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R. B. Matthews
N. C. Davis

October 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
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PNL-3210

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Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy $____*; Microfiche $3.00

*Pages	NTIS Selling Price
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FABRICATION OF ThO_2 and ThO_2-UO_2 PELLETS FOR PROLIFERATION RESISTANT FUELS

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Thoria based fuels are being considered by the Department of Energy's Fuels Refabrication and Development program for proliferation resistant fuel cycles. This report summarizes the development work carried out during FY 79 on fabrication of ThO_2 and $ThO-UO_2$ pellet fuels from commercially available powders.

The work was directed toward the definition and development of the unit operations required for the fabrication of ThO_2-based pellet fuels. The objective of the program was to define and optimize a reference flow sheet based on mixing of ThO_2 and UO_2 powders. The flow sheet will be used as a standard for judging other processes and will be the technique used for fabrication of ThO_2 fuels containing up to 30 wt% UO_2 for irradiation testing. Since previous work suggested that sintered density of ThO_2-UO_2 pellets decreased with increasing UO_2 concentration, techniques for milling and blending the oxide powders into a mix that will readily press and sinter to 93 - 95% TD with a homogeneous distribution of the fissile component needed to be developed.

To meet this objective, batches of ThO_2 powders were compared and milling parameters, pressing and sintering conditions were established. A method for blending ThO_2 and UO_2 into homogeneous powders that press and sinter into 95% TD pellets was determined. The effect of UO_2 additions on ThO_2-UO_2 pellet properties was determined and a process for fabricating irradiation test quality ThO_2-20 wt% UO_2 pellets containing CaO as a dissolution aid was established.

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FIGURES

FIGURES (contd)

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INTRODUCTION

A pellet fabrication study with ThO_2-based fuels was done as part of the Department of Energy's Fuels Refabrication and Development Program. The goal of this Program was to develop technology for the remote refabrication of proliferation resistant fuels. In order to meet proliferation resistance requirements, the ThO_2-based fuels will contain up to 30 wt% UO_2.

Several major fabrication campaigns for ThO_2 and ThO_2-UO_2 pellets have been completed for core loads for a critical facility,(1) the Bettis Light Water Breeder Reactor program,(2) the Borax IV Reactor,(3) the Elk River Reactor,(4) and the Indian Point I Reactor.(5) This past experience relied on hands-on operations, and most of these fuels contained less than 10 wt% UO_2. The flow sheets generally used oxalate-derived ThO_2 powders activated by jet milling or extensive ball milling. Binders were needed to enhance pellet integrity, and lengthy sintering cycles were sometimes needed to achieve high sintered densities. Most of these steps would be undesirable in a production scale, remotely operated fabrication facility. One of the objectives of this study was to evaluate these steps and to direct future development into areas where improvements can be made.

Although ThO_2 and UO_2 form a continuous series of solid solutions,(6) the limited work done with high U/Th ratios suggests that fabrication of the compositions needed for denatured fuel cycles can be more difficult than fabrication of either of the single oxides or compositions containing less than 10 wt% UO_2. The few sintering studies which have been carried out over the entire ThO_2-UO_2 composition range,(7-10) indicate that sintered density can decrease with increasing concentration of the second component with a minimum density occurring at about 50 wt% UO_2.

This report summarizes the development work carried out at PNL during FY 79 on fabrication of ThO_2 and ThO-UO_2 pellet fuels from commercially available powders. The ThO_2 pellet development work was directed toward the definition and development of the unit operations required for the fabrication of ThO_2-based pellet fuels. The objective of the program was to define and optimize a reference flow sheet based on the mixing of ThO_2

and UO_2 powders. The flow sheet will be used as a standard to judge other processes and to fabricate ThO_2 fuels containing up to 30 wt% UO_2 for irradiation testing. Based on a review of previous work, milling and blending of the oxide powders were considered to be the key steps for preparing a mix that will readily press and sinter to 93 - 95% TD(a) with a homogeneous distribution of the fissile component. Various batches of ThO_2 powders were compared, and milling parameters, pressing, and sintering conditions for the most promising batches were established. A method of homogeneous blending ThO_2 and UO_2 powders was then established, and the effect of UO_2 additions on ThO_2-UO_2 pellet properties determined.

(a) TD = theoretical density

EXPERIMENTAL

The various batches of ThO_2 and UO_2 powders evaluated are listed in Table 1 along with the suppliers. Batches TB-2 and TB-3 were made by thorium oxalate precipitation followed by thermal decomposition of the thorium oxalate to the oxide. Precipitation and calcining conditions were not available. No information was available on the history of the other ThO_2 powder batches. Batches TB-2 and TB-3 were used to establish blending and milling conditions with UO_2 powders. The UO_2 powders were produced by the conventional ADU process.

TABLE 1. ThO_2 and UO_2 Powder Batches

Batch Number	Material	Supplier
TB-2	ThO_2	Tennessee Nuclear Specialties, Jonesboro, TN
TB-3	ThO_2	Tennessee Nuclear Specialties, Jonesboro, TN
TA-1	ThO_2	VarLac Chemical Co., Elizabeth, NY
TC-1	ThO_2	Battelle, Pacific Northwest Laboratory, Richland, WA
TG-1	ThO_2	National Lead of Ohio, Cincinnati, OH
TH-1	ThO_2	Rhône-Poulence Chimie Fire, Paris, France
DF-1	UO_2	Exxon Nuclear Company, Inc., Richland, WA
DF-2	UO_2	Exxon Nuclear Company, Inc., Richland, WA

Dry ball milling was used to comminute ThO_2 and UO_2 powders to enhance pressing and sintering characteristics. Small (1-liter capacity) rubber-lined mills were loaded with 1 kg of powder and 6 mm tungsten carbide balls. The mills were run at approximately 100 rpm, and the powder was sampled and tested at 2 h intervals up to 16 h. Tap density, measured according to ASTM Standard D 527-70, was used as an indication of powder packing efficiency, flowability characteristics, and agglomeration of powder particles. Specific surface area of the powders was measured by BET gas absorption.

Pellet fabrication procedures were kept close to constant throughout this study. A press frame equipped with a 9 mm hydraulic cylinder was used with a punch and die set to press pellets. The die set was designed with spring supports to allow upper and lower punch action during pressing. The springs compressed for ejection of the pellet on a second cycle of the press. Pellets were pressed in an 11 mm diameter die sprayed with zinc stearate mold release at a compaction pressure of 150 to 200 MPa and a dwell time of about 10 s. The length-to-diameter ratio was held to about 1:1 on the various test pellets.

Several of the early tests were sintered in a cold wall refractory metal sintering furnace using Ar-50%H_2 at 1700°C for 8 h. In most of the tests, and in all cases where direct comparisons are made, sintering was done in a small graphite element laboratory furnace with an Al_2O_3 muffle tube operated at 1700°C for 4 h in Ar-4%H_2 flowing at 42 l/h. The two sintering conditions gave similar pellet densities.

