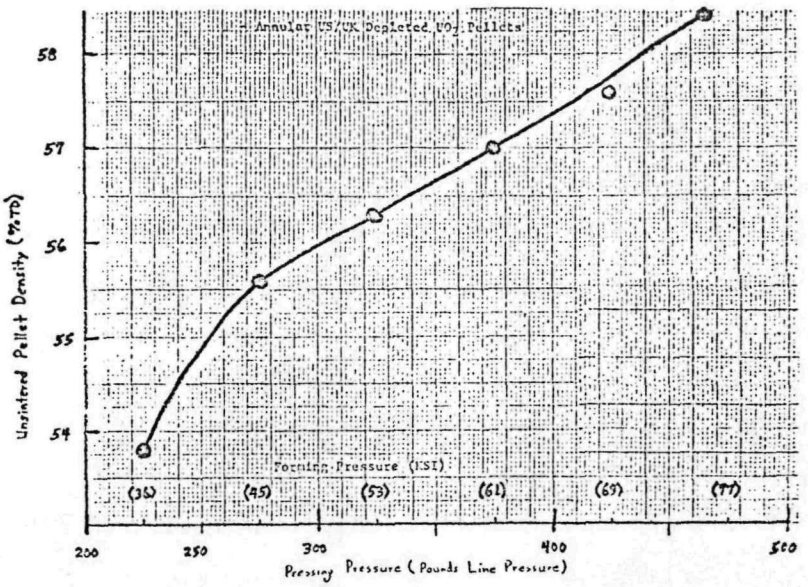

Figure 4. Green Depleted UO_2 Pellet Density as a Function of Final Pressing Pressure

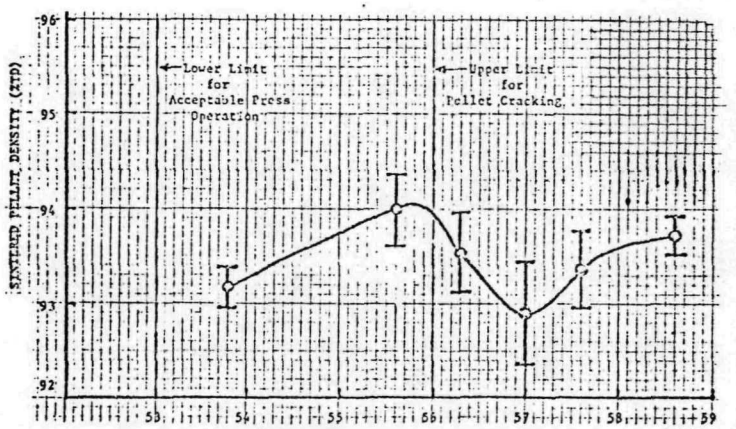

Figure 5. Sintered Depleted UO_2 Pellet Density as a Function of Green Pellet Density

Pellet Geometry. Pellet length and diameter can affect final pellet density. A decrease in pellet length without a corresponding decrease in pressing pressure causes an increase in pellet density. Similarly, an increase in length causes a reduction in pellet density and can cause pellet laminations due to powder compaction behavior. Pellet diameter is controlled by die size. In some cases, pressing pressure can be used to effect pellet diameter. Close control of tolerances on matching punch and die sets minimizes pellet defects such as lamination, cracking, and chipping. At HEDL, dimensions are controlled within tolerances that assure adequate control of pellet densities.

Sintering Temperature and Atmosphere. Sintered pellet density can be controlled by sintering temperature and atmosphere control. Pellet density increases with increasing temperature. Although our depleted UO_2 sintering furnace is limited to 1600°C, we have improved sinterability by using a 0°C ice bath bubbler through which AR-4% H_2 gas flows prior to entry to the furnace muffle. Others have also found that atmosphere control enhances solid-state sintering of metals and oxides (7-9).

Pellet Sintering Shrinkage. Control of sintering shrinkage is of concern because of die design and because of pellet diameter specifications. Pellets typically must meet a specification tolerance of ± 0.002 inch. Therefore, pellet shrinkage is closely monitored. Pressing pressure affects as-pressed pellet diameter and density as well as final pellet density and sintering shrinkage as shown in Figures 6 and 7.

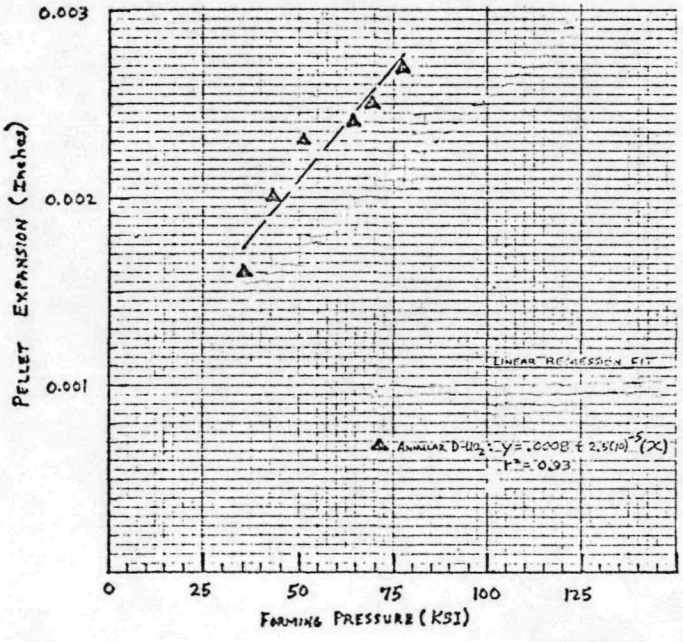

Figure 6. As-Pressed Depleted UO_2 Pellet Diameter Expansion as a Function of Pressing Pressure

