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SINTERING UO_3 TO DENSE UO_2

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SINTERING UO_3 TO DENSE UO_2

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ABSTRACT

Sintering was considered for converting separated UO_3 from Savannah River reactors into dense UO_2 granules suitable for vibrationally loaded fuel elements. However, sintering of compacted hydrated UO_3 at 1600°C in hydrogen produced $UO_{2.06}$ pellets with bulk density of only 90% of theoretical, 5% less than the UO_2 density desired. The effects on UO_2 density of temperature, hydration, compacting pressure, ball-milling, and additives are described.

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INTRODUCTION

A lower-cost process was sought for converting UO_3 into dense UO_2 suitable for vibrationally compacted fuel elements. Present processes generally require reduction of UO_3 to fine particles of UO_2, followed by pressing, sintering, crushing, and sizing to obtain suitable feed material for vibrational loading.[1] A more direct conversion process would simplify the recycle of granular UO_3 from the Savannah River separations plant to make reactor-grade UO_2 feed granules. Two methods were considered:

- Sintering of pelletized UO_3 under hydrogen or other atmospheres at 1600-2200°C.
- Arc fusion of UO_3.

A UO_2 product with density of 95% of theoretical was desired, to equal the density of commercial high-fired UO_2 used in irradiation tests of vibrationally compacted fuel elements.[2]

This report describes preliminary studies on the sintering method. The arc fusion process, which was investigated on a larger scale, is described in USAEC Report DP-1148.[3]

SUMMARY

Uranium dioxide pellets with bulk density of 90% of theoretical were produced when compacted pellets of ball-milled, completely hydrated UO_3 were sintered under hydrogen for four hours at 1600°C. Pellets similarly produced from partially hydrated UO_3 had lower density, but the density increased to 86% of theoretical when partially hydrated UO_3 was wet ball-milled with 0.1 wt % trisodium phosphate before the pellets were compacted and sintered. Sintering at 1600-2200°C in induction-heated crucibles did not increase the density.

During sintering under hydrogen, UO_3 was rapidly reduced to U_4O_9 at or below 600°C, major densification occurred at 1300-1600°C, and the U_4O_9 was slowly reduced at 1600°C.

The sintering process was not carried to the point of producing UO_2 suitable for reactor irradiation.

DISCUSSION

BACKGROUND

In recognized procedures for converting UO_3 to dense UO_2, powdered UO_3 is reduced to U_3O_8 and then to powdered UO_2 by heating to 800-1000°C in hydrogen, cracked ammonia, or carbon monoxide. Then, the UO_2 is compacted into pellets and sintered in hydrogen at 1300-1750°C to densify the UO_2 for fuel element use. However, no method has been reported for producing dense UO_2 pellets by compacting UO_3 into pellets and then reducing and sintering the pellets in a single heating step. The emphasis in commercial pellet production has been to produce a precisely dimensioned pellet so costly operations, such as centerless grinding, would be minimized.

In the work described in this report, dimensional control of the product pellets was not important because the pellets were to be crushed and compacted mechanically within the fuel cladding. The principal objective was to demonstrate that pellets compacted from Savannah River Plant UO_3, produced by denitration of uranyl nitrate, could be reduced and densified in a single treatment and still maintain sufficient mechanical integrity to be used in powder-compacted fuel elements.

PROCEDURES

Compacting and Sintering

The UO_3 powder was prepressed at 20,000 psi, granulated by forcing it through a 20-mesh sieve, and then compacted into cylindrical pellets 5/16 inch in diameter. Compaction pressures ranged from 30,000 to 100,000 psi. No binder was used. The die was lubricated with a solution of "Sterotex"* powdered animal fat.

Some pellets were heated to 1600°C on high purity alumina in a silicon carbide resistance furnace and held for four hours in flowing hydrogen. They were cooled in hydrogen to 200°C or below before discharge from the furnace.

Other pellets were sintered at 1600-2200°C by induction heating under hydrogen, helium-hydrogen, or nitrogen atmospheres in graphite, aluminum oxide, beryllium oxide, zirconium oxide, or molybdenum crucibles. After sintering, these specimens were cooled in the furnace atmosphere before exposure to air.

* Product of Capital City Products Co., Columbus, Ohio.

Density Measurements

Density, calculated from measured weight and dimensions, was the standard characteristic for evaluating the UO_2 produced. Densities measured by loss of weight in water were not sufficiently discriminatory because of (1) water penetration into small interstices and (2) surface absorption. Densities measured by mercury displacement were not reproducible because of the poor wetting characteristics of mercury.