Geometric densities were calculated from measurements on unground pellets; immersion densities and open porosity were determined using a modification of ASTM Standard C-373-72. Reported densities were calculated using 10.96 Mg/m^3 for UO_2 and 10.00 Mg/m^3 for ThO_2. All reported densities are geometric densities unless stated in the text and are an average of 4 to 8 pellets; ranges represent 95% confidence limits. Structures of powders and pellets were examined using standard ceramographic and SEM techniques.

RESULTS

ThO_2 POWDER PREPARATION AND PELLET FABRICATION

Preliminary tests carried out on Lot TB-2 ThO_2 powder showed that the as-received material could not be readily pressed without appropriate treatment. Flowability and pressing problems were encountered; and a large fraction of the green pellets had to be rejected due to cracking and breakage. After pre-slugging, granulation and mixing with 0.2% Sterotex, pellets could be pressed, and sintered densities as high as 90% TD were achieved. The as-received powder particles were large with a square platelet morphology (Figure 1a). The sintered pellet structure (Figure 1b) was coarse with random cracks and large pores. These results indicated that powder milling was needed to improve the pressing and sintering characteristics of the as-received powders.

Dry ball milling was used to enhance the pressing and sintering characteristics of Lot TB-2 powder. Figure 2 shows that a maximum pellet density was reached after 12 h milling. The yield of intact pellets continued to increase with milling time up to 16 h. Table 2 summarizes the effect of milling for 1 h on powder and pellet properties; milling resulted in significant improvements in tap density, surface area, green density and sintered pellet density.

TABLE 2. Change in ThO_2 Powder Properties After Milling

Material	Tap Density,(a) Mg/m^3	Surface Area, m^2/g	Green Density, %TD	Sintered Density, %TD
As-Received	2.7	1.8	60.1	77.0
12-h milled	3.6	5.5	62.4	97.7

The milled powder morphology and resulting pellet structure are shown in Figure 3. The milling broke down the platelets into fine particles as can be seen by comparing SEM micrograph of the as-received powder (Figure 1a) with milled powder (Figure 3a). The microstructure of the sintered pellet (Figure 3b) made from the milled powder shows a high density matrix consisting of a uniform

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(a) International System of Units are used exclusively in this report.

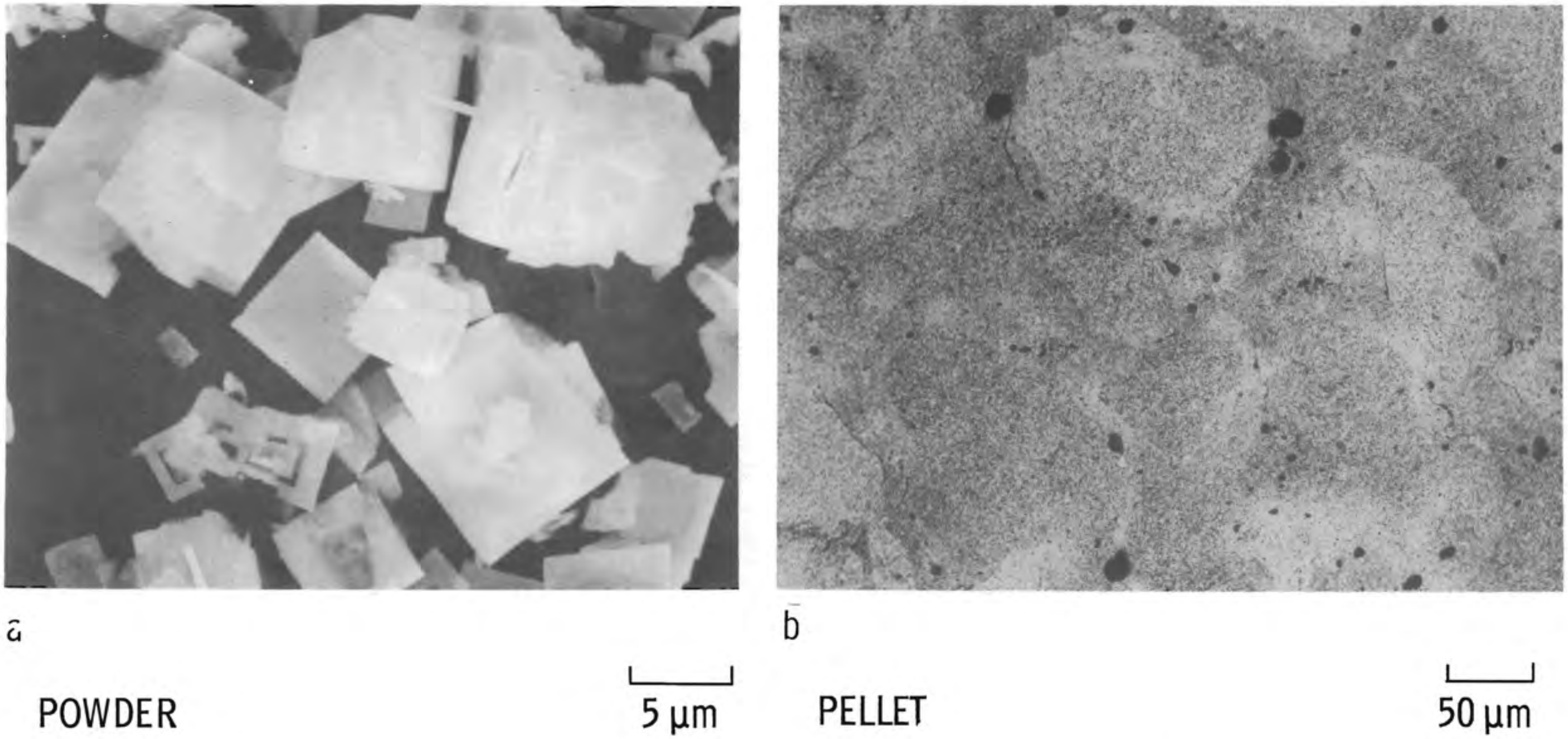


FIGURE 1. (a) SEM Micrograph of As-Received Lot TB-2 ThO_2 Powder
(b) Cross-Section of a Sintered Pellet Fabricated From As-Received TB-2 Powder, 87% TD