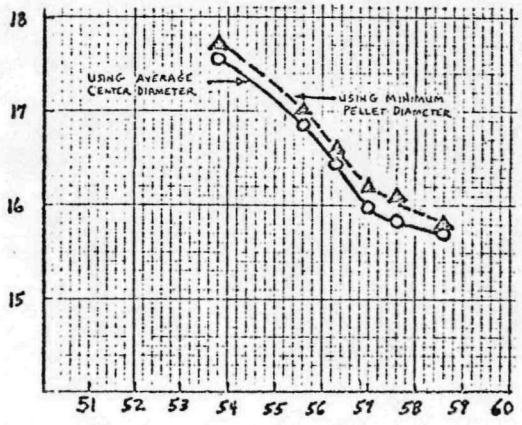

Figure 7. Depleted UO_2 Diametral Sintering Shrinkage as a Function of Green Pellet Density

Pellet Properties/Characteristics

Micrographs of typical depleted UO_2 insulator pellets are shown in Figures 8 and 9. Typical depleted UO_2 pellet sintered pellet properties are presented in Table 2. Fabrication parameters have been shown by other investigators to control nuclear fuel microstructures and resultant irradiation densification effects.[1-2, 10-11] Extensive mixed oxide fuel characterization measurements are performed as part of the continuing fabrication development program[2-5].

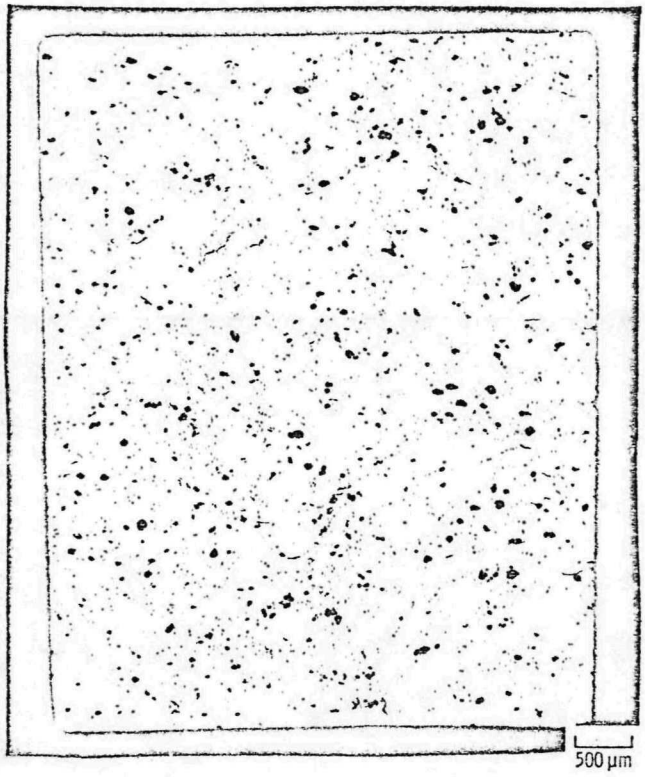

Figure 8. Optical Micrograph of Depleted UO_2 Pellet Polished Cross Section

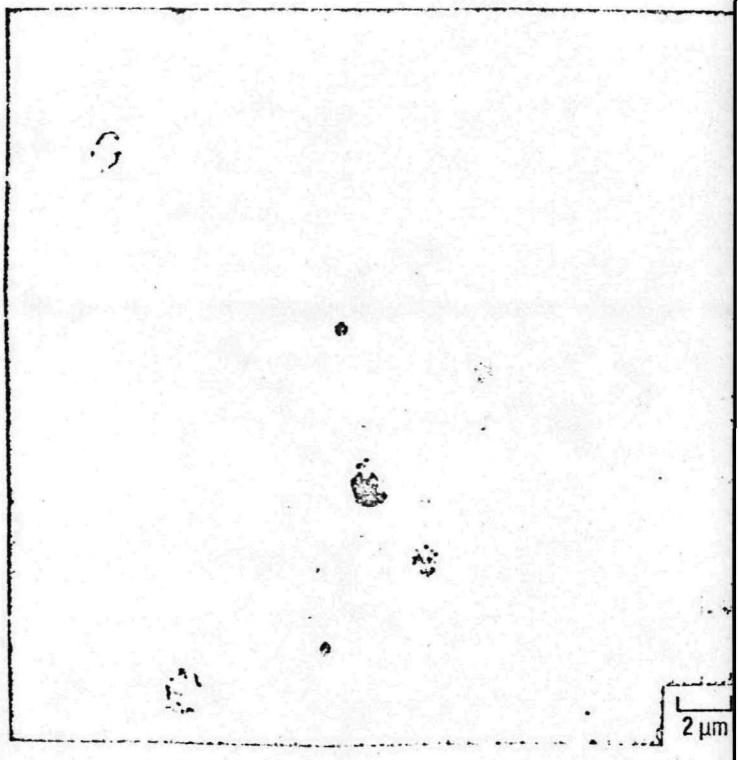

Figure 9. Scanning Electron Micrograph of Depleted UO_2 Pellet Polished Cross Section

Table 2. Properties of Depleted UO_2 Sintered Pellets

Density	94 %TD
Diameter	0.2200 inches
Length	0.5000 inches
Weight	2.6 grams
Geometry	Solid, Flat Ends; and Annular (0.062 in.)

ThO_2 INSULATOR PELLET FABRICATION

Safety Considerations

Thorium oxide powder and pellet operations are conducted within open-faced hoods with negative air flow away from the operator. Continuous air monitoring equipment is used to assure constant surveillance of the room atmosphere. Additional radiological control measures are being implemented at HEDL to further improve operations safety and to increase material processing rates.

Raw Material

The thorium oxide (thoria) used at HEDL for insulator pellet fabrication is white in color and was produced by the oxalate precipitation process. The ThO_2 powder more closely resembles PuO_2 powder than UO_2 powder, and has been used to simulate PuO_2 in mixed ThO_2-UO_2 studies elsewhere.[12-13] Powder shape and morphology are evident as seen in Figure 10. Particle size distribution is presented in Figure 11. Physical and chemical properties of ThO_2 as presented in Table 3.