SINTERING AT 1600°C

Effect of UO_3 Feed

The extent of hydration of the feed material was the most important variable that influenced the final pellet density. Three types of UO_3 were tested:

- Partially hydrated UO_3 from Mallinckrodt Chemical Works (MCW).
- Partially hydrated UO_3 produced at the Savannah River Plant (SRP).
- Completely hydrated UO_3 produced several years earlier at SRP.

The color of the UO_3 changed from orange to yellow with increasing hydration. X-ray analyses showed that orange UO_3 was a mixture of completely hydrated and anhydrous monoclinic gamma UO_3, and that yellow UO_3 was almost completely hydrated ($UO_3 \cdot 0.8\ H_2O$). The aged UO_3 had become hydrated during several years of exposure to ambient (moist) air.

The densities of the UO_2 pellets produced in the tests are summarized in Table I. The completely hydrated UO_3 produced pellets of higher density than did the partially hydrated UO_3. In general, the density was not affected by changes in compacting pressure between 30,000 and 100,000 psi, but the powder stuck to the rams and die above 50,000 psi.

Effect of Compacting Variables

Omission of the prepressing and granulating steps reduced the final pellet density by 1 to 3%. Therefore, these steps were retained as a part of the standard procedure.

Increasing the final compacting pressure from 30,000 to 100,000 psi increased the density of pellets prepared from partially hydrated UO_3, but did not increase the density of those from as-denitrated, completely hydrated UO_3 (Table I).

Effect of Ball-Milling

Dry ball-milling all varieties of UO_3 before compaction increased the density of the sintered pellets (Table I). Wet ball-milling partially hydrated UO_3 further increased the final pellet density and also changed the UO_3 color from orange to yellow (the color of completely hydrated UO_3).

TABLE I

Densities of UO_2 Pellets Compacted at 20,000-100,000 psi and Sintered at 1600°C

Starting Material	Density, g/cm³ (% of theoretical, 10.97 g/cm³) 20,000 psi	30,000 psi	50,000 psi	70,000 psi	100,000 psi
Aged SRP UO_3 (completely hydrated, yellow)					
As-denitrated		9.25 (84%)	9.15 (83%)		
Dry-ball-milled	10.02 (91%)	9.87 (90%)	10.04 (92%)		
Fresh SRP UO_3 (partially hydrated, orange)					
As-denitrated		8.34 (76%)	8.65 (79%)	8.96 (82%)	9.01 (82%)
Dry-ball-milled		8.82 (80%)	9.03 (82%)	9.08 (83%)	
Wet-ball-milled		9.20 (84%)			
Wet-ball-milled with 0.1% trisodium phosphate		9.41 (86%)			
MCW UO_3 (partially hydrated, orange)					
As-denitrated		7.72 (70%)	8.10 (74%)	8.43 (77%)	8.70 (79%)

Effect of Additives

One of the most effective process modifications tested was the wet ball-milling of partially hydrated SRP product with 0.1% trisodium phosphate additive. This additive increased the density of wet-ball-milled UO_3 from 84 to 86% of theoretical. The handling characteristics and green strength of the powder and pellets made with this additive were excellent.

Of four other organic binders added to the UO_3 pellet feed, "Mobilcer"* R wax emulsion was better than polyvinyl alcohol, methyl cellulose, or "Carbowax"** 4000. The as-compacted pellets with "Mobilcer" R had higher green strength and higher green density, but the density of the final sintered pellets was not higher.

Chemical Composition of Product

Excess oxygen was present in all pellets analyzed for oxygen-to-uranium ratio. Nitrogen content was low, and carbon analyses were contradictory. The impurity analyses are summarized in Table II.

TABLE II

Impurities in UO_2 Sintered in Hydrogen at 1600°C

	UO_2 From Completely Hydrated SRP UO_3	UO_2 From Partially Hydrated SRP UO_3	
		As-Denitrated	Wet-Ball-Milled
O/U			
Average	2.05	2.11	2.07
Range	2.03 - 2.09	2.10 - 2.12	2.03 - 2.10
Carbon, ppm			
Average	~120		
Range	<25 - 260		
Nitrogen (Kjeldahl), ppm	<25	<25	
Gases evolved on vacuum extraction at 1300°C, ppm(a)			
N_2	17	7	
CO	600	600	
CO_2	2900	1500	
H_2	50	23	
Ar	2	3	
CH_4	7	2	

(a) Determined mass spectrographically.

* Trademark of Socony Mobil Oil Co., Inc., Brooklyn, N. Y.
** Trademark of Union Carbide Corp.