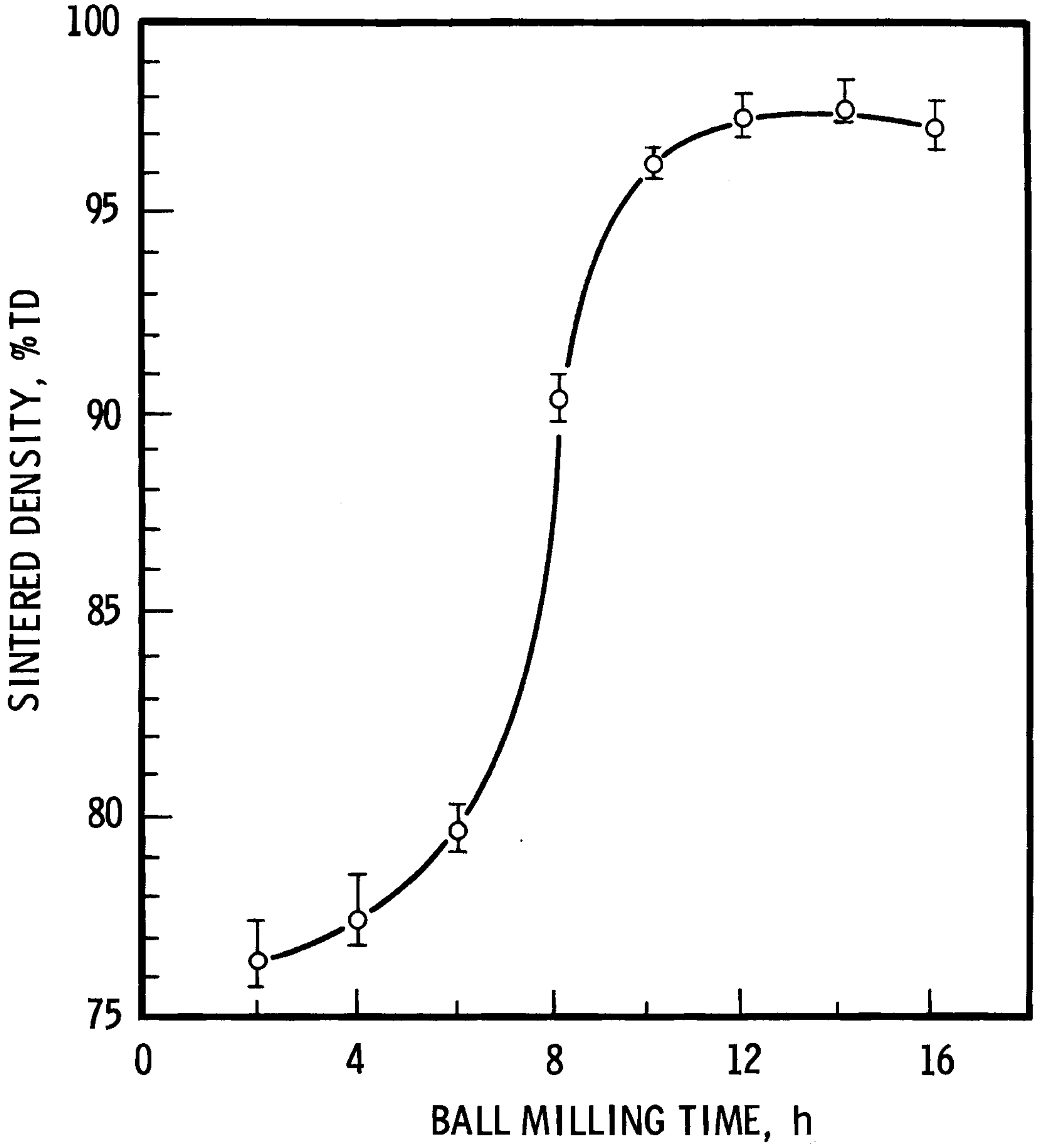


FIGURE 2. Effect of Ball Milling Time on the Sintered Density of ThO_2 Pellets. Data Points Show the Mean and Range of Geometric Densities of at Least Four Pellets.

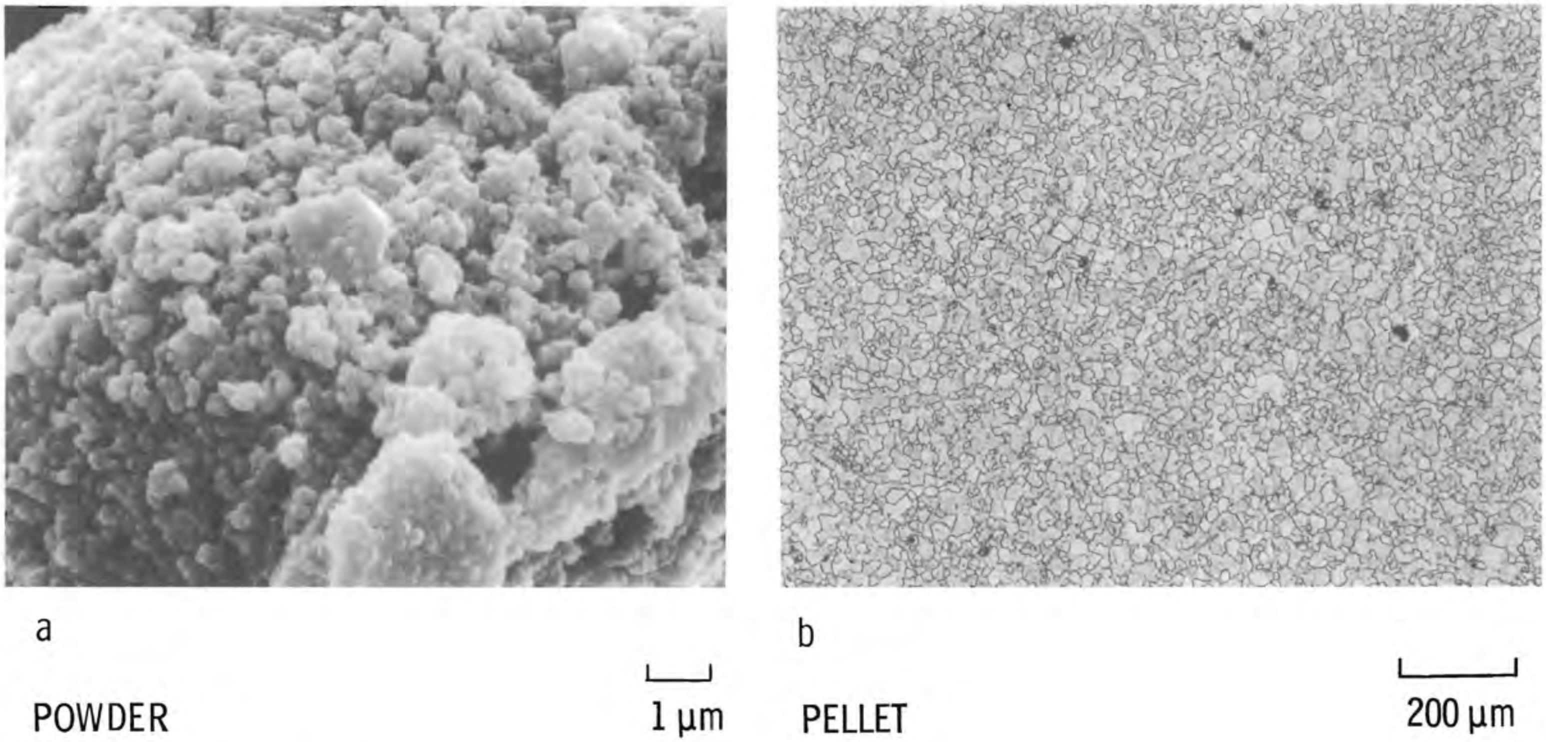


FIGURE 3. (a) SEM Micrograph of TB-2 Powder After 16 h Milling
(b) Cross-Section of a Sintered Pellet Fabricated From TB-2 Powder Milled for 16 h, 97% TD

grain size and occasional small pores with no evidence of cracking. The improvement in pellet microstructure can be seen by comparing the photomicrograph of a sintered pellet (Figure 1b) made from unmilled powder with that of a pellet (Figure 3b) made from 12 h milled powder.