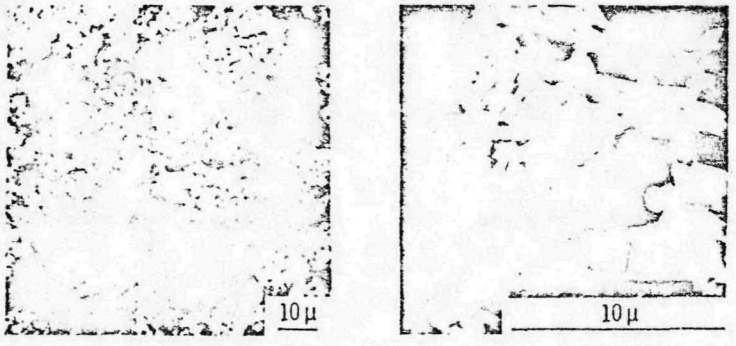

Figure 10. Scanning Electron Micrographs of As-Received ThO_2 Powder

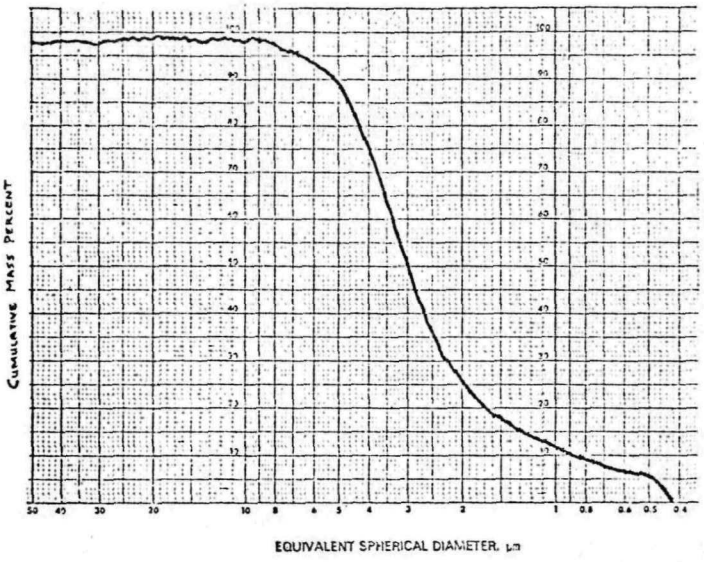

Figure 11. Particle Size Distribution of ThO_2 Powder

Table 3. Properties of ThO_2 Powder

Average Particle Size	3 µm
Surface Area	20.6 m^2/g
Total Impurities	<3120 ppm
Melting Point	3300°C
Theoretical Density	10.03 g/cc

Process Description

Because of time limitations on fabricating ThO_2 insulator pellets (92 ± 2% TD) for irradiation testing, ThO_2 pellets were processed using essentially the same equipment, facilities, and process as the depleted UO_2 described earlier. The process flowsheet is shown in Figure 12. Basically, the ThO_2 was preslugged, granulated, final pressed, and sintered in AR - 4% H_2 gas passing through a 0°C bath bubbler.

Process Parameter Effects

Generally speaking, the ThO_2 powder did not behave like UO_2 or mixed PuO_2-UO_2, but rather more like straight PuO_2, which is not unusual considering its particle size, shape, and morphology. Also, like straight PuO_2, it was more difficult to make a high-quality, high-density, pellet free of defects and mechanically strong. The various process adjustements and effects on pellet density and/or quality are described below.

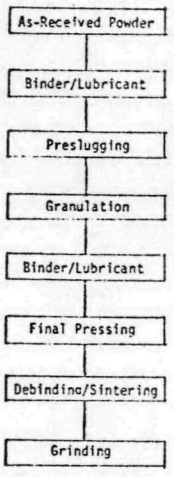

FIGURE 12. ThO_2 Insulator Pellet Fabrication Process Flowsheet

Precompaction Drying ??
Describe —

Drying. Because of the compaction characteristics during early testing, a drying operation was tested. Drying at 70°C for six hours did not significantly effect fabricability of the ThO_2 powder, and therefore, was not used.

Ballmilling. Ballmilling was also found to not significantly improve fabricability of the ThO_2 powder. This can be seen in the lack of effect on green and sintered pellet densities as presented in Figure 13. Ballmilled ThO_2 powder showed a tendency to increase pellet cracking and lamination as well as decrease green pellet strength.

Binder/Lubricant. Sterotex binder was added to the ThO_2 used prior to preslugging and prior to final pressing. A minimum of 0.2 weight percent and 0.4 weight percent were required for the preslugging and final additions to achieve satisfactory compaction characteristics, which is more than normally used for depleted UO_2 or natural UO_2 operations. Additional increases in Sterotex were found to first increase compaction and resultant sintered densities and then to finally cause a decrease in sintered density due to pore-forming. This behavior is evident in Figure 14.

