PNL-3134
UC-78

Hybrid Pellets: An Improved Concept for Fabrication of Nuclear Fuel

R. B. Matthews
P. E. Hart

September 1979

Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

Battelle

PNL-3134

DISCLAIMER

PNL-3134
UC-78

HYBRID PELLETS: AN IMPROVED CONCEPT FOR FABRICATION OF NUCLEAR FUEL

R. B. Matthews
P. E. Hart

September 1979

Prepared for
the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352

DOE Richland, WA

HYBRID PELLETS: AN IMPROVED CONCEPT FOR FABRICATION OF NUCLEAR FUEL

SUMMARY

The feasibility of fabricating fuel pellets using gel-derived microspheres as press feed was evaluated under the funding of the Department of Energy's Fuels and Refabrication Development Program. By using gel-derived microspheres as press feed, the potential exists for eliminating dusty operations like milling, slugging, and granulation, from the pelleting process. The free-flowing character of the spheres should also result in limited dust generation during powder transport and pressing operations.

The results of this study clearly demonstrate that fuel pellets can be successfully fabricated on a laboratory scale using UO_2 gel microspheres as press feed. Under moderate sintering conditions, 1,500°C for 4 h in Ar-4% H_2, UO_2 pellets with densities up to 96% TD were fabricated. A range of pellet microstructures and densities were achieved depending on sphere forming and calcining conditions. Based on these results, a set of necessary sphere properties are suggested: O/U less than 2.20, crystallite size less than 500 Å, specific surface area greater than 8 m^2/g, and sphere size 200 to 400 μm.

Preliminary attempts to fabricate ThO_2 and ThO_2-UO_2 pellets using microspheres were unsuccessful because the requisite sphere properties were not achieved.

Areas requiring additional development include: demonstration of the process on scaled-up equipment suitable for use in a remote fuel fabrication facility and evaluation of the irradiation performance of pellet fuels from gel-spheres.

CONTENTS

FIGURES

FIGURES (contd)

TABLES

INTRODUCTION

One of the anticipated problems in the fabrication of nuclear fuels containing high exposure plutonium or highly gamma-active materials is the dust accumulation and subsequent increase in exposure to personnel from the powder preparation and pellet pressing steps. This paper describes the development of an improved fabrication approach that may result in fewer dusty operations during remote fabrication of mixed oxide fuels. The concept combines the front-end of the gel-sphere flowsheet with the back-end of the standard pelleting flowsheet into a single, so-called hybrid process. Oxide microspheres fabricated by one of the sol-gel methods are dried and partially calcined. These microspheres become the press feed material for conventional pellet fabrication of oxide fuels thus eliminating the need for dusty operations like powder milling, slugging and granulation. The free-flowing character of the spheres should also improve powder transport and result in limited dust generation during transport and pressing operations.

Combined efforts are currently underway at Oak Ridge National Laboratory and the Pacific Northwest Laboratory under the Department of Energy's Fuels Refabrication and Development program to develop hybrid fuel pellets for ThO_2- and UO_2-based fuels. Two earlier reports[1,2] introduced the hybrid concept; this paper is a more complete description of the variables affecting the processing of UO_3 spheres into high density pellets. Preliminary results on ThO_2 and ThO_2-UO_2 microspheres are also presented. Previous studies[3-5] have demonstrated that ThO_2 and ThO_2-UO_2 pellets with densities as high as 95% TD can be fabricated from sol-gel shards. Sol-gel derived UO_2-PuO_2 pellets have also been successfully fabricated.[6] However, sol-gel shards require milling and lack the free-flowing character of microspheres, so there is a greater incentive to develop sol-gel microspheres as press feed material.

The feasibility of fabricating pellets from sol-gel microspheres depends on the properties and characteristics of the starting spheres. For example, sphere size, bulk density, and deformability influence pressing behavior while

stoichiometry, surface area, and crystallite size influence sintering behavior. These properties are primarily controlled by the sol preparation, gelation and drying conditions and partly by calcining conditions. The objective of this study was to demonstrate that sol-gel microspheres can be pressed and sintered into acceptable fuel pellets, to identify desirable sphere properties and optimum process conditions, and to develop a pellet fabrication process that is compatible with remote operations. The experimental approach was to characterize various types of spheres before and after calcining and assess the effect of these characteristics on pressing and sintering behavior.

EXPERIMENTAL

SPHERE PRODUCTION AND PROPERTIES

Uranium oxide microspheres,[a] made by an internal gelation process, were used for the calcining, pressing and sintering studies. Spheres were supplied as UO_3 in the as-dried state. Properties of the spheres varied depending on the formation, gelation and drying conditions used in the sol-gel process. The internal gelation process and the effect of process parameters on sphere properties is described in a recent ORNL publication.[7] Table I-A in Appendix A lists the sphere batches tested and their relevant as-received properties. Batches DD-5 and DD-7 were primarily used to establish the effect of calcining conditions on sphere properties as discussed in the Results Section. These batches were formed under similar conditions except that the DD-7 spheres were dried at a higher temperature resulting in a higher bulk density. Thorium oxide and ThO_2-25wt% UO_3 microspheres,[b] prepared by an external gelation process, were also tested. The external gelation process is described in general by Brambilla et al.,[8] but the details of the process used to fabricate the ThO_2 spheres are proprietary.

SPHERE CALCINING AND CHARACTERIZATION

Spheres were calcined in 50- to 100-gram batches by heating in Ar to temperature and soaking for various times and temperatures in Ar-4% H_2 flowing at 28 l/h. Weight changes were measured by thermogravimetric analysis (TGA) under conditions similar to calcining. Bulk density was measured according to ASTM Standard B 212-48; tap density was measured according to ASTM Standard D 527-70. Specific surface area was measured by BET gas adsorption and crystallite size was determined by x-ray line broadening of the (220) peak. Oxygen-to-metal ratios of calcined UO_2 spheres were determined by reduction at 1000°C in Ar-4% H_2 for 6 h and measuring weight change.

(a) Supplied by Oak Ridge National Laboratory, Oak Ridge, TN.
(b) Supplied by General Atomic Company, San Diego, CA.

PELLET FABRICATION

Pellet fabrication procedures were kept constant throughout this study except where noted in the Results Section. Green pellets were pressed at 150 MPa in a double-acting die sprayed with zinc stearate mold release. Pellets were sintered at 1500°C for 4 h in Ar-4% H_2 flowing at 42 l/h. Green and sintered pellet densities were calculated from measurements on unground pellets. An immersion technique, which is a modification of ASTM Standard C-373-72, was used to check sintered pellet densities; the immersion densities were 1 to 1.5% TD greater than the bulk densities. The pellets contained about 0.3 vol% open porosity. Theoretical densities (TD) were calculated using 10.96 Mg/m^3[(a)] for UO_2 and 10.00 Mg/m^3 for ThO_2. All stated densities are an average of the geometric densities of at least 8 pellets and ranges represent 95% confidence limits. Structures of spheres and pellets were examined using standard ceramographic and SEM techniques.

(a) SI units are used throughout this document. 1 Mg/m^3 = 1 g/cm^3, 1 MPa = 145 psi.

RESULTS

EFFECTS OF CALCINING CONDITIONS ON UO_2 SPHERE PROPERTIES

The first step needed to prepare UO_3 gel spheres for pressing is a calcining treatment to remove residual volatiles and reduce the UO_3 to UO_2. The thermogravimetric curve in Figure 1 shows that a 9 wt% decrease occurred in UO_3 spheres after heating to 500°C in Ar-4% H_2; further heating to 1000°C caused an insignificant weight decrease. Initial calcining runs were done at 600°C to assure complete reduction and outgassing. Sphere batches DD-5 and DD-7 were calcined at 600°C for 4, 8, 16 and 24 h to determine the effect of calcining time on sphere properties. Figure 2 shows that the O/U ratio of the calcined spheres measured after 2 to 4 days exposure to room temperature air decreased with increasing time at temperature. The high density DD-7 spheres reached a stable stoichiometry after 8 h at temperature while the DD-5 spheres required 16 h. X-ray analysis of the DD-5 spheres showed that the 4-h spheres contained about 50% U_3O_8, the 8-h spheres contained about 30% U_3O_8, and the 16- and 24-h spheres were 100% UO_2.

Surface areas and crystallite sizes of the same spheres are plotted against calcining time in Figure 3. The specific surface area decreases with time up to 16 h while the crystallite size shows a corresponding increase with time at temperature. The reason for the decrease in crystallite size and increase in surface area between 16 and 24 h is not clear. However, these results do suggest that the spheres are continuing to restructure during the long calcining times.

A similar series of calcining trials at 700, 800 and 900°C were run to determine the effect of temperature on sphere properties. Batches DD-5 and DD-7 were heated to temperature in air to effect reduction at the calcining temperatures and soaked at temperature for 4 h in Ar-4% H_2. Figure 4 shows that the O/U after calcining for 4 h drops off with increasing temperature and reaches a value of less than 2.10 at 800°C. Surface area decreases by a factor of about 5 with increasing temperature while the crystallite size grows to about 900 Å at 800°C as shown in Figure 5. These large changes indicated that

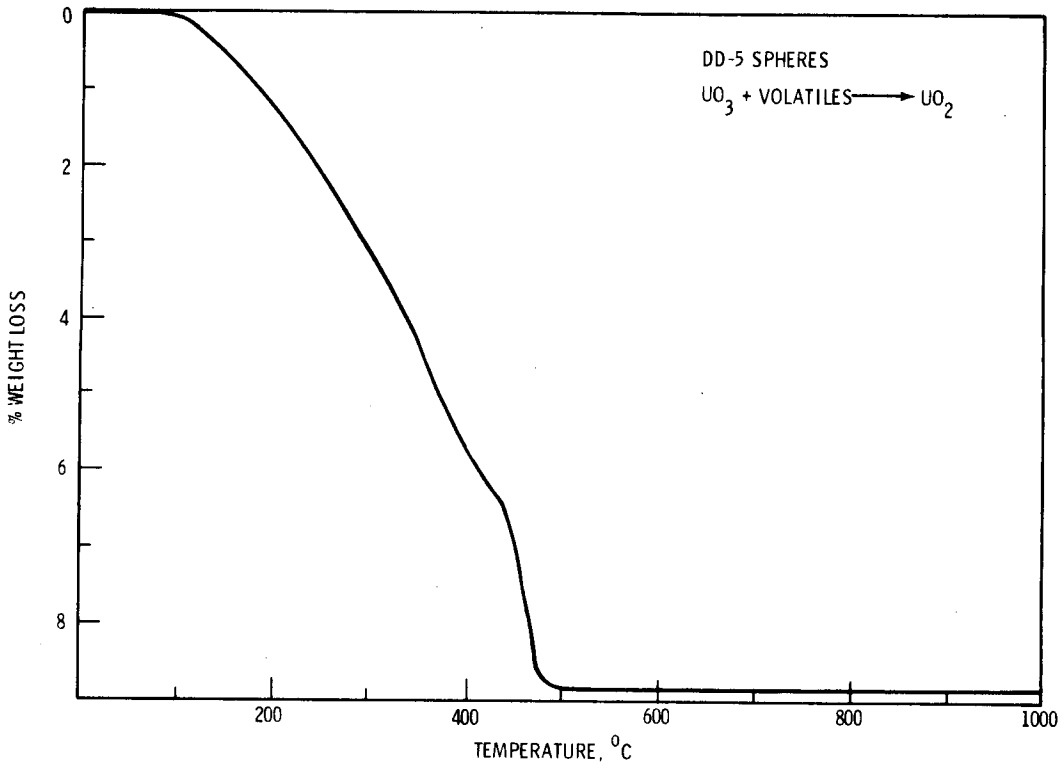


FIGURE 1. Weight Loss as a Function of Temperature for UO_3-gel Spheres in Ar-4% H_2

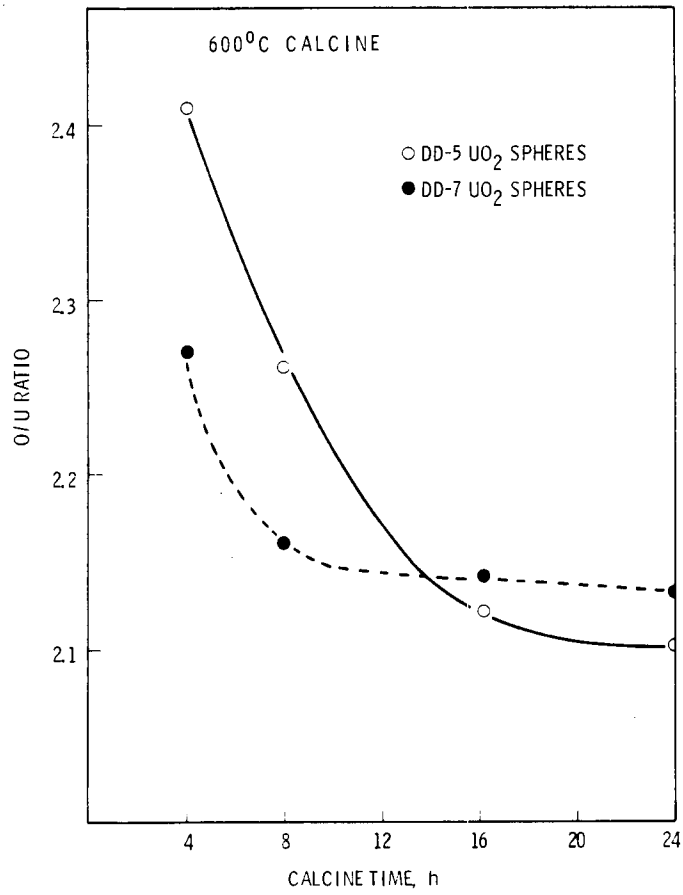


FIGURE 2. The Effect of Calcining Time at 600°C on the O/U Ratio of Uranium Oxide Spheres After Exposure to Room Temperature Air