Five additional batches of ThO_2 powders from various sources were evaluated and compared to the data established for Lot TB-2. Table 3 lists the powder characteristics, pressing and sintering behavior of as-received and ball milled material. A wide variation in powder properties was observed, for example, the surface area ranged from 1.8 m^2/g to 25.9 m^2/g and the structure of the as-received powders varied from flat platelets (TB-2, TA-1, and TH-1) to bulky cubic crystals (TB-3 and TG-1) to fluffy powder (TC-1). None of these powders could be sintered to high density pellets without milling. Extensive ball milling acted to break down the large crystals and increase surface area of the powder lots. The change in sintered pellet density of all these powder lots is plotted against ball milling time in Figure 4. All powders except TA-1 and TC-1 sintered to or exceeded a 95% TD target density after 16 h ball milling. These two lots had the highest surface areas and morphologies similar to that of milled TB-2 powder (Figure 3a). This demonstrates that a high surface area and a fine powder morphology do not guarantee sinterability. In fact, the TA-1 powder may have been over activated by milling. Microstructures of TB-3, TG-1, and TH-1 sintered pellets are nearly identical to that of TB-2 (Figure 3b). The microstructures of TA-1 and TC-1 sintered pellets are coarse with random large crystals

TABLE 3. Comparison of Properties of ThO_2 Powders Lots

Lot Number	Ball Milling Time, h	Surface Area, m^2/g		Tap Density, Mg/m^3		Green Density, %TD		Sintered Density, %TD	
		As-Received	Ball Milled	As-Received	Ball Milled	As-Received	Ball Milled	As-Received	Ball Milled
TB-2	12	1.8	5.5	2.7	3.6	60.1	62.4	77.0	97.7
TB-3	6	7.5	13.3	2.7	3.5	51.0	58.2	90.2	96.4
TA-1	16	7.6	20.7	2.7	3.3	47.7	55.4	70.7	85.7
TC-1	16	25.9	31.1	2.1	3.2	43.7	48.5	83.9	86.3
TG-1	16	5.2	9.6	2.4	3.6	54.9	62.0	79.4	96.7
TH-1	16	5.5	9.7	2.9	3.5	57.3	62.4	75.2	96.4

suggesting the presence of a second phase; however, spectrochemical analysis does not indicate any high impurity levels. This variability in powder properties is clearly undesirable and points out the need to define a consistent set of precipitation and calcining conditions that will yield uniform and repeatable powders.

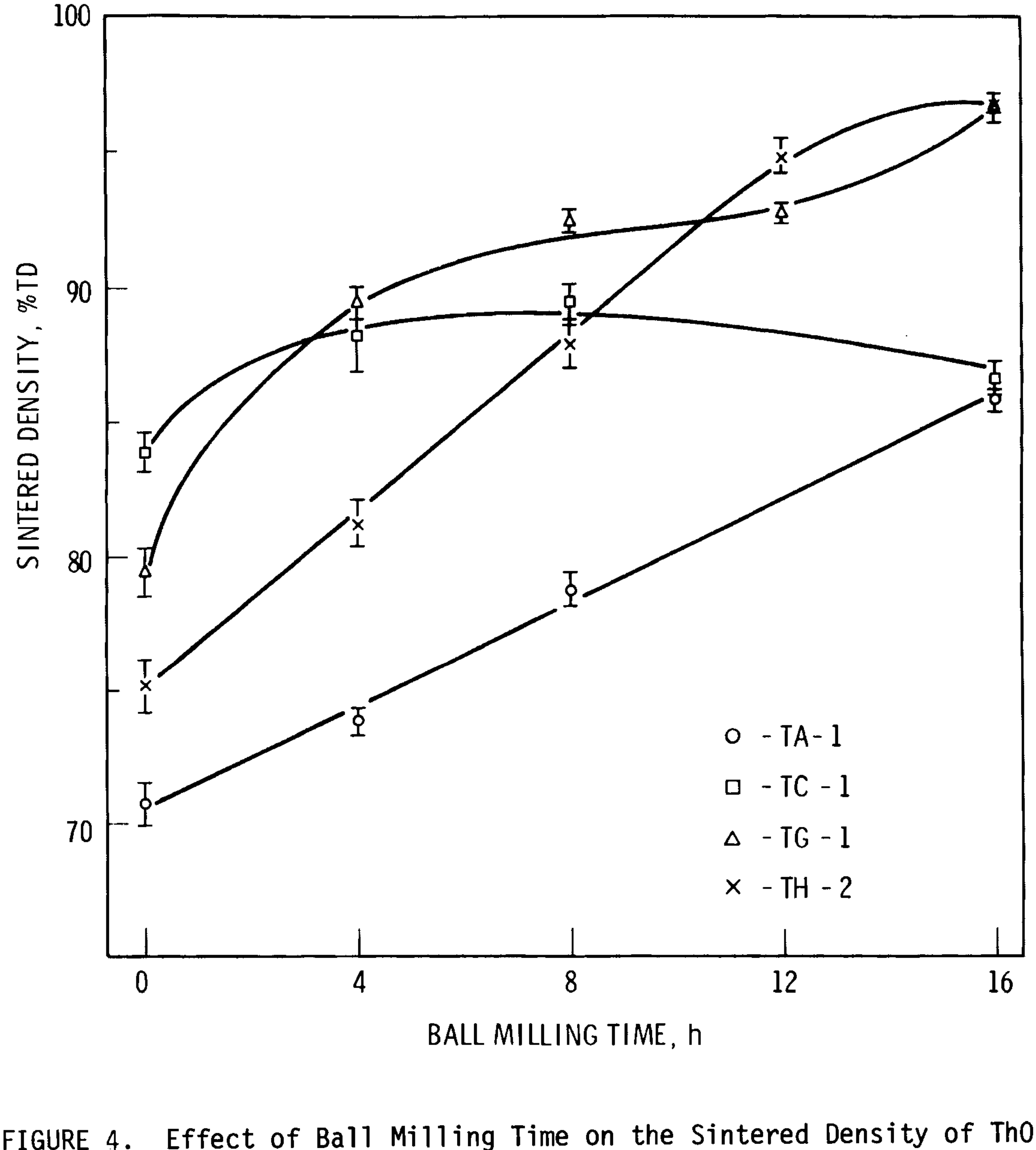


FIGURE 4. Effect of Ball Milling Time on the Sintered Density of ThO_2 Pellets Made From Various Lots of Powder. The Data Points Show the Mean and 95% Confidence Limits of Geometric Densities of Eight Pellets.