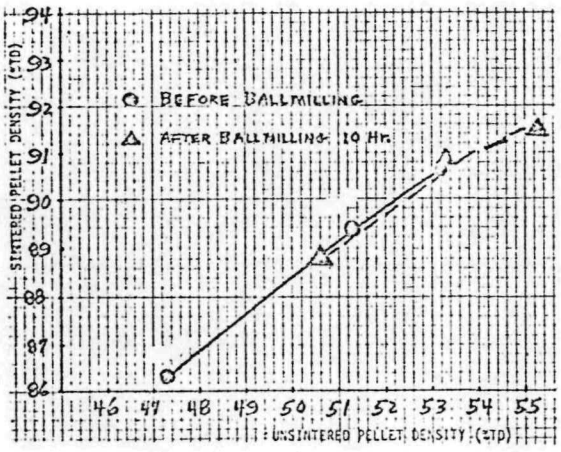

Figure 13. ThO_2 Sintered Pellet Density as a Function of Green Pellet Density for Ball Milled and Non-Ball Milled Powder

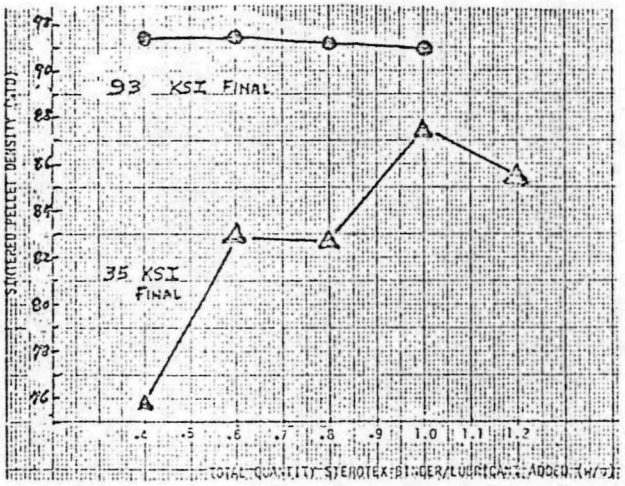

Figure 14. ThO_2 Sintered Pellet Density as a Function of Total Organic Binder Content

Compaction Pressures. As seen earlier with the depleted UO_2, pressing pressures were used to increase final green pellet density and resultant sintered pellet density. As with the depleted UO_2, once the powder properties are set (or adjusted by preslugging and granulation), pressing pressure is used as a secondary control. Effect of pressing pressure is shown in Figures 15-17. Pellet density increased with increased pressing pressure until extremely high pressures caused lamination.

Particle Granulation. ThO_2 showed subtle changes in fabricability with changes in the granulation step. Although more work is being done in this area, preliminary findings show that the presence of minus 40-mesh and minus-70 mesh fines aides pressing to higher green densities, which was not the case for depleted UO_2 fabrication. This effect is present in the sintered density versus green density curves shown in Figure 18.

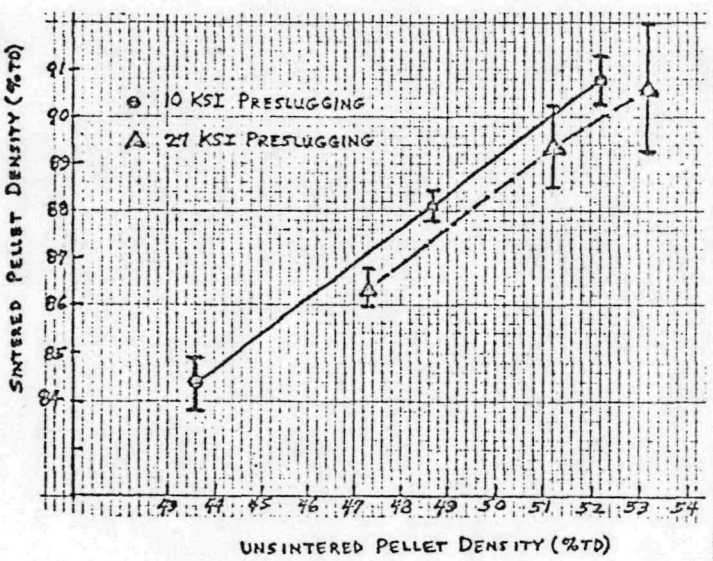

Figure 15. ThO_2 Sintered Pellet Density Versus Unsintered Density for Pellets Preslugged at Two Different Pressures.