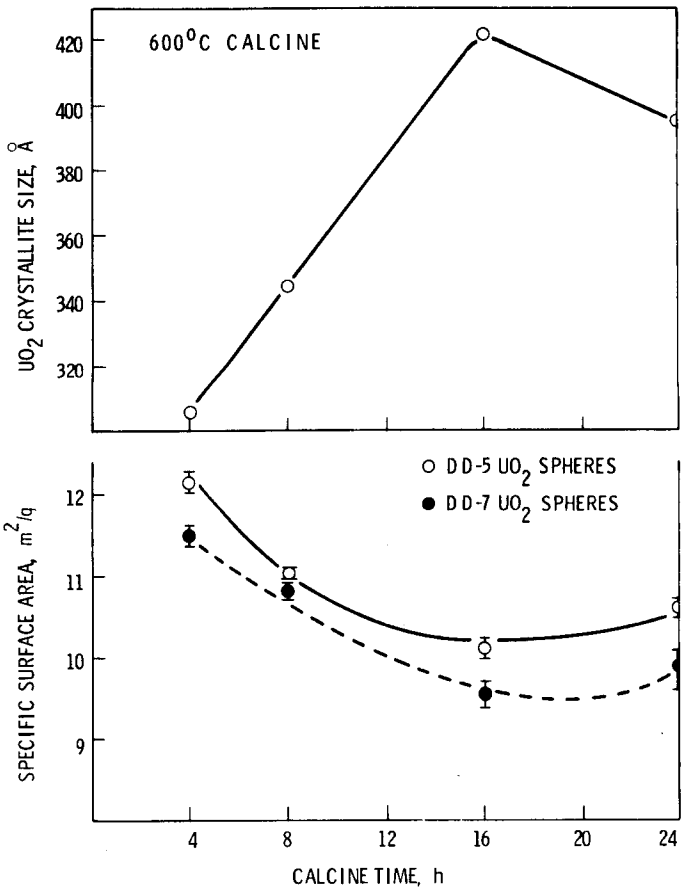


FIGURE 3. The Effect of Calcining Time at 600°C on the Surface Area and Crystallite Size of Uranium Oxide Spheres

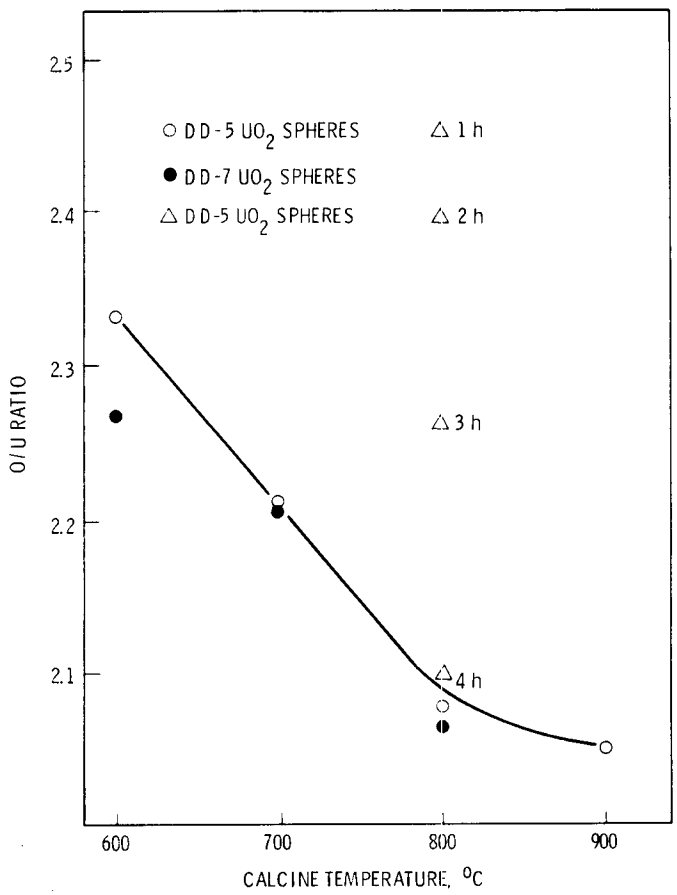


FIGURE 4. The Effect of Calcining Temperature on the O/U Ratio of Uranium Oxide Spheres After Exposure to Room Temperature Air. Calcining Time is 4 h Unless Noted.

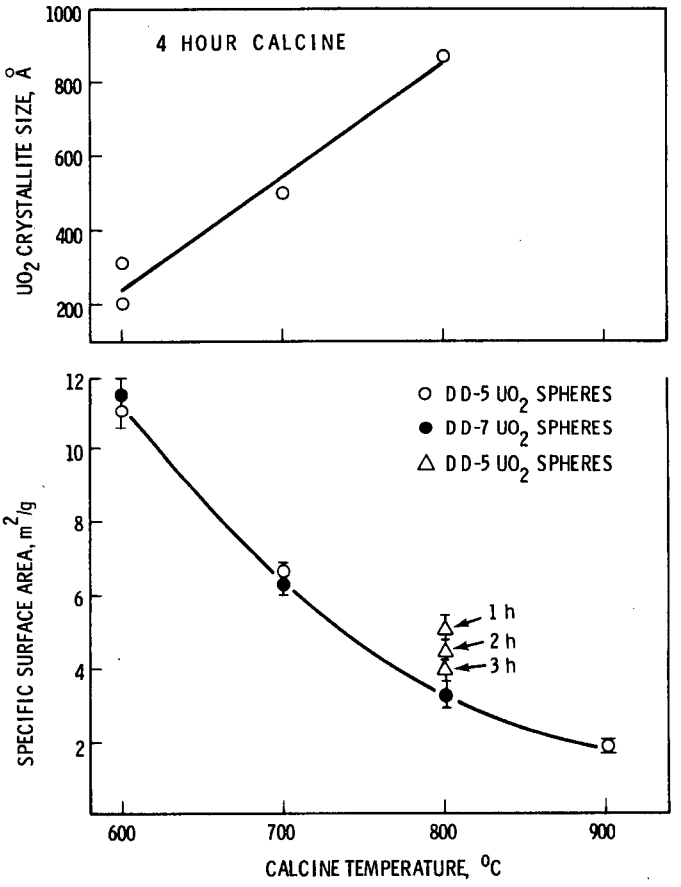


FIGURE 5. The Effect of Calcining Temperature on the Surface Area and Crystallite Size of Uranium Oxide Spheres

partial sintering occurs at temperatures above 600°C. The effects of calcining temperatures were nearly the same for both DD-5 and DD-7. The DD-5 spheres were calcined for 1, 2, 3 and 4 h at 800°C to determine the effect of time at the higher temperature. The triangular points of Figures 4 and 5 show that the surface area drops to about 5 m^2/g after only 1 h at 800°C, while the O/U remains above 2.25 up to 3 h at 800°C.

Figure 6a shows an optical micrograph of the DD-5 spheres after the 600°C - 16 h calcine; Figure 6b shows an SEM micrograph of the fracture surface of one of these spheres. SEM micrographs show that the surface structure of the calcined spheres has a coarse, grainy texture. Fracture surfaces of the spheres (Figure 6b) have an open structure that appears similar to fine-grained, sinterable UO_2 powders. Changes in this type of structure with various calcining conditions could not be resolved on the SEM.

EFFECT OF CALCINING CONDITIONS ON PRESSING AND SINTERING OF UO_2 SPHERES

Preliminary pressing studies indicated that the low bulk density of the spheres caused abnormally high compaction ratios and pellets with low length/diameter ratios. The pressing characteristics were sensitive to die lubricant additions, i.e., no lubricant resulted in a low end-capping threshold and surface microcracks, while 0.2 wt% lubricant mixed with the spheres prevented bonding and the pellets fell apart when ejected from the die. A light coating of zinc stearate mold release applied to the die was the most effective lubricant. Pressure had a positive effect on green density of pellets pressed from DD-8 spheres as shown in Figure 7; end caps began to appear at 250 MPa. However, sintered density of these pellets was independent of pressure, so 150 MPa was used as the standard forming pressure for all sphere batches. Pellets pressed at 150 MPa had smooth surfaces, clean edges and no significant cracks or chips; however, the green densities of the pellets are lower than routinely achieved with standard UO_2 powders.

The tap densities of spheres calcined at 600°C are plotted against calcining time in Figure 8. The small increase in tap density with time reflects the restructuring of the spheres. Note that density is reduced by the presence

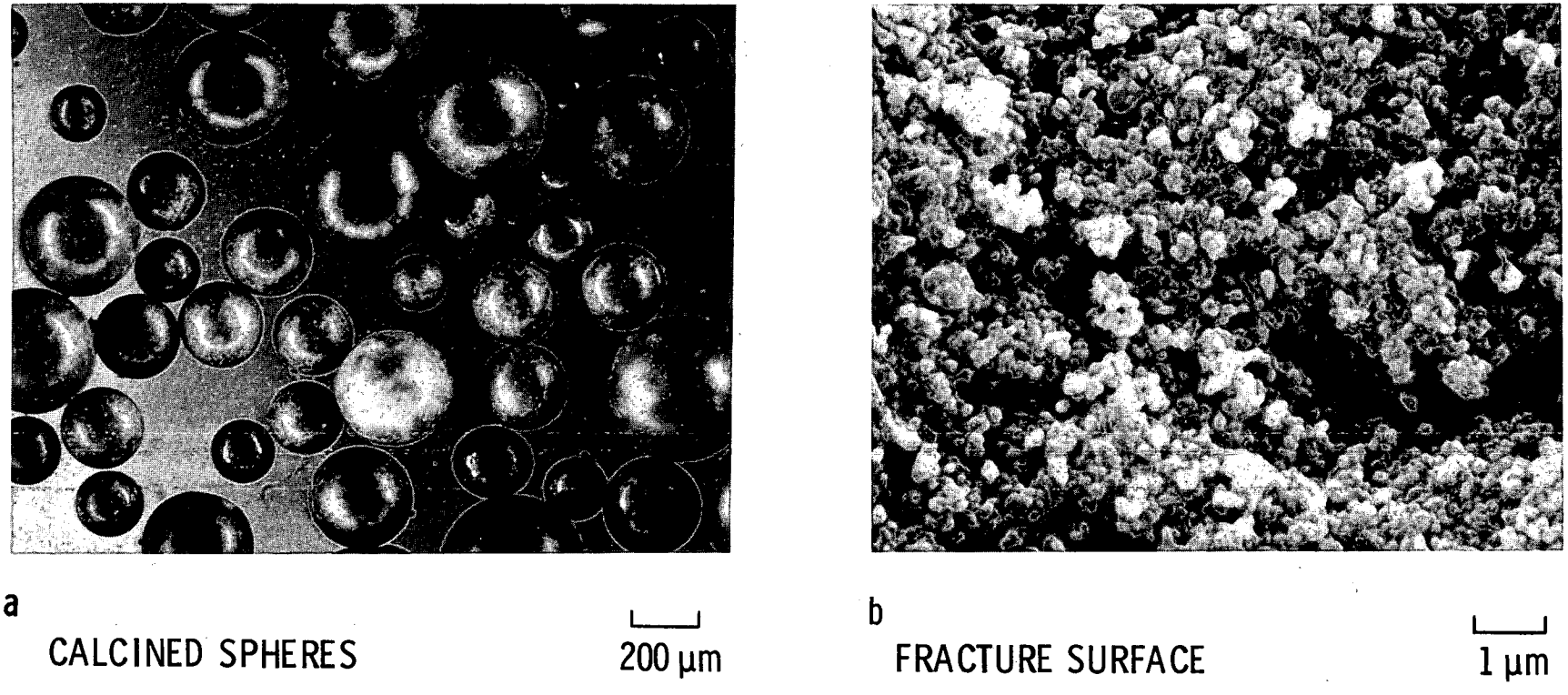


FIGURE 6. (a) Calcined UO_2 Gel Spheres, and
(b) SEM Micrograph of the Fracture Surface of a Calcined Sphere