A comparison of the physical properties and pressing and sintering behavior of Lot TB-3 ThO_2 powder with Lot TB-2 powder indicates that large variations in powder characteristics can occur between powder lots produced by the same process. The as-received TB-3 powder had a surface area of 7.5 m^2/g, smaller particles than TB-2, a blocky morphology, and pressed and sintered to 90% TD. After 8 h of ball milling, the TB-3 powder pressed and sintered to 95% TD. Figure 5 shows that the structure of the as-received TB-3 powder is considerably different than that of as-received TB-2 powder (see Figure 1a); however, morphology of 8 h milled TB-3 powder and microstructure of sintered pellets made from the milled powder are nearly identical to the 16 h milled TB-2 powder and pellets.

Further milling studies on the TB-3 powder showed that although surface area increased with milling time, the average particle size measured by sieve analysis also increased. Table 4 shows the sieve analysis and tap density for as-received and ball milled TB-3 powder. The SEM micrographs of as-received and 6 h ball-milled TB-3 in Figure 6a and b show that the powder particles tended to cluster into spherical agglomerates during milling. These clusters resulted in the apparent increase in particle size shown in Table 4. This agglomeration continued to occur up to 10 h of ball milling

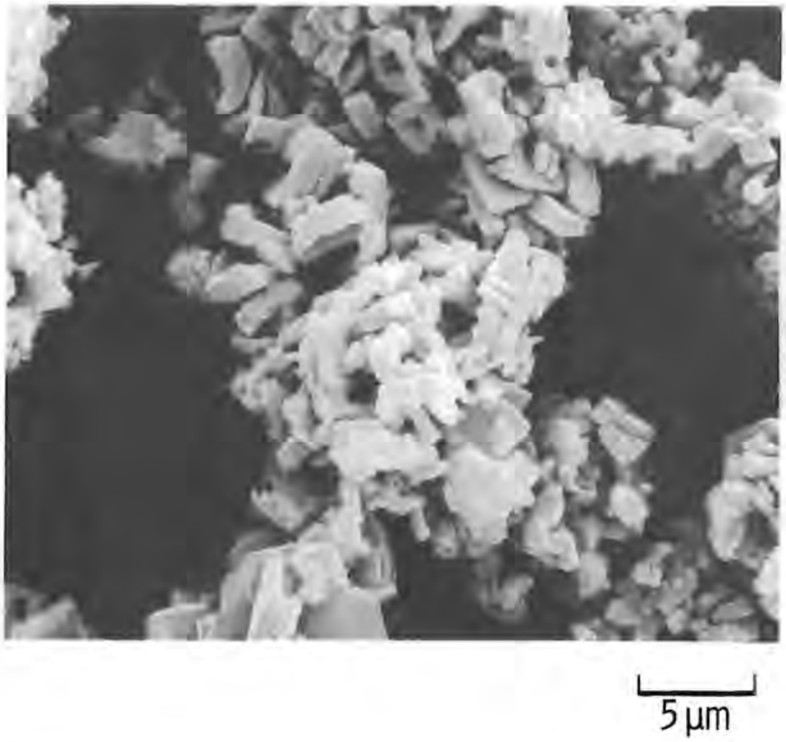


FIGURE 5. SEM Micrograph of As-Received Lot TB-3 ThO_2 Powder

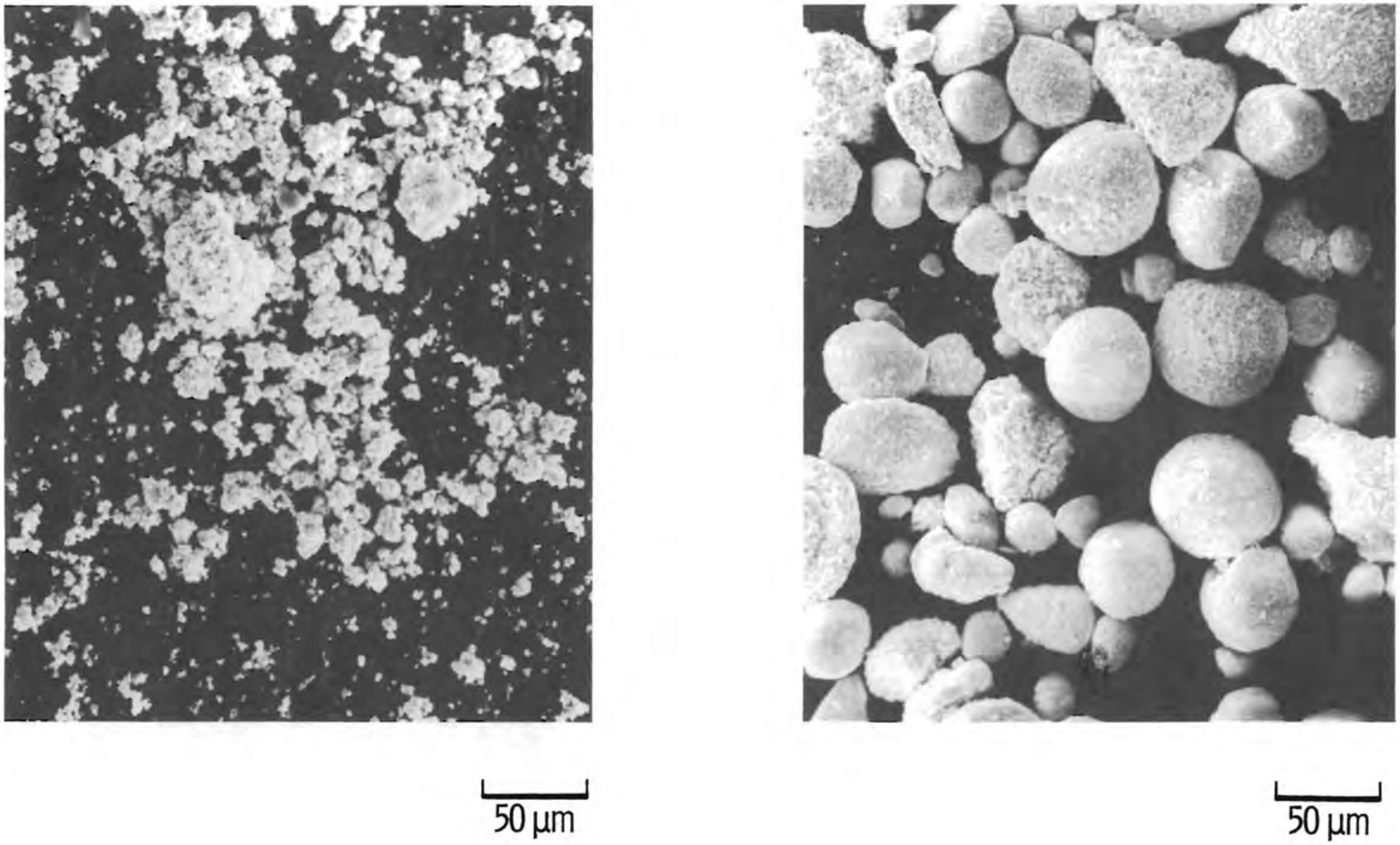


FIGURE 6. (a) SEM Micrograph of As-Received Lot TB-3 ThO_2 Powder
(b) SEM Micrograph of 6 h Ball Milled TB-3 Showing Clustering of Powders

TABLE 4. Effect of Milling on Sieve Analysis and Tap Density for TB-3 Powder

Milling Time, h	Sieve Analysis, wt%						Tap Density, Mg/m^3
	>212μm	<212->150μm	<150->106μm	<106->75μm	<75->45μm	<45μm	
As-Received	--	--	3.5	2.3	21.1	73.1	2.65
6h	1.4	2.9	9.4	8.3	27.1	51.0	3.42
10h	16.6	9.6	10.3	9.8	14.3	39.4	3.41

and acted to enhance the flowability of the powders. All the above milling studies were done with 1 kg powder batches. A test to assess the effect of ball mill load size on milling showed that milling efficiency decreased with increasing batch size. The data in Table 5 show that the sintered density of ThO_2 pellets dropped off with increasing batch size and that the sinterability of the large batch could be recovered by increasing milling time. One kg was judged to be the best batch size for milling ThO_2 powders in the laboratory size ball mills.

TABLE 5. Effect of Batch Size on Milling Efficiency

Batch Size, g	Milling Time, h	Tap Density, Mg/m^3	Green Density, %TD	Sintered Density, %TD
600	8	3.44	59.9	96.1±.1
1,000	8	3.46	58.7	95.5±.3
1,400	8	3.35	56.3	93.8±.5
1,400	12	3.61	59.2	95.5±.2

High energy, wet milling is capable of rapid and efficient reduction of coarse powders to submicron sizes. An attrition mill(a) was evaluated using a two level, three factorial (milling, speed, and slurry concentration) experiment with Lot TB-2 ThO_2 powder. The attritor consisted of a stationary 300 ml stainless steel vessel containing grinding balls. An intensifier bar with cross pieces was rotated at high speeds in the container thereby rotating the grinding balls and effecting the milling action. The powder to be milled was mixed with water to form a slurry. After grinding, the slurry was dried and the powder prepared for pressing.