The oxygen content ranged from 2.03 to 2.12, expressed as oxygen-to-uranium ratio (O/U). The excess oxygen was greater than normally expected for material sintered under hydrogen. The excess oxygen and the inconsistency of the oxygen concentrations indicate that the hydrogen may have been impure. Excessive moisture in the hydrogen could raise the equilibrium oxygen-to-uranium ratio above 2.00 during furnace cooling from 1600°C.

The nitrogen impurity content of the pellets was low. No nitrogen was detected by Kjeldahl (wet chemical) analysis (limit of detection: 25 ppm). Nitrogen evolved as gas during vacuum extraction at 1300°C was 17 ppm for pellets made from the completely hydrated SRP UO_3, and 7 ppm for pellets made from partially hydrated SRP UO_3 (average of three values in each case).

Evidence concerning carbon content is conflicting. The mean value by the standard combustion analysis was 120 ppm, but CO and CO_2 released on vacuum extraction at 1300°C indicated carbon content of about 1000 ppm.

Reduction and Sintering Kinetics

The progress of reduction and sintering was investigated by heating groups of pellets to successively higher temperatures. Several groups of pellets of completely hydrated SRP UO_3 and dry-ball-milled partially hydrated SRP UO_3 were started along the sintering cycle; stopped at 600, 1000, 1300, or 1600°C; held for 30 minutes; and then cooled. The densities and oxygen-to-uranium ratios of the pellets were then measured (Table III).

TABLE III

Progress of Reduction and Sintering in Pellets of SRP UO_3

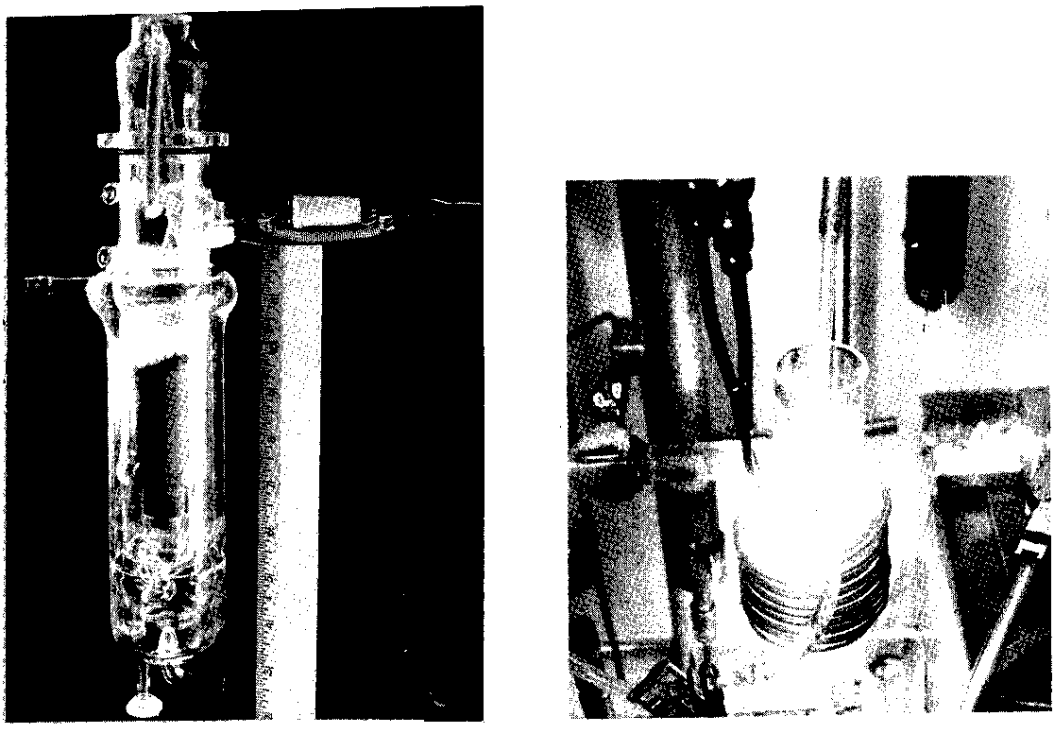
SRP UO_3	As-Compacted	After 30 min in Hydrogen at 600°C	1000°C	1300°C	1600°C	After 4 hr in Hydrogen at 1600°C
Completely hydrated						
Density, g/cm³	4.6	5.6	5.8	7.2	8.9	9.4
O/U	3	2.28	2.25	2.20	2.06	2.04
Partially hydrated						
Density, g/cm³	5.3	6.0	6.3	7.1	8.2	8.2
O/U	3	2.28	2.24	2.20	2.12	2.08

Most of the oxide was reduced from UO_3 to U_4O_9 rapidly below 600°C, and the major densification took place at 1300-1600°C. Reduction below U_4O_9 (O/U = 2.25) proceeded slowly even at 1600°C, but was more rapid for the completely hydrated SRP UO_3 than for the partially hydrated SRP UO_3.