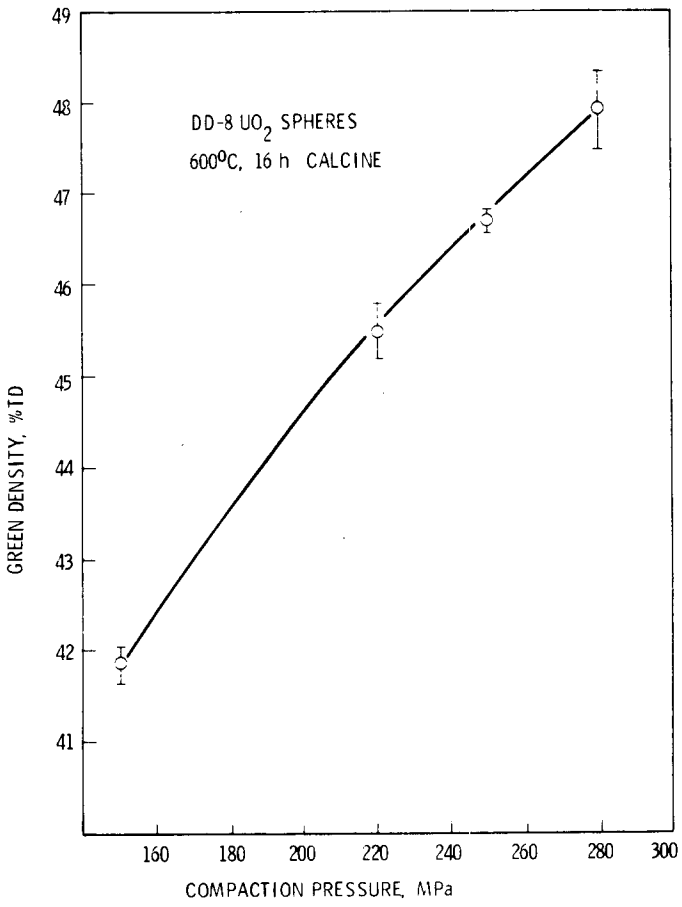


FIGURE 7. The Effect of Compaction Pressure on the Green Density of UO_2 Hybrid Pellets

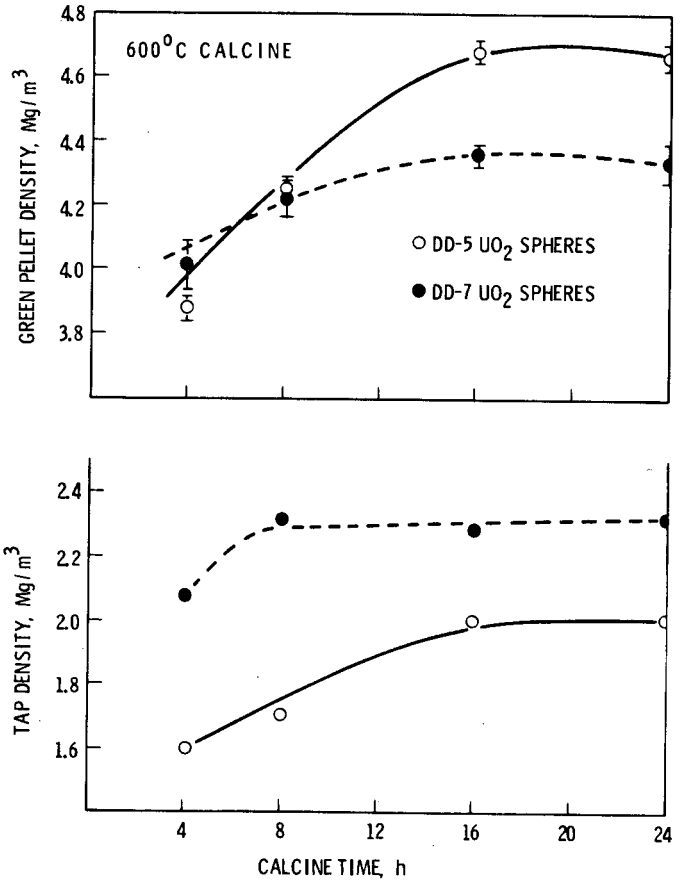


FIGURE 8. The Effect of Calcining Time at 600°C on the Tap Density and Green Pellet Density of Uranium Oxide Hybrid Pellets

of U_3O_8 so the apparent density change plotted in Figure 8 is magnified by spheres with O/U greater than 2.25. Higher calcining temperatures made a significant improvement in tap density, as shown in Figure 9, due to the partial sintering that occurs at 800°C and above. Green pellet densities showed a similar increase with increasing time and temperature as shown in Figures 8 and 9. Although the tap densities of the DD-7 spheres are greater than DD-5, the green density of the DD-5 pellets were equal or exceed those of DD-7. This is due to the enhanced deformability and bonding of the low density DD-5 spheres.

Micrographs of fractured surfaces of green pellets made from DD-5 spheres calcined at 600°C for 24 h show that the spheres deform into ellipsoids during pressing and extremely tight packing and intimate contact between spheres occurs throughout the pellet (see Figure 10a). Green pellets made from DD-5 spheres calcined at 800°C for 4 h contain undeformed, intact spheres with cracks surrounding the sphere interfaces as shown in the SEM micrograph in Figure 10b.

Sintered densities of pellets made from spheres calcined at 600°C are plotted against calcining time in Figure 11. Density of pellets made from DD-5 spheres increases significantly with calcining time up to 16 h. Pellets fabricated from spheres with O/U greater than 2.2 (4- and 8-h calcine runs for DD-5 spheres) were severely cracked after sintering with cracks surrounding individual spheres and running through the pellets as shown in Figure 12a. However, the microstructure in Figure 12b contains areas of very high density with no cracking or porosity at sphere interfaces. Pellets fabricated from spheres with O/U less than 2.2 (16- and 24-h calcine runs for DD-5 spheres) were crack-free and microstructures show a high density structure with some porosity outlining sections of residual sphere interfaces as shown in Figure 13 for DD-5 spheres. The DD-7 spheres behave similarly to the DD-5 spheres. Pellets fabricated from the DD-7 spheres with low O/U ratios (8-, 16- and 24-h calcine runs) sintered to about 93% TD, while those with high O/U ratios cracked during sintering. Microstructures of these sintered pellets showed less bonding between spheres and obvious remanent sphere outlines.

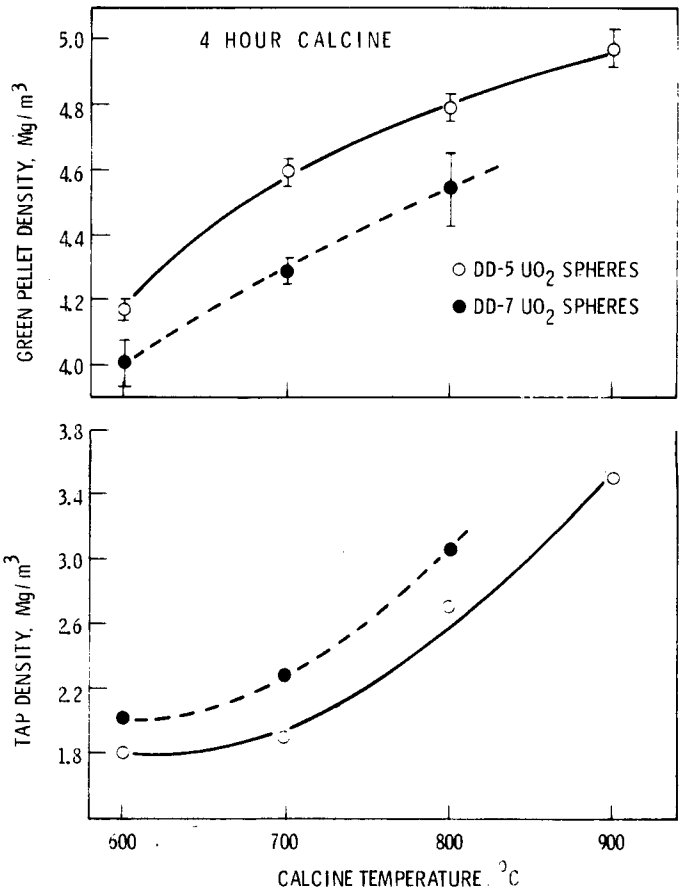


FIGURE 9. The Effect of Calcining Temperature on the Tap Density and Green Pellet Density of Uranium Oxide Hybrid Pellets

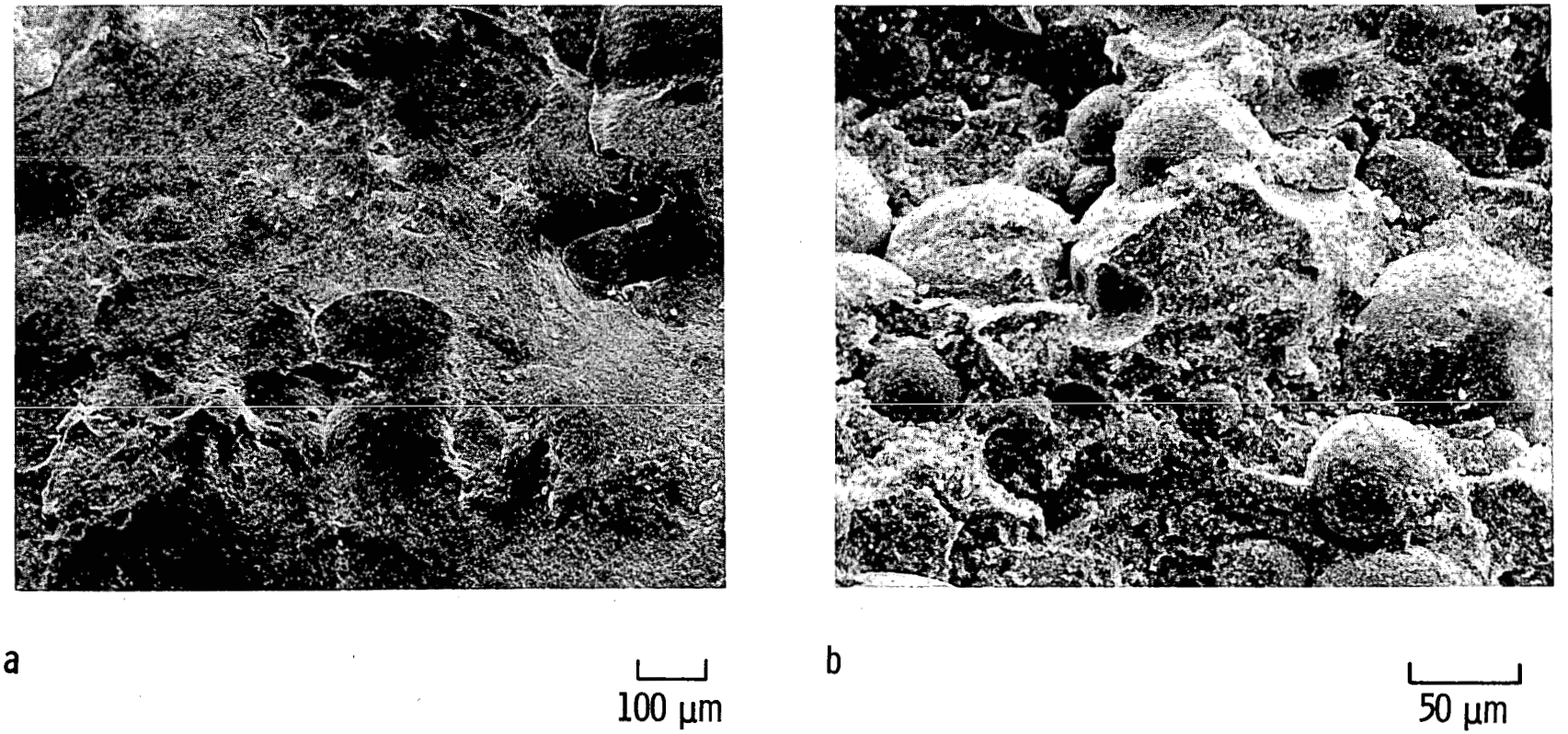


FIGURE 10. SEM Micrographs of the Fracture Surface of Green Pellets
(a) UO_2 Spheres Calcined at 600°C for 16 h
(b) UO_2 Spheres Calcined at 800°C for 4 h

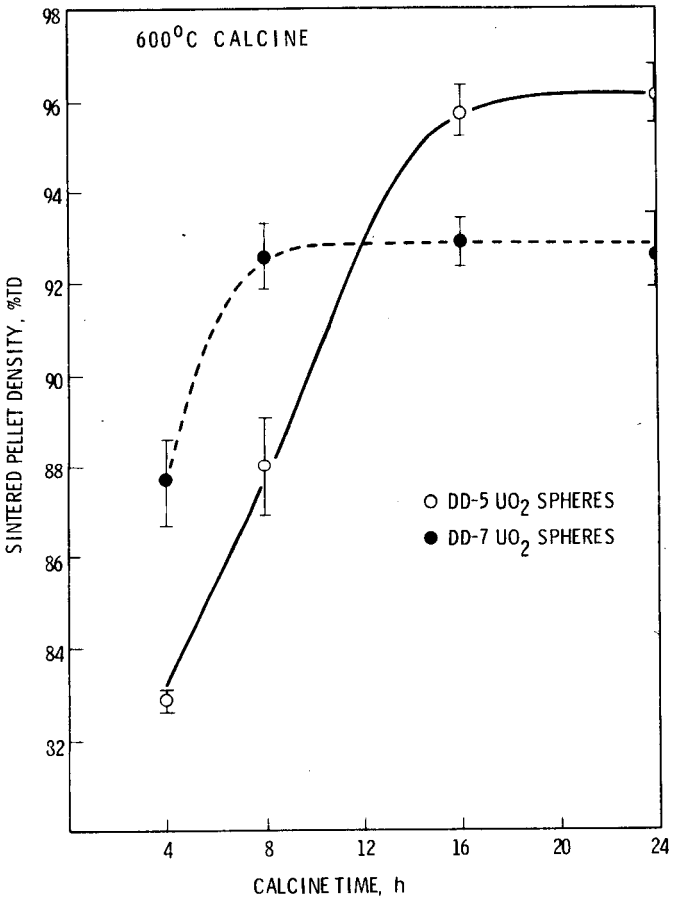


FIGURE 11. The Effect of Calcining Time at 600°C on the Sintered Density of UO_2 Hybrid Pellets