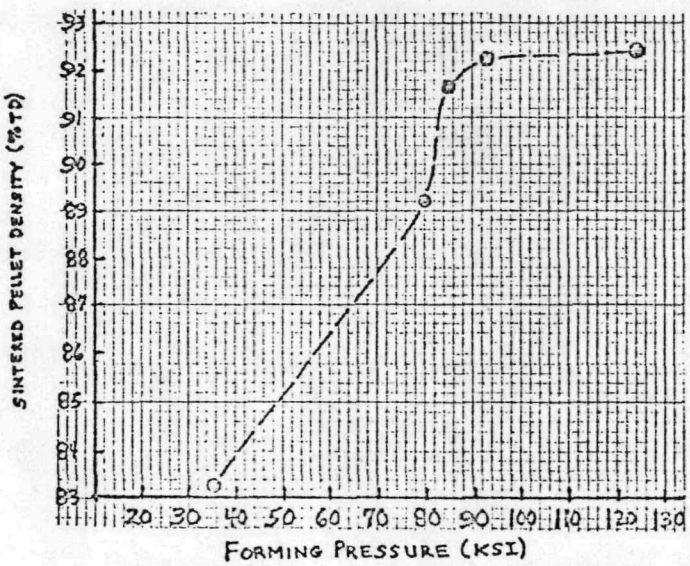

Figure 16. ThO_2 Sintered Pellet Density as a Function of Fressing Pressure

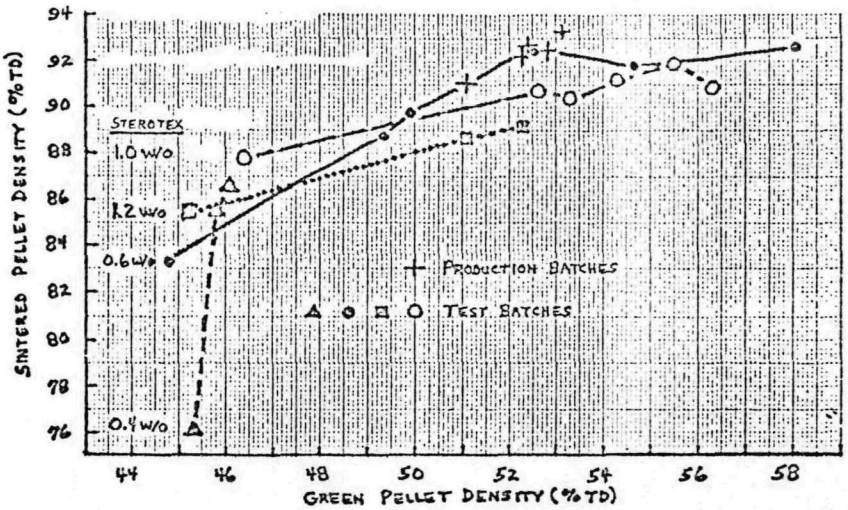

Figure 17. ThO_2 Sintered Pellet Density as a Function of Green Pellet Density

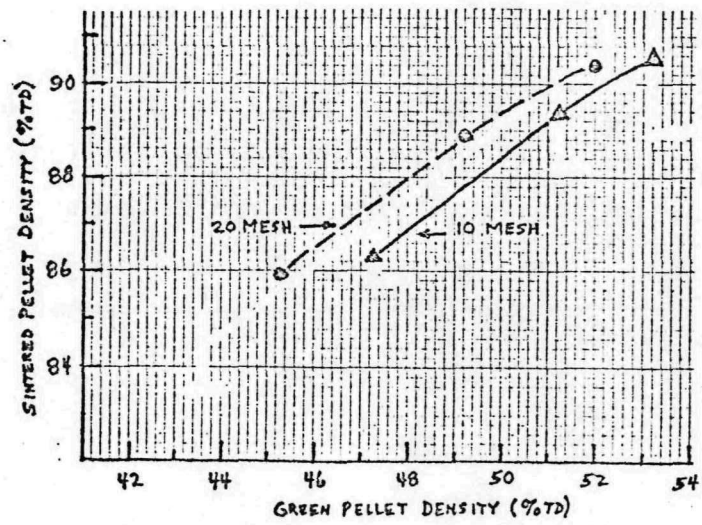

Figure 18. ThO_2 Sintered Pellet Density as a Function of Green Pellet Density for Powder Granulated through Different Size Sieves

Pellet Geometry. Control of pellet dimension and densities followed the same behavior and guidelines as described earlier for depleted UO_2.

Sintering Temperature and Atmosphere. Although ThO_2 is known to be more refractory than UO_2, our production batch furnace sintering temperature was limited to 1600°C. Therefore, we sintered ThO_2 pellet samples from several test batches in a small research furnace at 1800°C in He atmosphere. Pellets sintered at 1800°C exhibited higher sintered densities and longer etch times to show grain structure. Density curves are shown in Figure 19.

What does this mean? How does it relate to T_{sinter}?

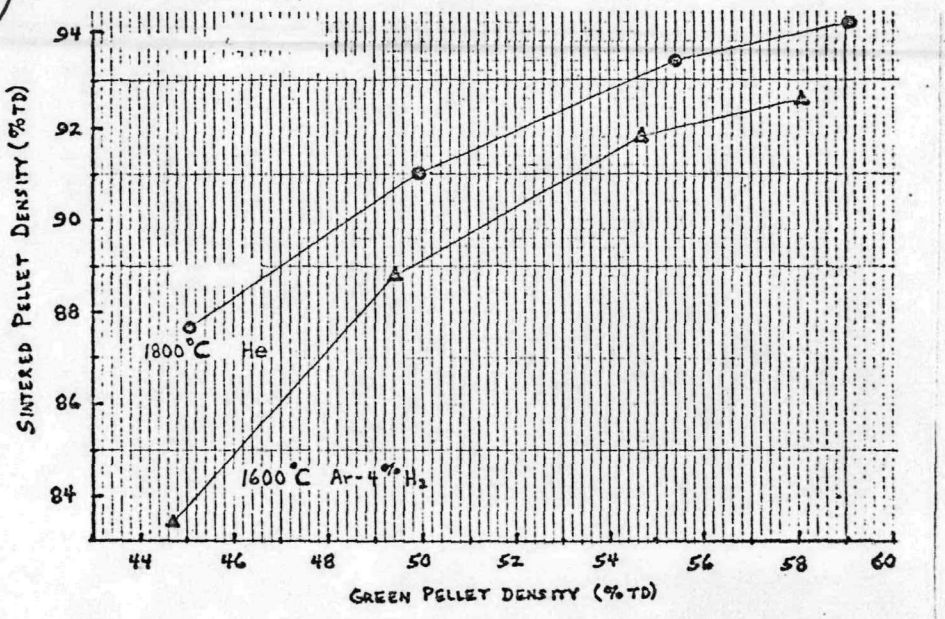

Figure 19. ThO_2 Sintered Pellet Density as a Function of Green Pellet Density for Pellets Sintered at 1600°C in Ar - 4% H_2 and at 1800°C in He.

Pellet Sintering Shrinkage. ThO_2 pellet sintering shrinkage behavior showed the same trends as for UO_2, as expected. Increasing pressing pressure caused an increase in pellet density and a corresponding decrease in sintering shrinkage as shown in Figures 20 and 21.