SINTERING AT 1600-2200°C

Technique and Crucible Selection

The possibility of producing UO_2 of higher density by sintering at higher temperatures than the 1600°C limit of the resistance furnace was studied by sintering pellets at 1600 to 2200°C in the glass apparatus shown in Figure 1. In this apparatus, refractory crucibles containing the pellets were heated by induction with a 10-kw, 400-kc power supply. Temperatures were measured with calibrated optical pyrometers sighted into black body holes in the crucible.



a. Glass Cell to Provide Controlled Atmosphere

b. Sintering Operation

FIG. 1 INDUCTION HEATING APPARATUS FOR SINTERING UO_3 PELLETS IN HYDROGEN

Crucibles of various materials were tested for corrosion and oxidation resistance, but all had limitations:

- Graphite crucibles eroded badly because of CO_2 formation and nitrogen attack, and reacted with UO_2 on contact at 1750°C.
- Alumina crucibles reacted with UO_3, melted at 2050°C, and reacted with the graphite susceptor sheath at lower temperatures.
- Molybdenum and tungsten crucibles reacted with UO_3 below 1000°C, producing a dense smoke of volatile molybdenum and tungsten oxides.
- Graphite-sheathed zirconia or beryllia crucibles, shown in Figure 2, were most suitable for the sintering studies but were limited to 2200°C because of reaction between the oxides and the graphite susceptor.

The crucibles were closed except for a small vent hole for slow oxygen removal from the UO_3 either as H_2O or CO_2 and O_2, depending on whether the UO_3 was sintered under hydrogen or inert gas or in the presence of graphite. Slow loss of oxygen was necessary to prevent disintegration of the UO_3 pellets.

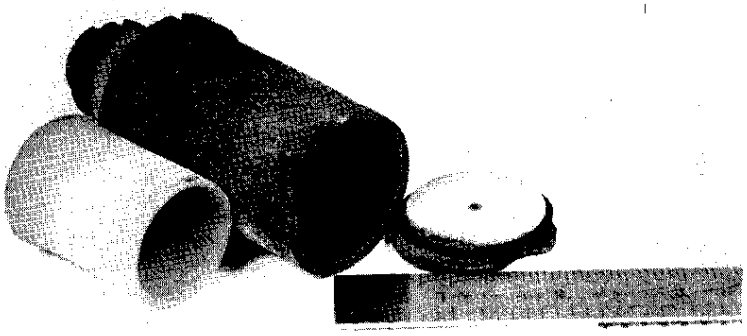


FIG. 2 GRAPHITE - SHEATHED ZrO_2 CRUCIBLE USED TO SINTER UO_3 PELLETS IN HYDROGEN AT TEMPERATURES ABOVE 1600°C

Effect of High Sintering Temperatures

Compacted pellets were heated at 1775°C or at 1600°C for six hours in carbon-sheathed zirconia crucibles under flowing hydrogen. Very little difference in density was produced by sintering at the higher temperature (Table IV). The effect of oxide hydration, ball-milling, and compacting pressure on pellets sintered at 1775°C was the same as for pellets sintered at 1600°C.

Densities of UO_3 pellets sintered above 1775°C were generally lower (Table V).

TABLE IV

Comparison of Densities of UO_2 Pellets Sintered at 1600 and 1775°C

	Ball-Milled	Compacting Pressure, psi	UO_2 Pellet Density, % of theoretical: Sintered at 1600°C(a)	Sintered at 1775°C(b)
Completely hydrated SRP UO_3	Yes	30,000	88-92	87-91
Partially hydrated SRP UO_3	Yes	50,000	83	83
	No	50,000	80	74-77
	No	100,000	82	84

(a) Resistance heating under hydrogen for 4 hr.
(b) Induction heating under hydrogen for 6 hr.

TABLE V

Effect of Increasing Temperature on Densities of UO_2 Pellets(a)

Sintering Temperature, °C	Time, hr	Density, % of theoretical
1850-1950	2	72-75
2000	3	83
2200	1	75

(a) Pellets produced by sintering as-denitrated partially hydrated SRP UO_3 in carbon-sheathed zirconia crucibles under flowing hydrogen. Compacting pressure: 30,000 psi.

Effect of Step Sintering

An attempt to produce a higher density by sintering in two steps was unsuccessful. Pellets previously fired at 1600°C in hydrogen for four hours to densities of 81-83% of theoretical were refired at 1900°C for two hours under hydrogen in a carbon-sheathed zirconia crucible. Final bulk density was increased only to 84% of theoretical.

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