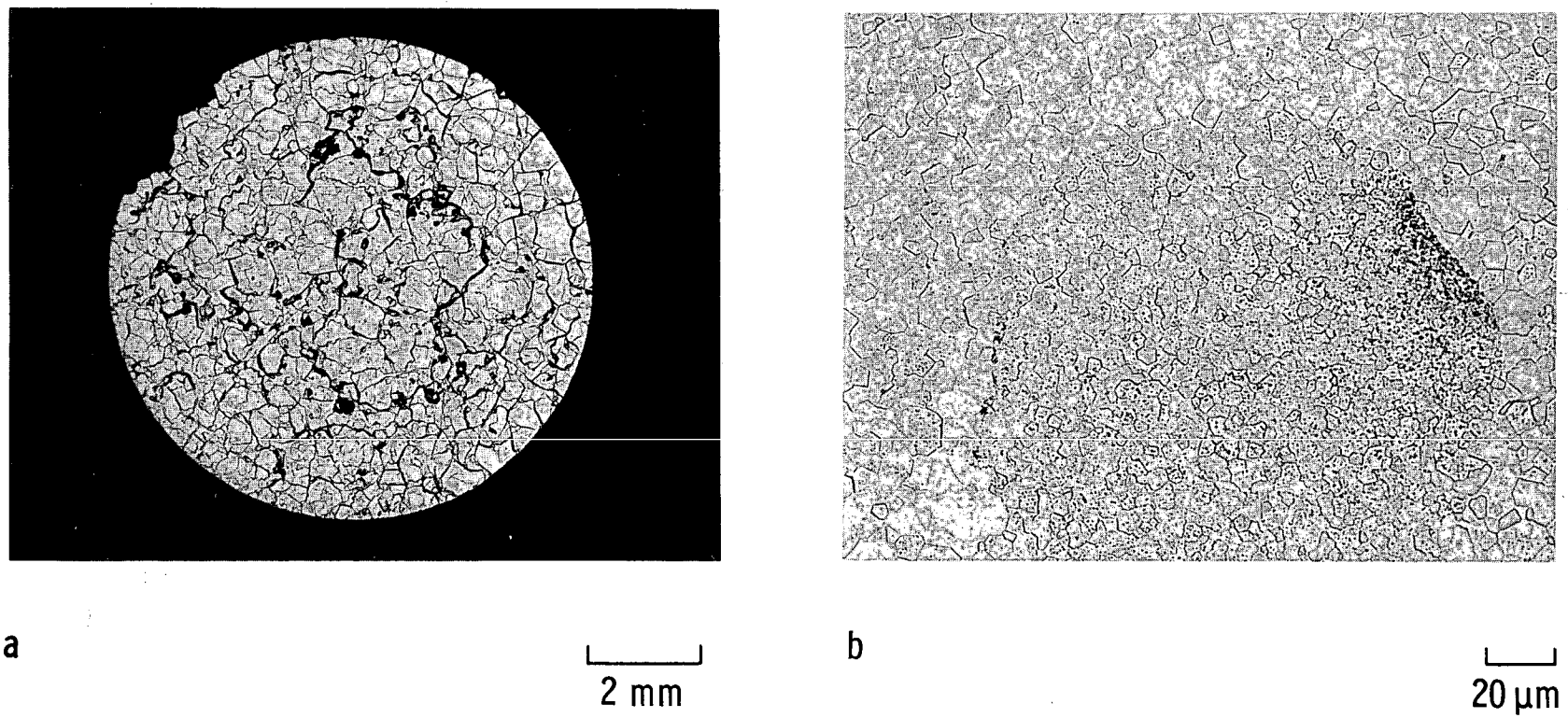


FIGURE 12. Micrograph of a UO_2 Hybrid Pellet Made from Spheres Calcined at 600°C for 4 h
(a) Shows the Gross Cracking Throughout the Pellet
(b) Shows an Area of High Density and Good Sintering Between Spheres (83% TD)

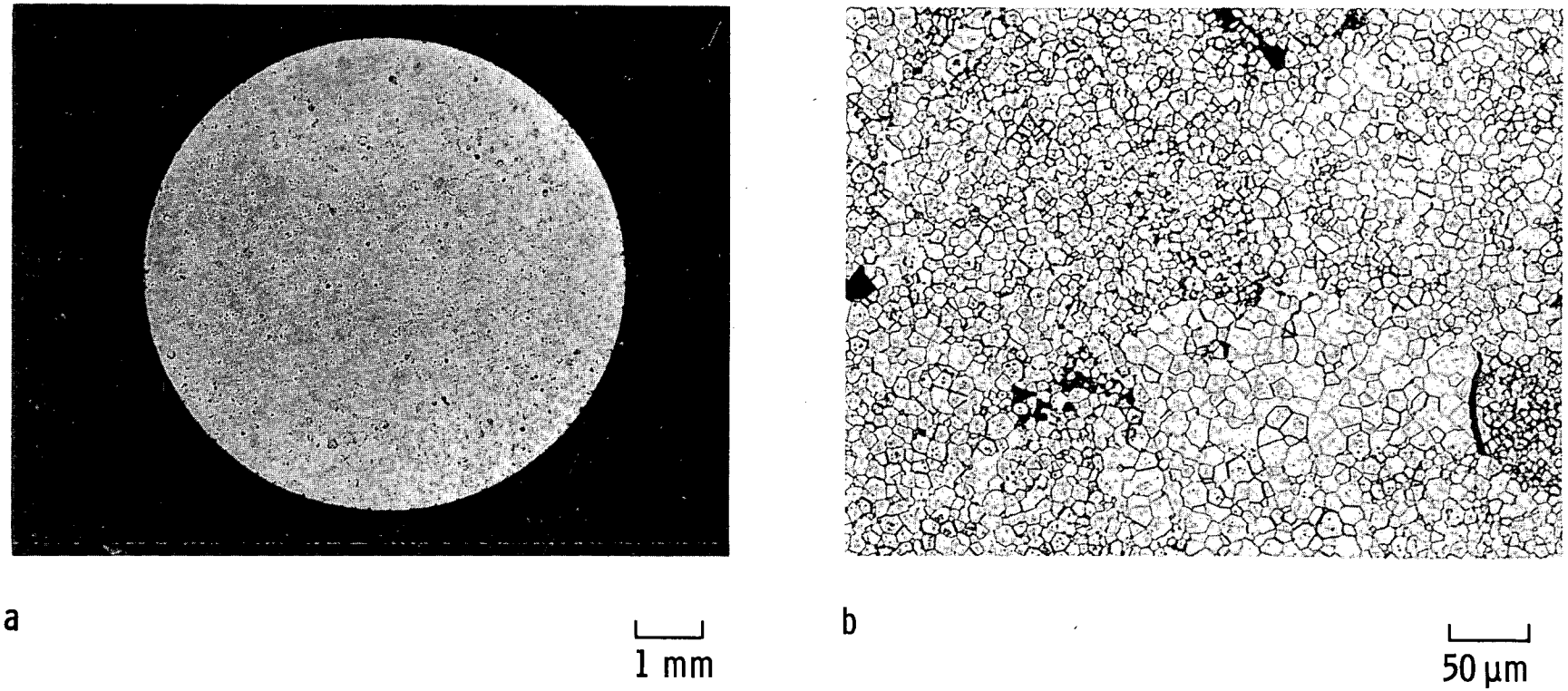


FIGURE 13. Micrograph of a UO_2 Hybrid Pellet Made from Spheres Calcined at 600°C for 24 h
(a) Shows the Cross-Section of an Intact Pellet
(b) Shows a High Magnification Etched Section (96% TD)

The effect of sphere calcining temperature on sintered pellet density is plotted in Figure 14; the sintered density falls off with increasing temperature. Pellets made from spheres calcined for 4 h at temperatures below 700°C cracked during sintering. Calcining temperatures above 700°C gave low density pellets with poor sintering between sphere interfaces as shown in the micrograph in Figure 15. The entire series of pellets fabricated from the DD-5 spheres calcined at 800°C for 1 to 3 h sintered to less than 85% TD as shown by the triangular point in Figure 14.

EFFECTS OF SPHERE PROPERTIES ON PRESSING AND SINTERING BEHAVIOR

Tap density is an important powder characteristic affecting pressing conditions, so a similar series of calcining and pellet fabrication tests was done using high bulk density, DD-7 spheres. The effect of calcining conditions on DD-7 sphere properties are plotted in Figures 2 through 5 along with the DD-5 results. As discussed in the previous section, the trends for the two types of spheres are similar. The lower sintered density of the DD-7 pellets reflects the low green pellet density. Gelation and drying conditions have a significant effect on tap density and the subsequent microstructure of UO_2 hybrid pellets. Appendix A summarizes the data from calcining, pressing and sintering tests done on various batches of UO_3 gel spheres. The lowest tap density spheres came from steam dried batches (DD-3A, DD-9 and DD-14) and these spheres yielded pellets with the highest sintered densities. In addition, remanent sphere outlines were nearly eliminated from the microstructure of sintered pellets made from steam dried spheres as shown in Figures 1-A, a, h and 1. The low tap densities of the spheres resulted in high compaction ratios during pressing and pellets with low length/diameter ratios.

Another important powder characteristic is particle size of the press feed granules, so evaluations were done on 50 to 800 μm UO_3 spheres formed under similar conditions. The 50 μm spheres were difficult to handle and press because they did not flow smoothly due to the effect of electrostatic charges. Sphere properties and sintered densities for selected sphere batches for the best calcining times at 600°C are listed in Table I. Sphere properties and calcining trends were similar for all sizes, but sintered pellet

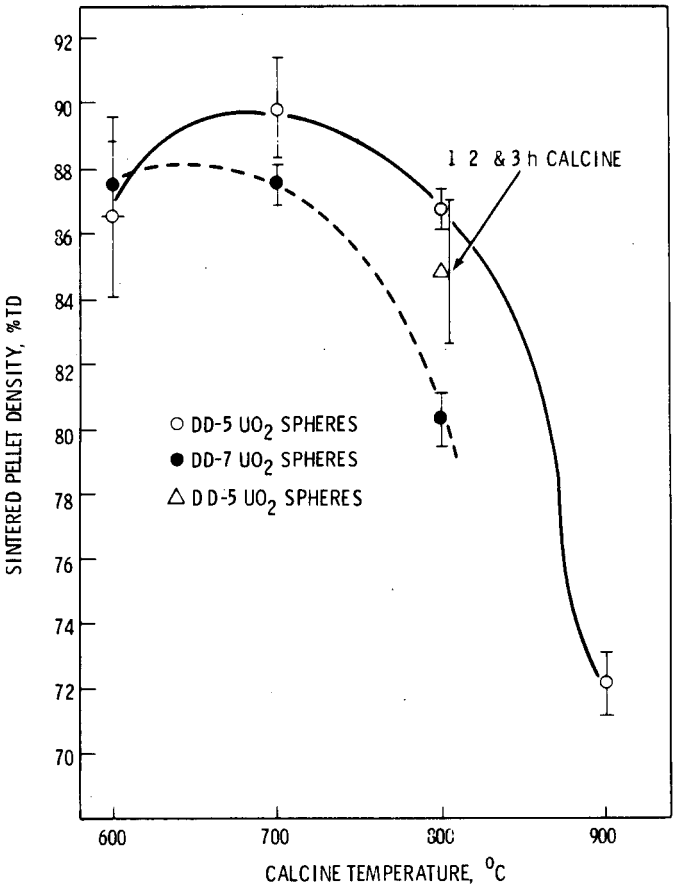


FIGURE 14. The Effect of Calcining Temperature on the Sintered Density of UO_2 Hybrid Pellets. Calcining Time is 4 h Unless Noted.