(a) Research Model 01 Attritor, Union Products, Inc., Akron, Ohio.

The results of the experiment are compared with ball milling results in Table 6. A statistical analysis of the data showed that milling time had the most significant effect on both surface area and sintered density. Increased slurry concentration and speed had a minor positive effect. Spectrochemical analysis showed that impurity levels did not increase during the milling times studied. Pre-slugging at 50 MPa and granulation of the milled powder to less than 425 µm was needed to eliminate pellet cracking during sintering. The green densities of pellets pressed at 150 MPa ranged from 53 to 55% TD. All pellets were intact after sintering at 1700°C for 4 h and had densities from 94.7 to 97.6%

TABLE 6. Results of Attrition Milling

Trial	Slurry Concentration, wt% ThO_2	Time, min	Speed, RPM	Average Surface Area, m^2/g	Average Green Density, %TD	Average Sintered Density, %TD
As-Received Powder				7.5	51.8	90.0
1	50	10	60	9.43	53.7	95.2
2	67	10	60	9.92	52.8	94.7
3	50	120	60	11.71	54.6	96.7
4	67	120	60	11.75	54.0	97.3
5	50	10	910	9.54	53.1	95.2
6	67	10	910	9.57	52.8	96.8
7	50	120	910	17.94	54.6	97.2
8	67	120	910	11.94	55.4	97.6
9	60	65	610	12.55	54.4	97.1
Ball Milled	100	360	100	12.54	58.2	96.0
Ball Milled	100	600	100	14.97	59.5	95.9

Pellets which sintered to 95% TD were fabricated from powders attrited for only 10 min; pellets approaching 98% TD were fabricated from powders attrited for 2 h. At least 6 h of ball milling of TB-3 powders was needed to achieve densities greater than 95% TD. Therefore, the attritor is a significantly more efficient milling unit than the ball mill; however, when total processing time and operator steps are considered, high energy wet milling is less attractive than dry ball milling because the slurry must be dried and granulated prior to pellet pressing. Attempts to use dry powders in the attritor proved unsuccessful; work on this milling technique was discontinued.

UO_2 EVALUATION

Two lots of depleted UO_2 powder (DF-1 and DF-2) were used for subsequent ThO_2-UO_2 pellet development studies. The powders were produced by the conventional ADU process. Examination of the powders showed that milling of the powders was required to reach target density. After 8 h of ball milling, Lot DF-1 had a tap density of 3.57 Mg/m^3, pressed to 54% TD at 180 MPa, and sintered to 95% TD at 1700°C. Milling times greater than 12 h seemed to cause cracking in the sintered pellets. Lot DF-2 required 12 h of ball milling to achieve sintered densities greater than 94% TD (tap density = 3.75 Mg/m^3; green density = 58% TD). No evidence of cracking was seen in the DF-2 pellets.

ThO_2-UO_2 PELLET FABRICATION

Lot TB-2 thoria powder, ball milled 16 h, was used as the matrix material in preliminary ThO_2-UO_2 pellet development study. The as-received UO_2 was screened to minus 100 mesh and mechanically blended by tumbling with the milled ThO_2 to form compositions of 5, 10, 15, 20, and 30% UO_2 in ThO_2. These powders were pressed and sintered under the same conditions as the pure ThO_2 powders. Both the green and sintered densities of the pellets decreased with increasing UO_2 concentration, as shown in Figure 7.