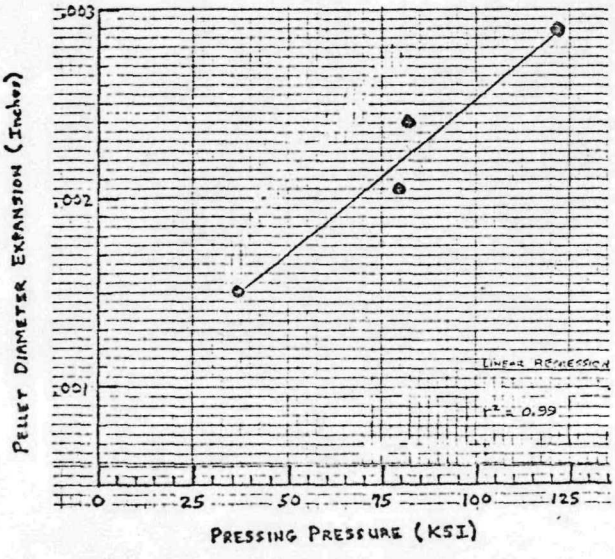

Figure 20. As-Pressed ThO_2 Pellet Diameter Expansion as a Function of Pressing Pressure

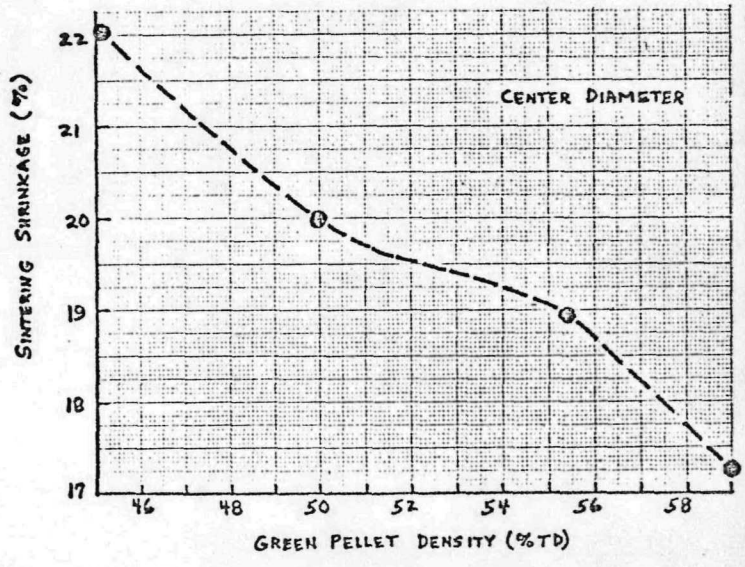

Figure 21. ThO_2 Pellet Diametral Sintering Shrinkage as a Function of Green Pellet Density

Pellet Properties/Characteristics

Typical as-pressed ThO_2 pellets are shown in Figure 22. Thoria pellets showed a slight translucent nature which made microscopic image focusing more difficult. Micrographs of typical thoria pellet polished cross sections are shown in Figures 23 and 24. Pellet properties are summarized in Table 4.

FIGURE 22. As-Pressed ThO_2 Insulator Pellets

Table 4. ThO_2 Pellet Properties

Density	91-93 %TD
Diameter	0.1900, 0.2005, and 0.2595 inches
Length	0.500 inches
Weight	2.0 grams
Geometry	Solid, Flat Ends

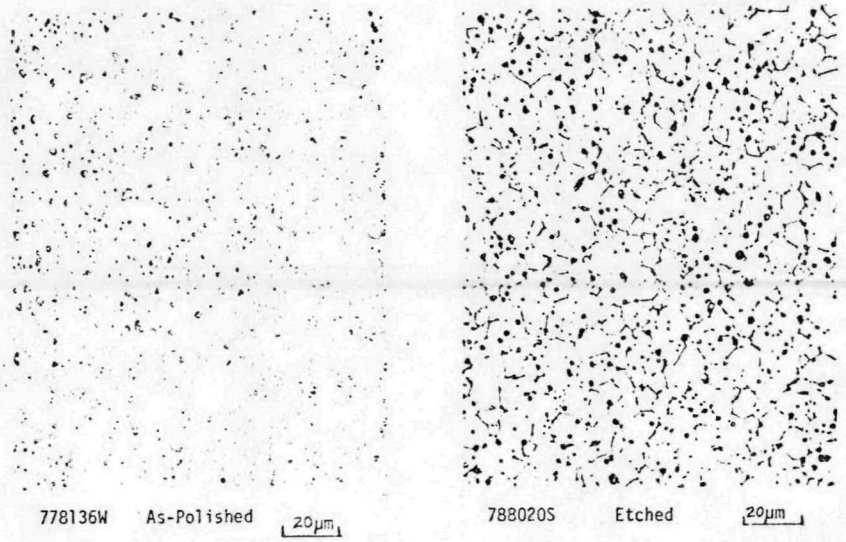

FIGURE 23. Optical Micrographs of ThO_2 Pellet Polished Cross Section

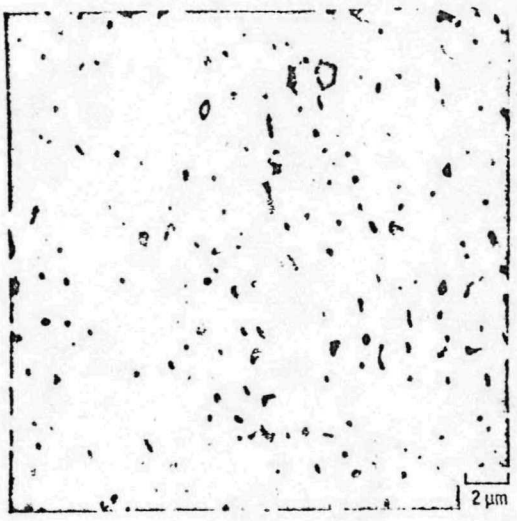

FIGURE 24. Scanning Electron Micrograph of ThO_2 Pellet Polished Cross Section (Cathodic Vacuum Etched)

MIXED OXIDE (PuO_2-UO_2) FABRICATION FOR PROTOTYPE FAST REACTOR IRRADIATION TESTING

Safety Considerations

Many procedures and precautions are applied to the fabrication of mixed oxide (PuO_2-UO_2) fuel pellets in a safe and orderly manner. These have been reported extensively elsewhere and include such things as glovebox operations, criticality control, and elaborate laboratory atmosphere flow control systems.[14]

Raw Material

To date, two materials have been used for fabrication of mixed oxide (PuO_2-UO_2) fuel for irradiation testing in PFR. First, natural UO_2 which was produced by Oak Ridge's diuranate ammonium process and second, PuO_2 produced by Atlantic Richfield Hanford Company's oxalate precipitation. The PuO_2 contains about 16% ^{240}Pu in Pu. One composition has been made to date; that is 27.7 w/o PuO_2-UO_2.