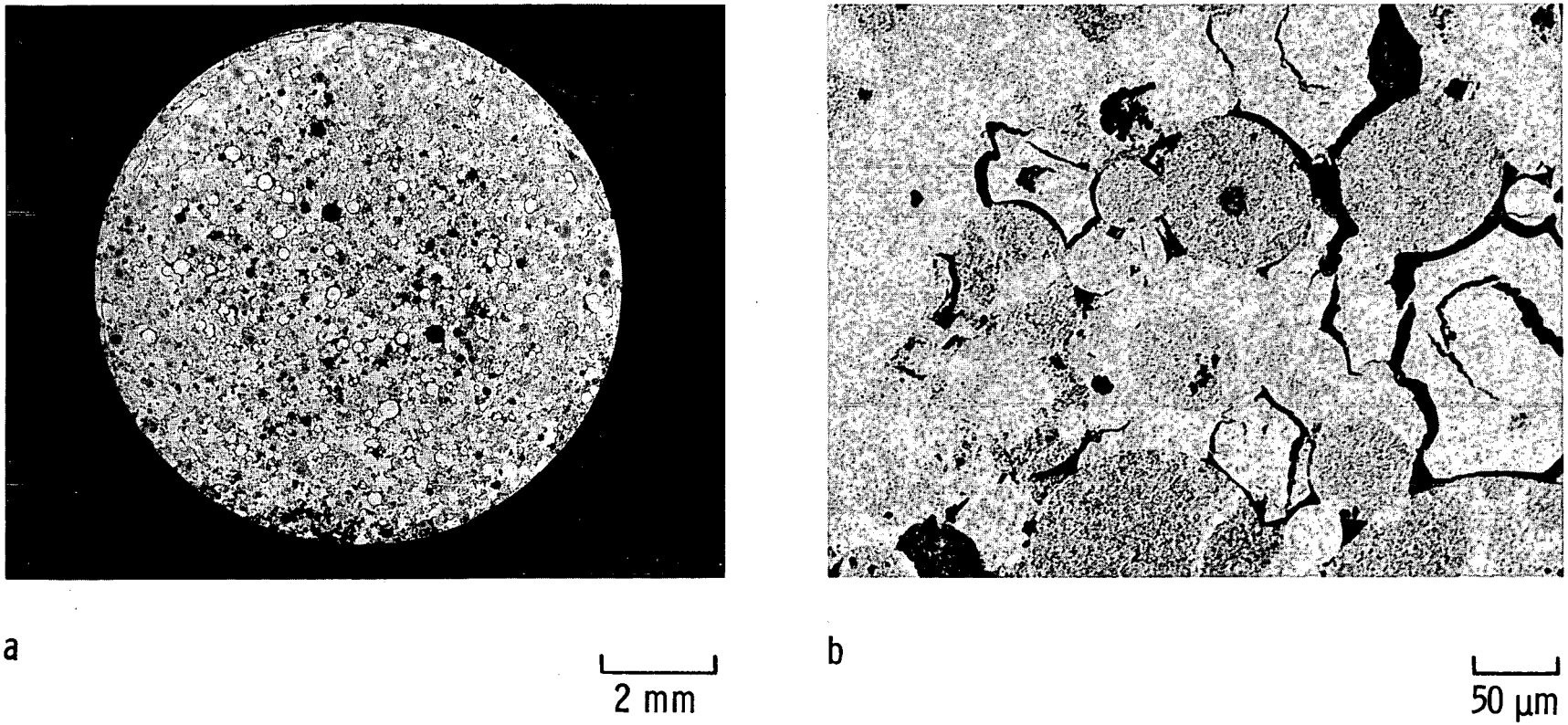


FIGURE 15. Micrograph of a Hybrid UO_2 Pellet Made from Spheres Calcined at 800°C for 4 h
(a) Shows the Cross-Section of the Pellet
(b) Shows the Lack of Sintering Between Spheres (87% TD)

TABLE I. Comparison of Sphere Properties and Sintered Pellet Densities for 50 to 800 μm Gel Spheres

Batch	Approximate Sphere Size (μm)	Calcining Time at 600°C (h)	Tap Density (Mg/m^3)	O/U	Specific Surface Area (m^2/g)	Average Sintered Pellet Density (%TD)
DD-4	50	8	1.7	2.15	10.4	91.6
DD-5	200	16	2.0	2.12	10.1	95.7
DD-8	400	16	2.1	2.06	7.8	95.5
DD-13	600	16	2.1	2.13	8.4	93.7
DD-15	800	16	2.1	2.09	7.1	94.4

densities were lower for the finest and coarser spheres. Photomicrographs of these pellets are shown in Figure 1-Ac, d, g, k and m in Appendix A. The 200 to 400 μm spheres give pellets with the most acceptable microstructures. Pellets made from the coarse spheres contain large pores at residual sphere interfaces, resulting in the lower densities. Additional calcining runs at 700 and 800°C further deactivated the finest and coarser spheres and reduced sintered pellet densities below 90% TD.

Four additional UO_3-gel sphere types were calcined, pressed and sintered in an attempt to identify sphere formation conditions best suited for fabrication of press feed spheres. Data summarizing calcining conditions, sphere properties and pellet densities are listed in Table II. The surface area decreased and the UO_3 was reduced to UO_2 with prolonged 600°C calcining cycles. Intact, crack-free pellets were pressed from each batch and sintered densities greater than 95% TD were readily achieved with all batches except DD-10 which had the highest tap density. In all cases, O/U of less than 2.2 was required to yield intact pellets. The DD-8 pellets, which were pressed at higher compaction pressures, (see Figure 7) all sintered to 95% TD. These results suggest that sphere formation conditions that lead to high density spheres are not favorable for hybrid pellet fabrication.

As shown in the micrographs of Appendix A, pellets pressed from the various sphere batches exhibited a range of microstructures. In general, the spheres

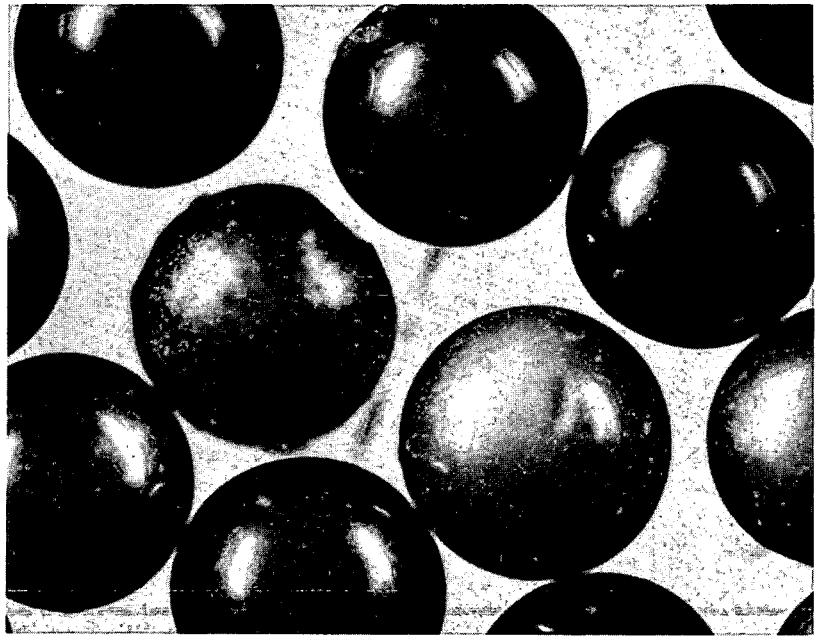
TABLE II. Comparison of Sphere Properties and Pellet Densities for Various Types of UO_3-gel Spheres Calcined at 600°C

Batch	Calcine Time (h)	Tap Density (% TD)	O/U	Specific Surface Area (m^2/g)	Green Density (%TD)	Sintered Density (%TD)	Observations
D-8	4	1.8	2.32	9.2	38.5	87.0	Cracked pellets
	16	2.1	2.06	7.8	43.0	95.5	Intact pellets
DD-9	4	1.4	2.21	10.6	43.5	96.1	Intact pellets
	16	1.5	2.18	9.5	44.0	95.8	Intact pellets
DD-10	4	2.2	2.43	8.7	34.6	79.9	Cracked pellets
	16	2.6	2.05	7.0	39.2	88.0	Intact pellets
DD-11	4	1.9	2.21	9.4	40.6	90.3	Cracked pellets
	16	2.1	2.07	8.3	42.9	95.8	Intact pellets

sintered to high densities and contained little internal porosity with most of the porosity being located between the spheres. Similar structures are achieved in UO_2 fuels when powders are precompacted at high pressures, crushed and granulated into press feed material.

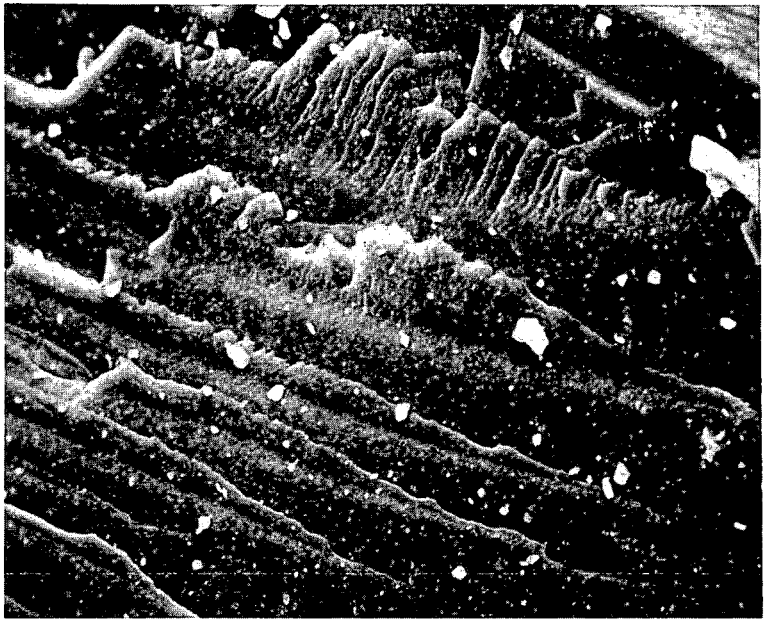
FABRICATION OF ThO_2 AND ThO_2-UO_2 HYBRID PELLETS

Thorium oxide spheres, formed by the external gelation process, were used for preliminary ThO_2 pressing studies. Spheres were supplied in the as-dried state in sizes from 100 to 700 μm. Density of the spheres was higher than for UO_2, i.e., 2.8 Mg/m^3 tap density for all sizes. The ThO_2 spheres had a glassy texture, and SEM micrographs (Figures 16b) show that the fracture surface has a brittle fracture pattern and no porosity or grains can be resolved. The crystallite size was 50 Å, and the surface area was about 100 m^2/g. TGA runs show that the spheres lose about 7% by weight after heating in Ar-4% H_2 to 1000°C, and that outgassing is 91% complete by 550°C. However calcining to moderate temperatures (200-400°C) decreased the green and sintered pellet densities by about 5% TD. Further pressing and sintering of as-received ThO_2 spheres into pellets showed that the pellets crumbled below a threshold compacting pressure of 115 MPa. The density of pellets sintered at 1500°C ranged from 72.9% TD for as-received 100-μm spheres to 82.3% TD for as-received 700-μm



(a) AS-RECEIVED SPHERES

200 µm



(b) FRACTURE SURFACE

10 µm

FIGURE 16. (a) As-Received ThO_2 Gel Spheres
(b) SEM Micrograph of the Fracture Surface of a ThO_2 Sphere

spheres, and increasing sintering temperature to 1700°C did not increase density. Small CaO additions (0.5 wt%) increased sintered density by about 5%, while communition of spheres into fine powders by extensive ball milling increased sintered density by about 4%. The ThO_2-25 wt% UO_3 spheres had properties similar to the ThO_2 spheres and pellets sintered to only 70 to 75% TD.

The photomicrograph in Figure 17 shows that some of the ThO_2 spheres shattered during pressing while others remained intact, and that no sintering took place between spheres or fractured shard; densification of the pellet occurred solely by sintering of the individual spheres or sphere fragments.