Microstructural examination (Figure 8) and microprobe analysis (Figure 9) showed that the ThO_2-20 wt% UO_2 pellet made from the blended powders consisted of high density, coarse (up to 3500 μm) ThO_2 particles surrounded by a matrix

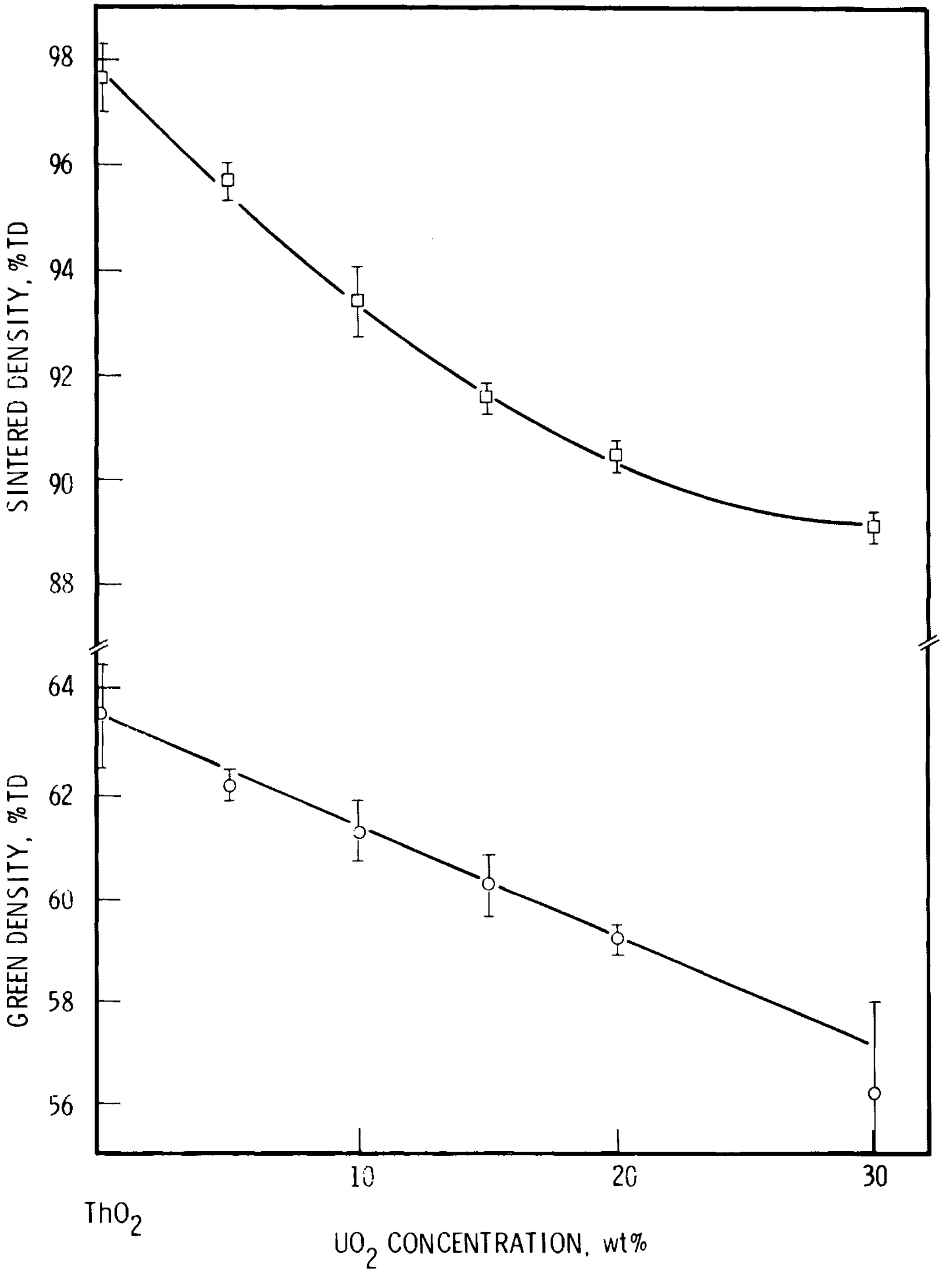


FIGURE 7. The Effect of UO_2 Concentration on the Green and Sintered Pellet Densities of ThO_2-UO_2 Compositions Prepared by Mechanical Blending of the Powders

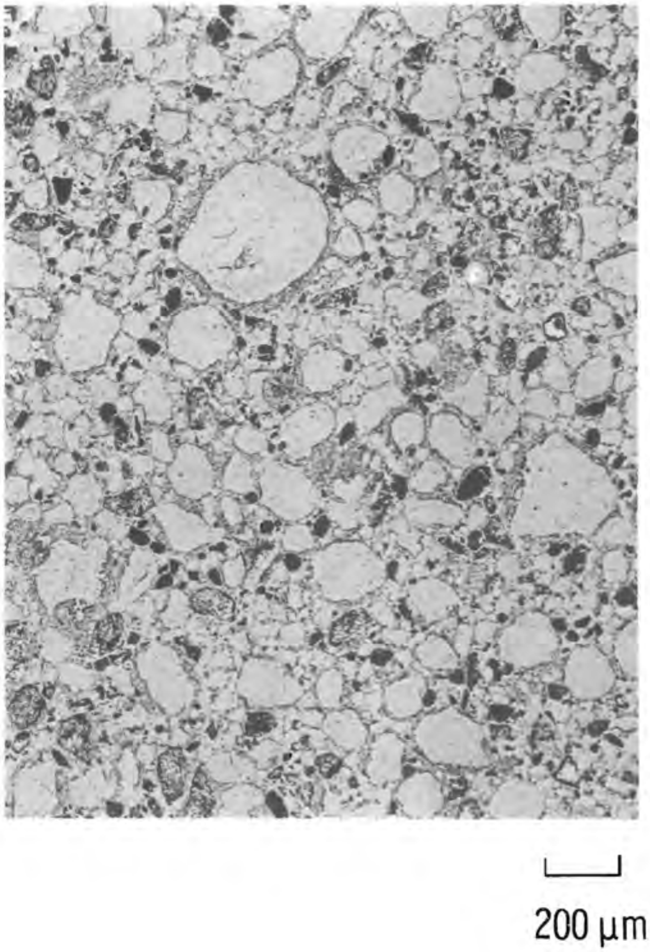
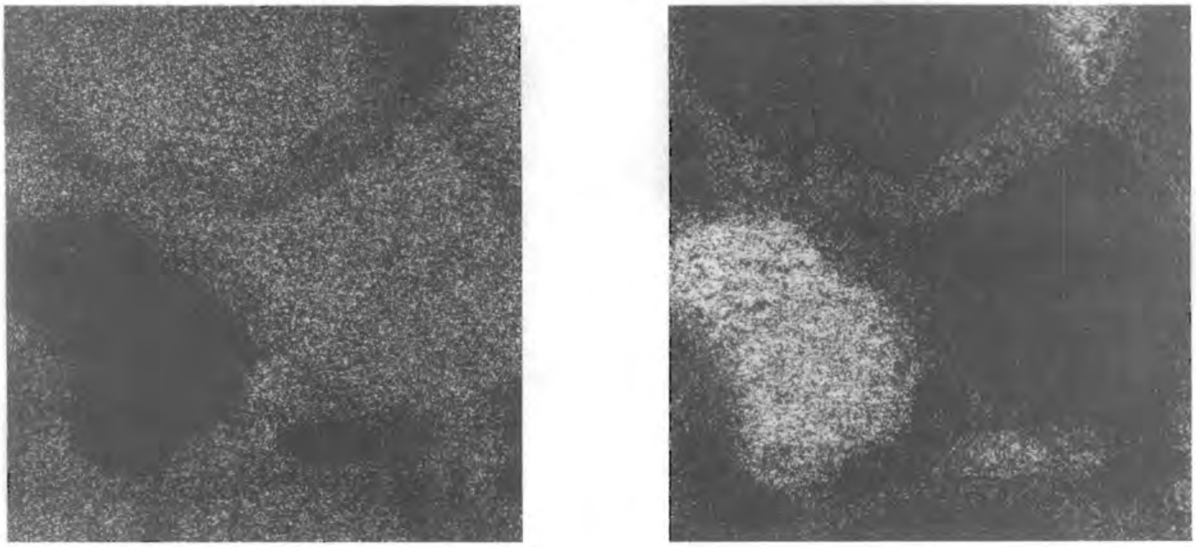