Process Description

The PuO_2 was ballmilled for 10 hours prior to mixing with the natural UO_2. This was necessitated by the sintering activity of the PuO_2 powder. Sintered pellet densities increased from 90 to 92% TD. Particle size, shape, and morphology before and after ballmilling are shown in the scanning electron micrographs in Figures 25 and 26, respectively. Particle size distributions before and after ballmilling are shown in Figure 27. After ballmilling of the straight PuO_2, it was manually blended with natural UO_2 and ballmilled as PuO_2-UO_2 for 20 hours to assure the high degree of PuO_2-UO_2 homogeneity required for controlled irradiation testing. Further processing followed the same dry powder processing scheme described earlier. The mixed oxide was preslugged, granulated, and final pressed as usual. Sterotex binder was added before and after preslugging. Sintering was performed in a glovebox furnace at 1690°C for six hours in 3 cfh of AR-8% H_2 gas with a cryostat atmosphere control system set at -35°C. The cryostat system was used to help increase pellet density and control pellet stoichiometry.

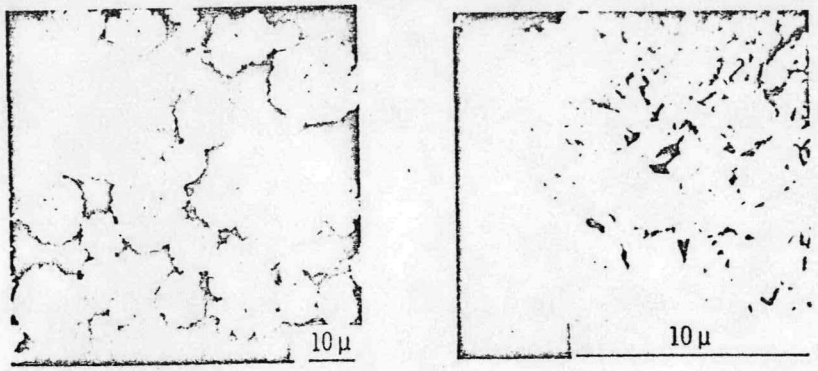

FIGURE 25. Scanning Electron Micrographs of PuO_2 Powder (16% ^{240}Pu in Pu) Before Ballmilling

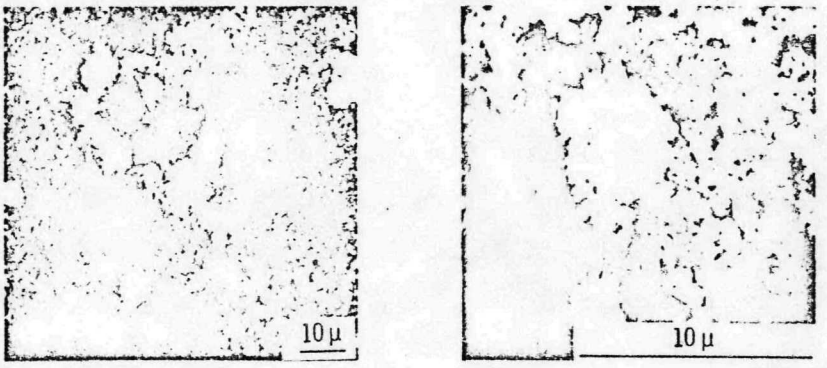

FIGURE 26. Scanning Electron Micrographs of PuO_2 Powder (16% ^{240}Pu in Pu) After Ten Hours Ballmilling

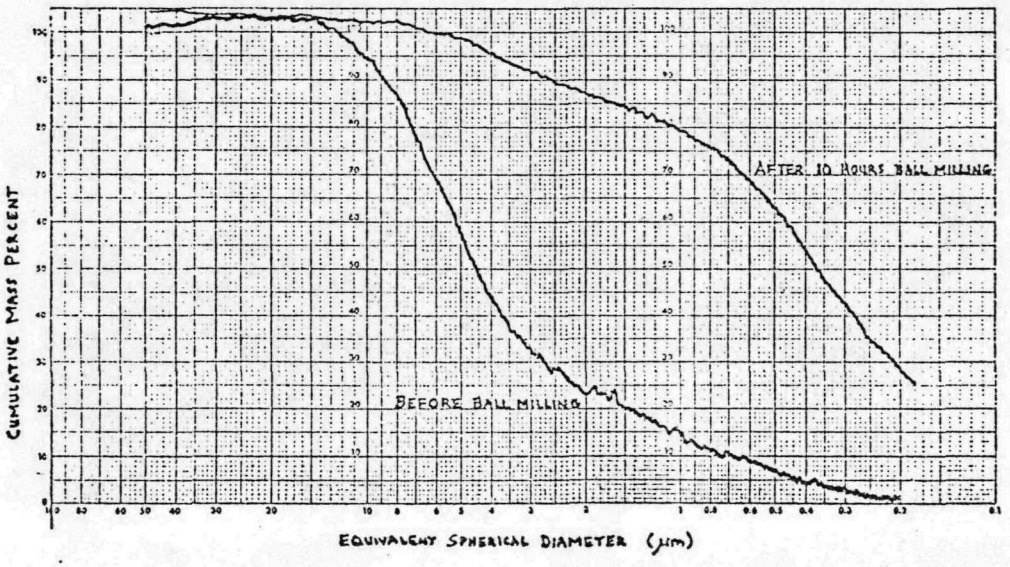

FIGURE 27. PuO_2 Particle Size Distributions Before and After Ten Hours Ballmilling

Pellet Properties/Characteristics

Pellets were sintered to nominal 92% TD. Micrographs of typical pellet polished cross sections are shown in Figures 28 and 29. Pellet properties are summarized in Table 5. Fuel microstructure characterization measurements are scheduled to provide preliminary information on the irradiation densification potential of these PuO_2-UO_2 fuels[1-4].