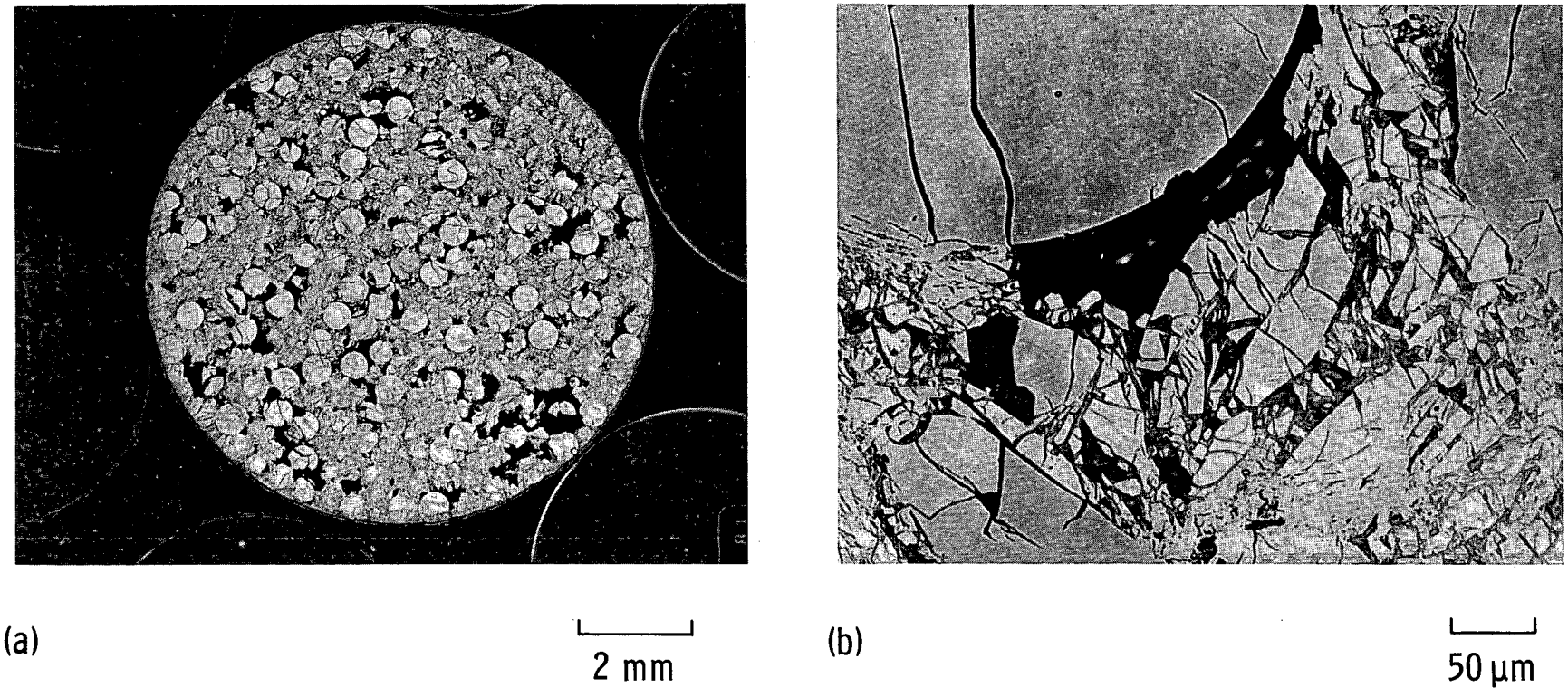


FIGURE 17. Micrograph of a ThO_2 Hybrid Pellet
(a) Shows the Cross-Section Through the Pellet
(b) Shows a High Magnification Detail of the Shattered Spheres (82% TD)

DISCUSSION

Thermal gravimetric analysis of UO_3 spheres showed that the reduction to UO_2 was complete after heating to 500°C in Ar-4% H_2, however the high O/U ratios of calcined spheres suggest that UO_2 spheres can oxidize in room temperature air. It has been established that the stoichiometry of UO_2 powders can change during storage in air,[9] and the amount of oxygen uptake increases with the specific surface area of the powders.[10] Pyrophoric reactions have been reported,[10] and the partial transformation of UO_2 to UO_3 under long term storage in air has been observed.[11] Apparently, the high surface area of the spheres calcined for short times promotes rapid oxidation and partial transformation of UO_2 to U_3O_8. The results of the calcining studies indicated that increased calcining times and/or temperatures reduce surface area and thereby inhibit rapid oxididation. Analysis of DD-7 spheres calcined for 24 h at 600°C that have been stored in closed containers in air for several months showed that the O/U increases slowly with time (i.e., from $UO_{2.13}$ to $UO_{2.24}$ after 4 months). Higher calcining temperatures also act to stabilize the stoichiometry of UO_2 spheres by decreasing surface area.

The high O/U ratios of the spheres calcined for 4 h at 600°C could be explained by incomplete reduction during the calcining cycle. In order to confirm that the calcined spheres were fully reduced, DD-5 spheres were calcined for 4 h at 600°C in Ar-4% H_2 and removed under argon cover gas to prevent air contamination. The O/U ratio of these spheres was 2.01 thereby confirming that reduction was complete during the 600°C-4 h calcining cycle. Thermogravimetric analysis confirmed that UO_2 spheres reoxidize on exposure to room temperature air. UO_3 gel spheres were heated in Ar-4% H_2 to 600°C, held at temperature for 4 h, cooled to room temperatures and exposed to air while recording weight change. Figure 18 shows that the spheres were reduced at temperature but a weight increase which corresponds to an O/U of 2.28 occurred soon after exposure to air. This curve confirms that the spheres oxidize rapidly in air.

Calcining temperature is the most important parameter affecting pressing behavior of the UO_2 spheres. The spheres calcined at 600°C pressed equally

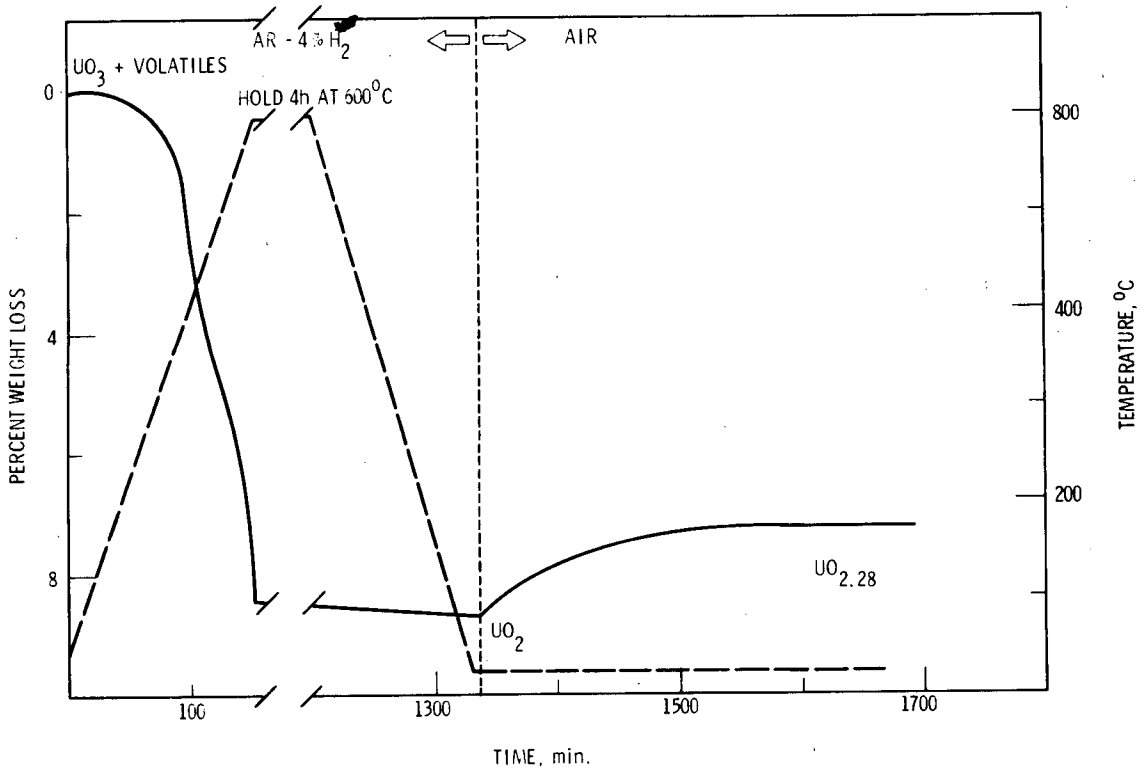


FIGURE 18. Thermogravimetric Analysis of UO_3-gel Spheres Showing Weight Loss During a Standard Calcine Cycle and Reoxidization After Exposure to Room Temperature Air

well regardless of calcining time or O/U. The low green densities after short 600°C calcining times (see Figure 8) are due to the presence of U_3O_8 which has a density of 8.4 Mg/m^3. The increase in green density with calcining temperature (see Figure 9) is largely due to partial sintering of the individual spheres, and in fact, the integrity of the pellets decreased with increasing calcining time. The SEM micrographs of fracture surfaces of green pellets (Figure 10a and b) suggest that the strength of the spheres is the key factor in pressing good green pellets. Deformable spheres favored by low calcining temperatures, readily compact during pressing and form intimate mechanical bonds between spheres. Higher strength spheres, attained by high calcining temperatures, do not deform or adhere together during pressing. The brittle, spheres formed by external gelation of ThO_2 and ThO_2-UO_2 sols, shatter during pressing and do not lend themselves to pellet fabrication. The pressed-in green structure of UO_2 hybrid pellets made from low O/U spheres is retained during sintering, and sphere properties which promote deformation and intimate sphere contact during pressing result in the homogeneous microstructures achieved with the steam dried spheres. In general, higher tap density spheres (greater than 2.3 Mg/m^3) give lower density pellets with a porous microstructure due to decreased bonding between spheres.

Sintering behavior of UO_2 hybrid pellets is influenced by both the stoichiometry and activity of the spheres. When the O/U is greater than 2.2 and U_3O_8 is present in the calcined spheres, offgassing and volume reduction that occurs from the transformation of U_3O_8 to UO_2 during sintering is sufficient to crack the pellets. When the O/U is less than 2.2 the pellets remain intact during sintering and the density and microstructure of the sintered pellets depends on the activity of the spheres and the characteristics of the as-pressed structure. The prolonged calcining times reduce the rate of sphere oxidization in room temperature air and thereby permit longer storage time before pellet fabrication. Pellets made from low activity spheres (surface area less than 8 m^2/g) retained the porous, pressed-in structure; pellets made from active spheres (surface area greater than 10 m^2/g) sintered to high density and had structures similar to standard UO_2 pellets made from powders slugged and granulated prior to pressing. One of the draw backs of this process is the low tap density of the spheres and the subsequent high compaction

ratios needed to press pellet with length-to-diameter ratios equal to or greater than 1. The low tap densities also lead to low green pellet densities and large shrinkage during sintering. Tap density is sensitive to calcining temperature as shown in Figure 9, but increasing tap density reduces sintered pellet density. Calcining conditions were adjusted in an attempt to increase tap density while maintaining pellet sinterability. Calcining parameters of heat up rate, atmosphere, temperature and time were varied systematically and the relative effects of calcining conditions were established (see Table III). Using similar calcining conditions, tap densities up to 2.4 Mg/m^2, with green pellet densities of about 45% TD and sintered pellet densities up to 94% TD have been achieved.

TABLE III. Favored Calcining Conditions

Parameter	Positive Effect	Intermediate Effect	Negative Effect
Heat up rate	300°C/h	200°C/h	30°C/h Heat Up
Heat Up Atmosphere	Ar	Ar-4%H_2	Air
Soak Atmosphere	Ar-4%H_2	Ar-2%H_2	Ar
Soak Temperature	700°C	600°C	<600°C >700°C
Soak Time	4h	3 - 6h	<3h >6h

The data discussed in this paper suggest a set of necessary properties before UO_2 gel spheres can be fabricated into pellets:

- O/U less than 2.20,
- crystallite size less than 500 Å,
- specific surface area greater than 8 m^2/g,
- sphere size 200 to 400 μm.

Given these properties and the open grainy structure and deformability of the UO_2 spheres made by the internal gelation process, high density hybrid pellets can be fabricated using the calcining, pressing and sintering conditions established.

Additional series of calcining and pellet fabrication tests done on other sol-gel sphere types, various sphere sizes and higher sphere densities showed that any significant deviation from the conditions and sphere properties discussed above compromised the hybrid process. For example, ThO_2 spheres made by external gelation could not be fabricated into good pellets; small spheres were difficult to press and sintered to low density; and the higher density spheres yielded low density sintered pellets.

The need for a novel, dust-free hybrid process for fabrication of mixed oxide fuels has been mentioned previously.[12,13,14] The present work has established the feasibility of the hybrid process and defined necessary sphere characteristics and fabrication conditions for producing high density UO_2 pellets. The hybrid process has several attractive features which make it particularly suited for remote operations. The potential for low dust buildup means lower radiation levels, less exposure to operators and easier equipment maintenance than with conventional pelleting. The spheres have better flow properties than powders so transport problems should be reduced and consistent die full should be achieved. Hybrid pellets sinter to high density at lower temperatures than possible with pellets made from conventional powders, so problems with sintering furnaces should be reduced. At the same time, the fuel retains the familiar pellet configuration and is anticipated to exhibit irradiation behavior similar to pellet fuels. Several important areas need development before the process can be considered suitable for remote fabrication. The technology needs to be transferred to mixed oxide fuels; current results with ThO_2-UO_2 spheres have not been positive and the nature of UO_2-PuO_2 spheres has not been assessed. The potential advantages of low dust generation, low personnel exposure and improved transport properties need to be evaluated. In addition, the UO_2 hybrid process needs to be demonstrated on scaled-up fabrication equipment, and the irradiation performance needs to be evaluated and compared with standard pellet fuels.

CONCLUSIONS

The following conclusions may be drawn from this work:

- The feasibility of fabricating fuel pellets from gel-derived microspheres was clearly demonstrated on a laboratory scale.
- UO_2 fuel pellets were successfully fabricated when spheres, formed by internal gelation, had the following properties: O/U less than 2.20, crystallite size less than 500Å, specific surface area greater than 8 m^2/g and sphere size 200 to 400 μm.
- A range of pellet microstructures and densities were achieved depending on sphere formation and calcining conditions.
- Attainment of these sphere properties depended on sphere calcining and forming conditions. Sphere formation conditions, other than those used in this study, may yield spheres with properties outside the specific range of values which are amenable to pellet fabrication.
- Preliminary attempts to fabricate ThO_2 and ThO_2-UO_2 hybrid pellets were not successful. The properties of the spheres fell outside the range of values established for UO_2.

REFERENCES

1. S. M. Tiegs, "Fabrication of UO_2 Fuel Pellets from Gel Microspheres," paper presented at the Pacific Coast Regional Meeting of the American Ceramic Society, Nov. 1978, San Diego, CA.

2. P. E. Hart, R. B. Matthews, G. D. White and N. C. Davis, "ThO_2-Based Pellet Fabrication Development for Proliferation Resistant Fuels," PNL-SA-7395, paper presented at the Annual Meeting of the American Ceramic Society, April 1979, Cincinnati, OH.

3. H. H. Crain and C. R. Hutchison, "Fabrication of Fuel Pellets from Sol-Gel Powders," WARD-TM-531, Bettis Atomic Power Laboratory, Pittsburgh, PA, (1966).

4. J. M. Robbins and J. G. Stradley, "Fabrication of Sol-Gel Derived Thoria-Urania by Cold Pressing and Sintering," ORNL-4426, Oak Ridge National Laboratory, Oak Ridge, TN (1969).

5. W. Burkhardt, G. G. Briggs, A. L. Clavel and J. F. White, "Production of Dense Thoria," NLCO-1029, National Lead Company of Ohio, Cincinnati, OH (1969).

6. W. J. Lackey and R. A. Bradley, "Microstructure of Sol-Gel Derived $(U,Pu)O_2$ Microspheres and Pellets," Nuclear Technology, 14, 257-268 (1972).

7. P. A. Haas, J. M. Begovich, A. D. Ryon and J. S. Vavruska, "Chemical Flowsheet Conditions for Preparing Urania Spheres by Internal Gelation," ORNL/TM-6850, Oak Ridge National Laboratory, Oak Ridge, TN, (1979).

8. G. Brambilla, P. Gerontopulos and D. Neri, "The SNAM Process for the Preparation of Ceramic Nuclear Fuel Microspheres: Laboratory Studies," Energ. Nucl. (Milan) 17, 216-224 (1970).

9. J. Belle, ed., Uranium Dioxide: Properties and Nuclear Applications, Chapter 3, U.S. Atomic Energy Commission, Washington DC (1961).

10. M. J. Bannister, "The Storage Behavior of Uranium Dioxide Powders-Review Article," J. Nucl. Mater., 26, 174, (1968).

11. T. Wadston, "The Oxidization of Polycrystalline Uranium Dioxide in Air at Room Temperature," J. Nucl. Mater. 64, 315, (1977).

12. R. L. Nelson, N. Parkinson, W. C. Kent and H. A. Taylor, "U. K. Development Toward Remote Fabrication of Breeder Reactor Fuel", Trans. Amer. Nuc. Soc., 32, 227, (1979).

13. E. Vanden Bemden, "Fabrication of Plutonium-Enriched Fuels at Belgonucleaire", Trans. Amer. Nuc. Soc., 32, 236, (1979).

14. D. W. Brite, "Fuels Refabrication and Development Program for Proliferation Resistant Fuels", Trans. Amer. Nuc. Soc., 32, 244, (1979).

ACKNOWLEDGMENTS

The support of T. D. Chikalla and S. Goldsmith of the Fuels and Refabrication Development Program office is gratefully acknowledged. Experimental assistance from C. W. Griffin, E. H. Shade, and D. E. Smith is also gratefully acknowledged. This study would not have been possible without the cooperation of the ORNL personnel who supplied the spheres and information needed to complete the development work.

APPENDIX A

Thirteen batches of UO_3-gel spheres made at ORNL by the internal gelation process were calcined, pressed, and sintered into hybrid pellets. The batches, their formation and drying conditions and as-received properties are listed in Table I-A along with the calcining treatment and sphere and pellet properties. Representative microstructures from each batch are shown in Figure 1-A.

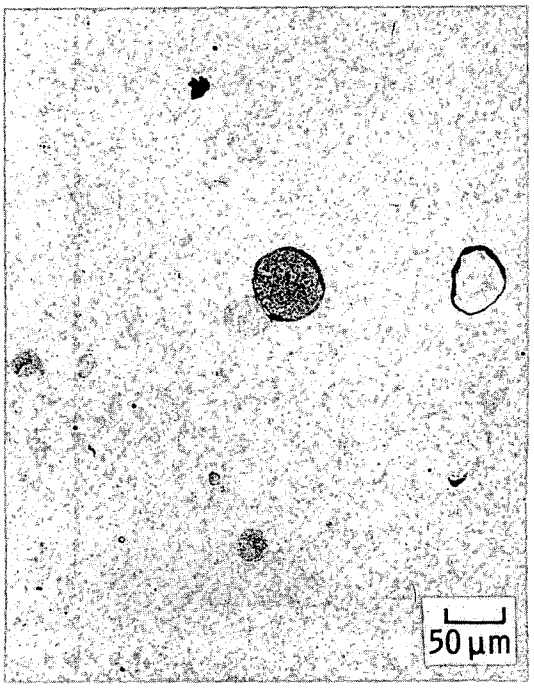
TABLE I-A. Summary of Evaluation Tests for Various Types of UO_3-Gel Spheres

	Formation Conditions		As-Received Sphere Properties			Calcining Conditions		Calcined Sphere Properties			Pellet Properties	
Batch	Gelation Media	Drying Atmosphere	Approximate Size (μm)	Bulk Density (Mg/m^3)	Surface Area (m^2/g)	Temperature (°C)	Time (h)	TAP Density (Mg/m^3)	O/U	Surface Area (m^2/g)	Green Density (%TD)	Sintered Density (%TD)
DD-3A	2-EH*	Steam	200	--	--	600	20	1.40	2.10	--	43.7	97.4
DD-3S	2-EH	Air	200	--	--	600	20	2.36	2.11	--	41.4	93.2
DD-4	2-EH	Air	50	1.1	38	600	8	1.68	2.15	10.4	40.0	91.6
DD-5	2-EH	Air	200	1.3	56	600	16	2.00	2.12	10.1	42.8	95.7
DD-6	2-EH	Air	50	1.5	33	600	16	2.44	2.08	8.0	40.0	90.3
DD-7	2-EH	Air	200	1.5	46	600	16	2.29	2.14	9.8	39.8	92.9
DD-8	TCE+	Air	400	1.4	33	600	16	2.06	2.06	7.8	42.0	95.5
DD-9	TCE	Steam	400	0.9	35	600	16	1.46	2.18	9.5	44.0	95.8
DD-10	TCE	Air	400	1.7	37	600	16	2.60	2.05	7.0	39.2	88.0
DD-11	TCE	Air	400	1.1	33	600	16	2.05	2.07	8.3	42.9	95.8
DD-13	TCE	Air	600	1.4	38	600	16	2.13	2.13	8.4	41.5	93.7
DD-14	TCE	Steam	800	1.2	31	600	16	1.45	2.14	7.1	45.0	96.0
DD-15	TCE	Air	800	1.4	34	600	16	2.14	2.09	7.1	43.3	94.4

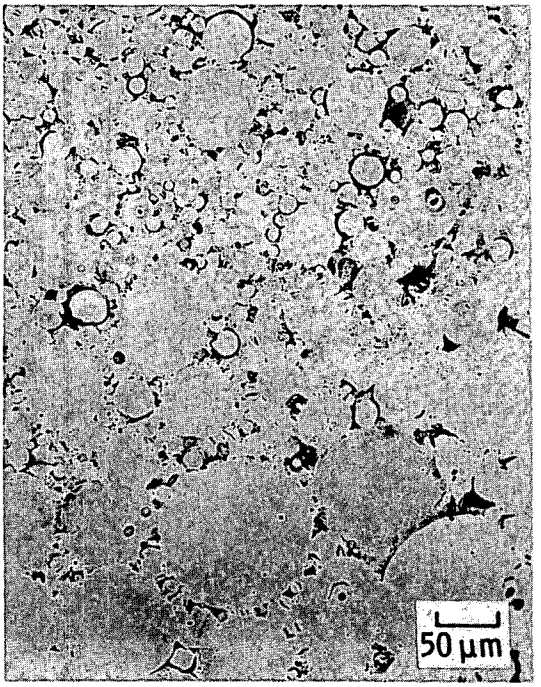
* 2-Ethylhexanol

\+ Trichloroethylene

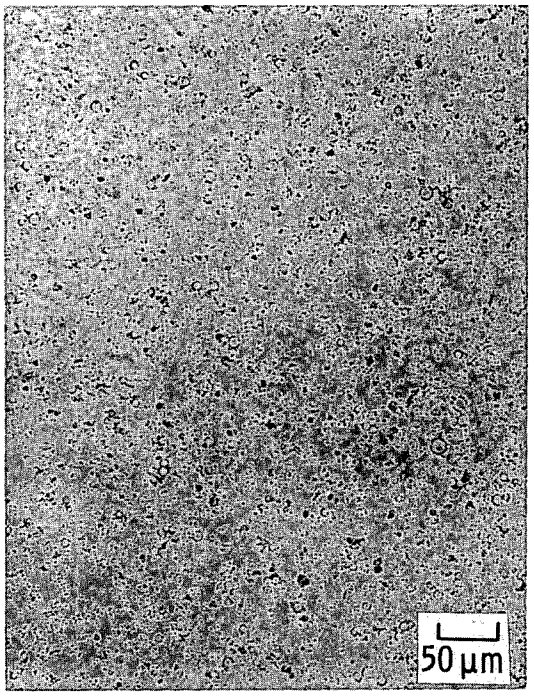
(a) DD-3-A



(b) DD-3-B



(c) DD-4



(d) DD-5

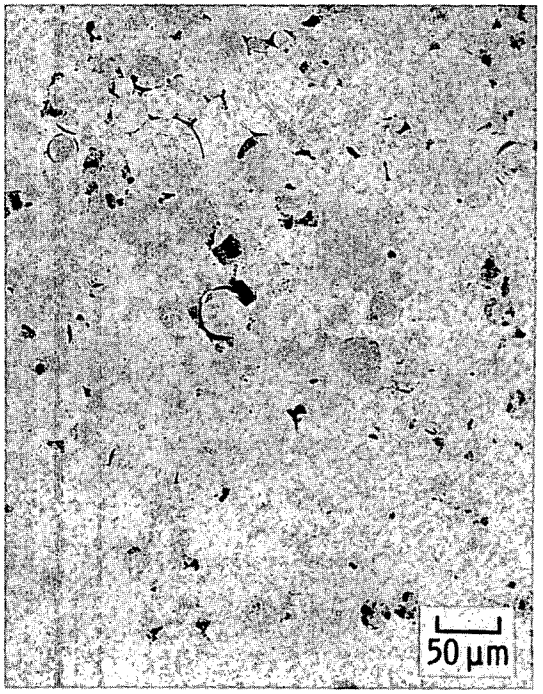
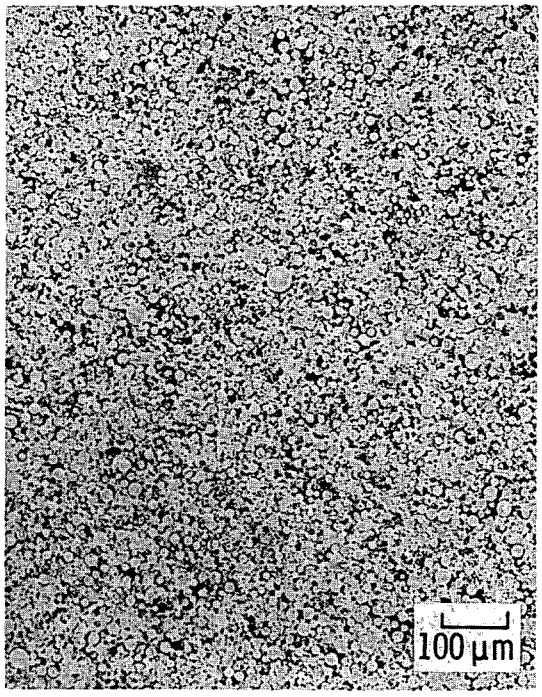
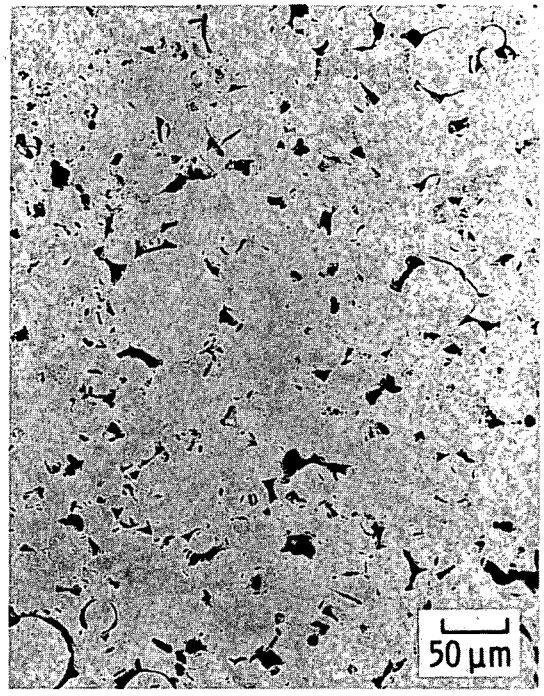