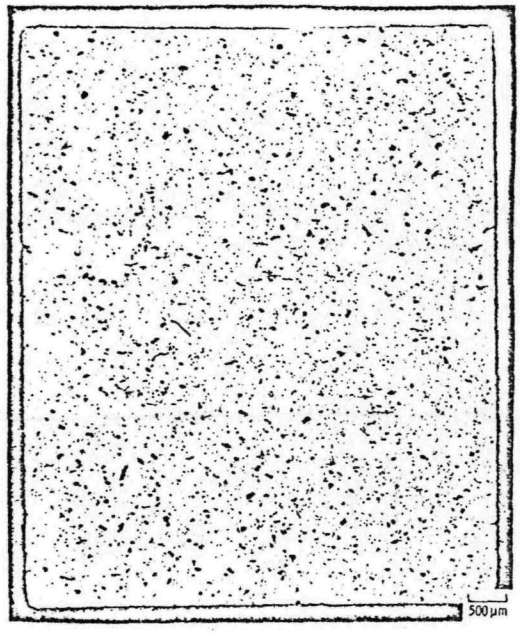

FIGURE 28. Optical Micrograph of 27.7 w/o PuO_2-UO_2 Pellet Polished Cross Section

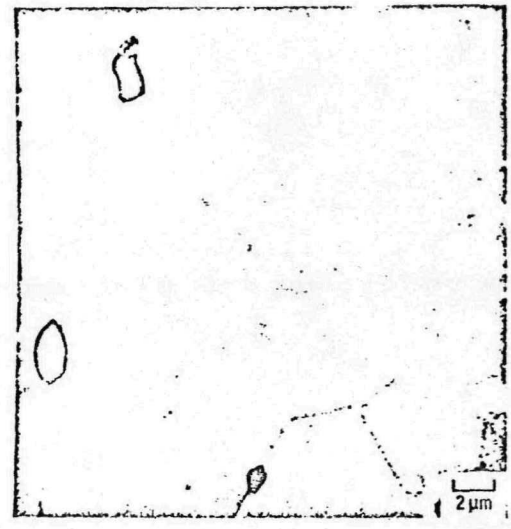

FIGURE 29. Scanning Electron Micrograph of 27.7 w/o PuO_2-UO_2 Pellet Polished Cross Section (Cathodic Vacuum Etched)

Table 5. Properties of 27.7 w/o PuO_2-UO_2 Pellets

Density	92 %TD
Diameter	0.2218 inches
Length	0.2500 inches
Weight	1.2 grams
Geometry	Dished Ends

REFERENCES

1. R. A. Graham, D. E. Rasmussen, and M. C. J. Carlson, "Microstructural Aspects of Nuclear Fuel", Pages 404-413 in Ceramic Microstructures '76, Edited by R. B. Fulrath and J. A. Pask, Westview Press, Boulder, Colorado, 1977.

2. D. E. Rasmussen, E. W. Gerber, and R. B. McCord, "Microstructure Characterization of Advanced Oxide Fuel", HEDL-SA-1171-FP, Paper presented at 79th Annual American Ceramic Society Meeting, Chicago, Illinois, April 23-28, 1977.

3. M. C. J. Carlson, "Densification In Mixed Oxide Fuel During Fast Reactor Irradiation", Nuclear Technology, 22: 335-359 (1974).

4. H. A. Treibs, "Porosity Characterization of Ceramic Nuclear Fuel", Practical Metallography 14 (1977).

5. W. E. Warden, "Process Development to Fabricate 90% Dense Fuel for Irradiation Testing", USAEC Report, HEDL-TME 71-149, WADCO Corporation, Richland, Washington, October, 1971.

6. H. A. Davis and L. J. Ferrell, "Microstructures of As-Fabricated UO_2 Fuel Pellets", Pages 389-403 in Ceramic Microstructures '76, Edited by R. M. Fulrath and J. A. Pask, Westview Press, Boulder, Colorado, 1977.

7. K. C. Radford and J. M. Pope, "Ammonia As A Sintering Aid for UO_2", Ceram. Bull. 56 (2): 197-200, 1977.

8. W. I. Stuart and R. B. Adams, "Effect of Sintering Atmosphere On the Density of Uranium Dioxide Pellets", J. Nuc. Mat. 58 (1975): 201-204.

9. R. A. Gregg and F. N. Rhines, "Surface Tension and the Sintering Force in Copper", Met. Transactions 4 (1973): 1365-1374.

10. P. E. Hart and J. L. Daniel, "The Influence of UO_2 Fuel Pellet Microstructure on Irradiation Induced Densification", Pages 710-720 in Ceramic Microstructures '76, Edited by R. M. Fulrath and J. A. Pask, Westview Press, Boulder, Colorado, 1977.

11. K. C. Radford, J. M. Pope, and L. R. Fleischer, "Influence of Powder Properties on the Dimensional Stability of UO_2 Pellets", Pages 208-222 in Ceramic Microstructures '76, Edited by R. B. Fulrath and J. A. Pask, Westview Press, Boulder, Colorado, 1977.

12. J. M. Pope and K. C. Radford, "Blending of UO_2-ThO_2 Powders", Ceram. Bull. 53 (8): 574-578 (1974).

13. K. C. Radford and R. J. Bratton, "Properties, Blending and Homogenization of (U, Th)O_2-UO_2 Powder", J. Nuc. Mat. 57 (1975): 287-302.

14. D. W. Brite, "Plutonium Fuel Technology, Part I-Plutonium Fuel Technology", Nuc. Tech. 18 (1973): 87-96.