FIGURE 1-A. Microstructures of Sintered Hybrid Pellets Made From Various Types of UO_3 Spheres

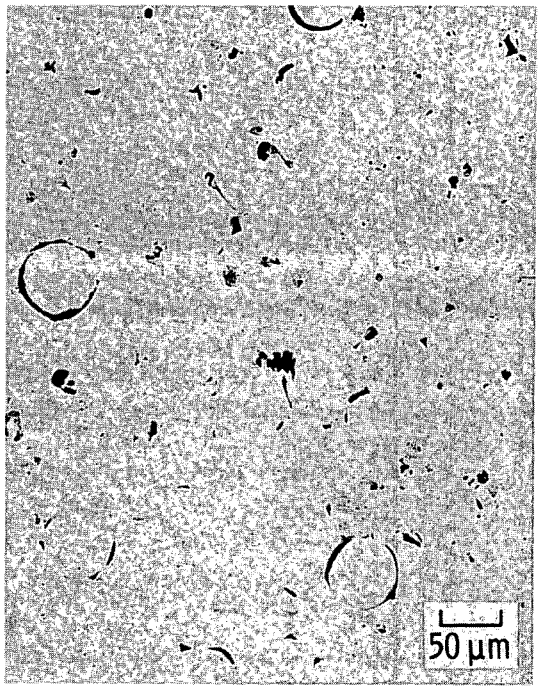
(e) DD-6



(f) DD-7



(g) DD-8



(h) DD-9

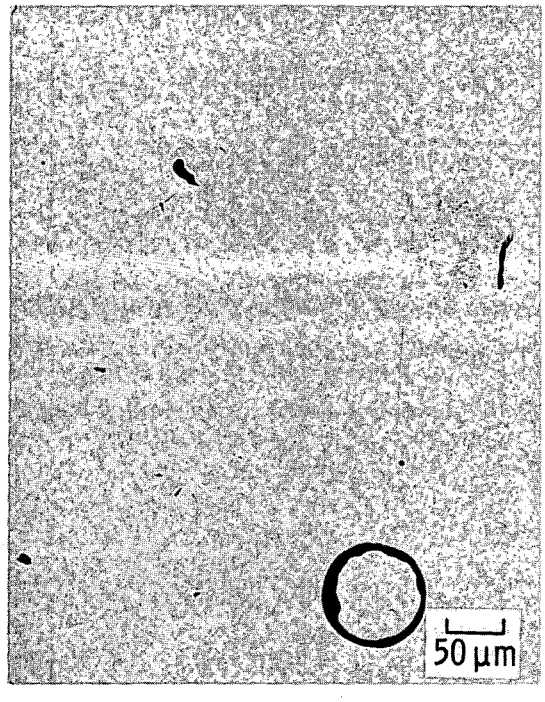
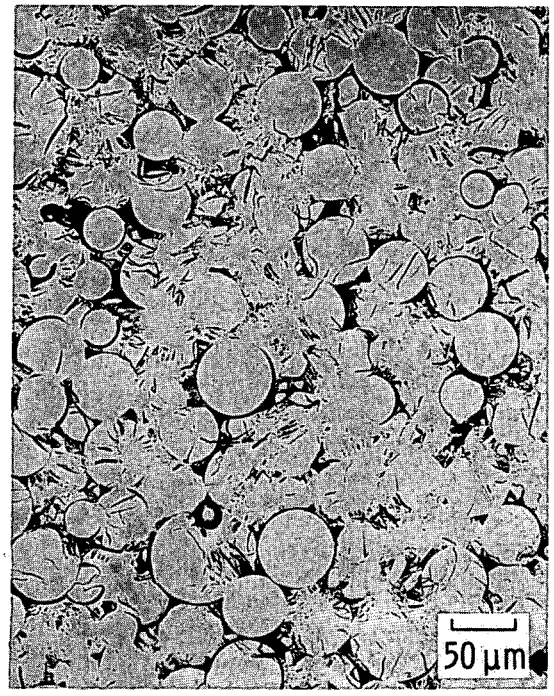
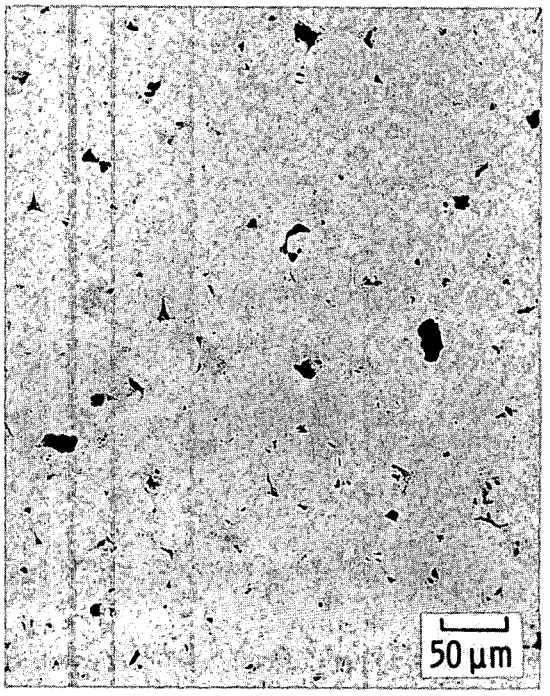


FIGURE 1-A. (contd)

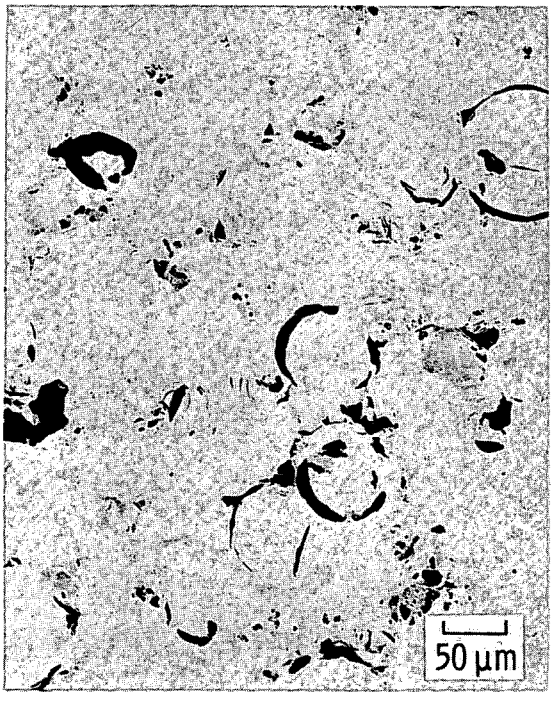
(i) DD-10



(j) DD-11



(k) DD-13



(l) DD-14

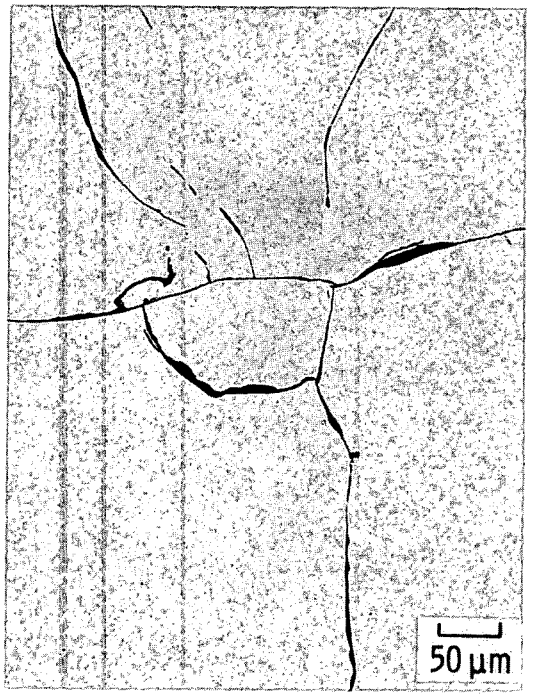


FIGURE 1-A. (contd)

(m) DD-15

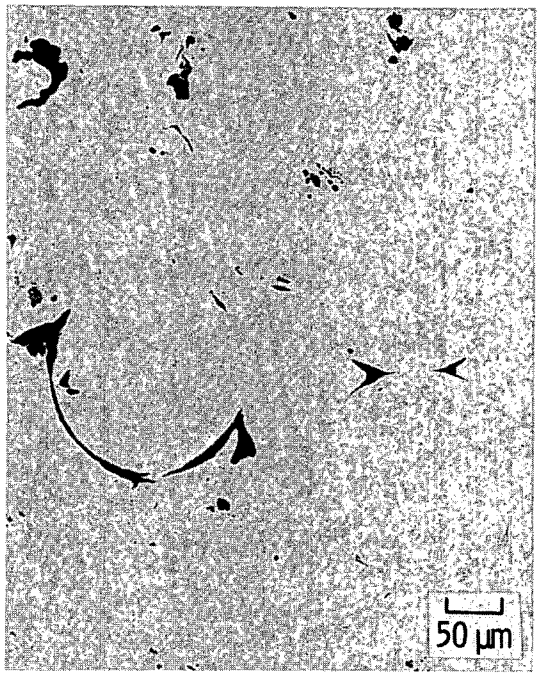


FIGURE 1-A. (contd)

DISTRIBUTION

No. of Copies

OFFSITE

M. J. Steindler
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

A. L. Lotts
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37830

J. D. Spencer
Savannah River Laboratory
E. I. DuPont DeNemours & Company
Aiken, SC 29801

A. Camp
Sandia Laboratory
Albuquerque, NM 87184

W. A. Weinreich
Bettis Atomic Power Laboratory
Westinghouse Electric Corporation
P.O. Box 79
West Mifflin, PA 15122

G. R. Keepin
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM 37545

D. J. Groetch
Knolls Atomic Power Laboratory
P.O. Box 1072
Schenectady, NY 12301

C. Youell
Babcock & Wilcox
Lynchburg, VA 24505

No. of Copies

P. Miller
General Electric Company
175 Curtner Avenue
San Jose, CA 95125

C. Palmer
Westinghouse NFD
Westinghouse Electric Company
P.O. Box 355
Pittsburgh, PA 15230

E. Zebroski
Electric Power Research Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94304

W. V. Goeddel
General Atomic Company
P.O. Box 81608
San Diego, CA 92138

E. W. Neben
Fluor Engineers & Constructors, Inc.
3333 Michelson Drive
Irvin, CA 92730

DOE

2 W. W. Ballard
U.S. Department of Energy - HQ/FCD
Washington, DC 20545

S. McDowell
U.S. Department of Energy - HQ/OSS
Washington, DC 20545

No. of Copies

2 P. R. Clark, R. H. Steele
U.S. Department of Energy - HQ/DNR
Washington, DC 20545

D. E. Bailey
U.S. Department of Energy - HQ/RRT
Washington, DC 20545

T. Hindman
U.S. Department of Energy
Savannah River Operations Office
P.O. Box A
Aiken, SC 29801

S. W. Ahrends
U.S. Department of Energy
Oak Ridge Operations Office
P.O. Box E
Oak Ridge, TN 37830

A. Mravca
U.S. Department of Energy
Chicago Operations Office
9800 South Cass Avenue
Argonne, IL 60439

A. A. Churm
DOE Chicago Patent Group
9800 South Cass Avenue
Argonne, IL 60439

6 U.S. Department of Energy
Technical Information Center
Washington, DC 20545

27 DOE Technical Information Center

K. L. Kighfill
Gas Cooled Reactor Associates
3344 N. Torrey Pines Ct.
Suite 300
La Jolla, CA 92037

No. of Copies

ONSITE

T. T. Claudson
Hanford Engineering Development Laboratory
P.O. Box 1970
Richland, WA 99352

E. A. Evans
Hanford Engineering Development Laboratory
P.O. Box 1970
Richland, WA 99352

O. Kruger
Exxon Nuclear Company, Inc.
2101 Horn Rapids Road
Richland, WA 99352

2 P. A. Craig, H. E. Ransom
U.S. Department of Energy
Richland Operations Office
P.O. Box 550
Richland, WA 99352

J. J. Keating
U.S. Department of Energy
FFTFPO
P.O. Box 550
Richland, WA 99352

53 Pacific Northwest Laboratory

J. O. Barner
D. W. Brite
J. R. Carrell
T. D. Chikalla (2)
N. C. Davis
R. M. Fleischman
S. Goldsmith
C. M. Hagen
C. R. Hann
P. E. Hart (5)
R. S. Kemper
L. R. Lambert
R. C. Liikala
R. P. Marshall
R. B. Matthews (18)
T. I. McSweeney
R. K. Johnson

No. of
Copies

Pacific Northwest Laboratory (continued)

J. R. Nesbitt
D. R. Newman
R. E. Schreiber
R. E. Sharp
G. D. White
Publishing Coordination (2)
Tech. Information Files (5)