FIGURE 8. Microstructure of a Sintered ThO_2-20 wt% UO_2 Pellet Made From Milled ThO_2 Powder Mechanically Blended with As-Received UO_2 Powder, 89% TD

ThO_2 - 20 wt% UO_2 20 μm



THORIUM MAP 20 μm URANIUM MAP 20 μm

FIGURE 9. Microprobe Analysis of ThO_2-20 wt% UO_2 Sintered Pellet Prepared by Mechanical Blending of the Powders

of $(Th,U)O_2$ and islands (about 60 µm) of pure UO_2. Most of the porosity was associated with the UO_2 phase. This segregated structure indicates that clustering of the ThO_2 component occurred during the mechanical mixing step.

A milling and blending study was undertaken to improve the homogeniety of the blended powders and increase pellet density. Both UO_2 and ThO_2 powders, which were separately milled for 12 h, could be pressed and sintered to >95% TD. When ThO_2-20 wt% UO_2 powders were co-milled for 16 h without any prior treatment, pellets sintered to only 93% TD. When the single oxide powders were separately milled for 12 h then co-milled for an additional 4 h, pellets sintered to 96% TD. Therefore, the key to fabricating high density ThO_2-UO_2 fuels with the particular powders used is proper preparation of the single oxide powders followed by thorough co-milling of the powders. Figure 10 shows the microstructure of a sintered ThO_2-20 wt% UO_2 pellet made from co-milled powders. The microstructure is homogeneous with random pores and uniform grains. Microprobe x-ray maps (Figure 11) show that the UO_2 is distributed throughout the ThO_2 with occasional 10 µm clusters of high UO_2 concentration. Further milling tests indicate that the 12 h separate milling of UO_2 and ThO_2 powders can be reduced to 8 h but that 4 h co-milling is necessary to reach sintered densities greater than 95% TD.

The effectiveness of thorough milling was confirmed by fabricating ThO_2-UO_2 pellets containing 10, 20, 30, 50, and 80 wt% UO_2 from powders that were separately milled for 12 h and co-milled for 4 h. Single oxide control pellets were fabricated from ThO_2 and UO_2 powders milled for 16 h. Green and sintered pellet densities decreased with increasing UO_2 concentration as shown in Figure 12 but less rapidly than with the powders that were only mechanically mixed (see Figure 7). The density of sintered pellets decreased slightly with UO_2 concentration and microstructures were homogeneous with random pores and uniform grains. About 50% of all ThO_2-UO_2 pellets contained microcracks, and the cracking seemed to increase with increasing UO_2 concentration. These cracks probably account for the slight decrease in density with high UO_2 concentrations.

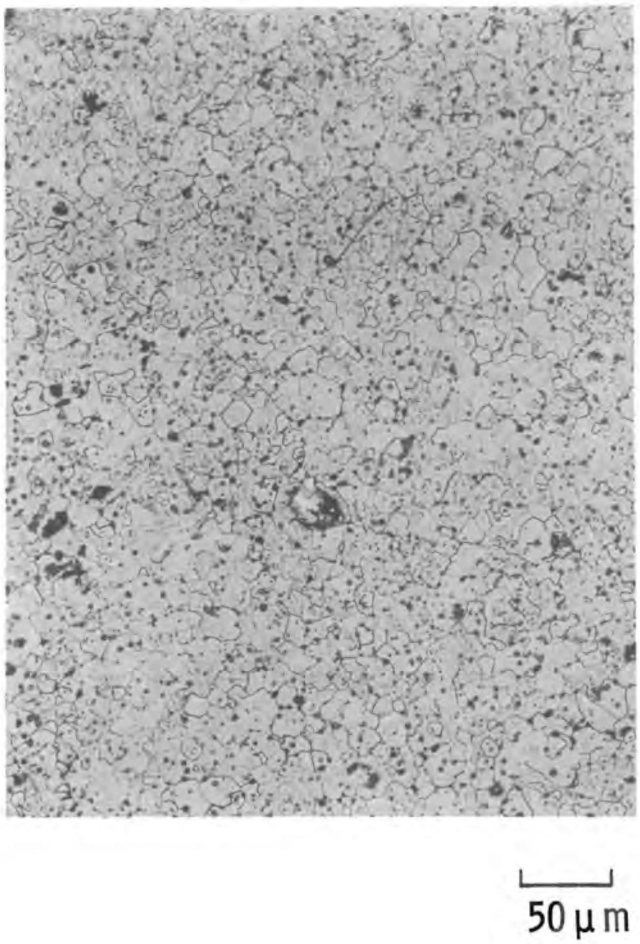
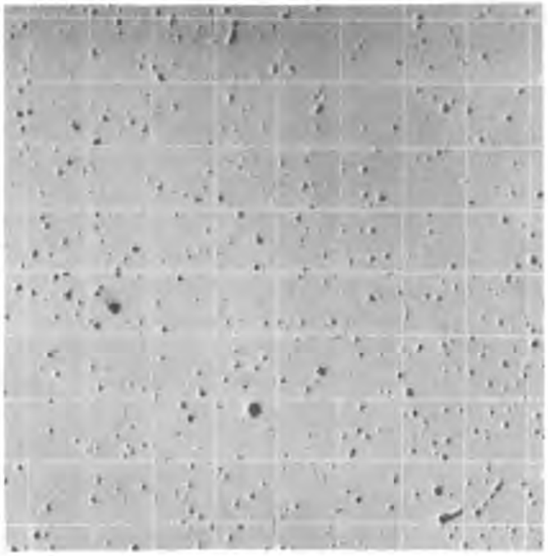
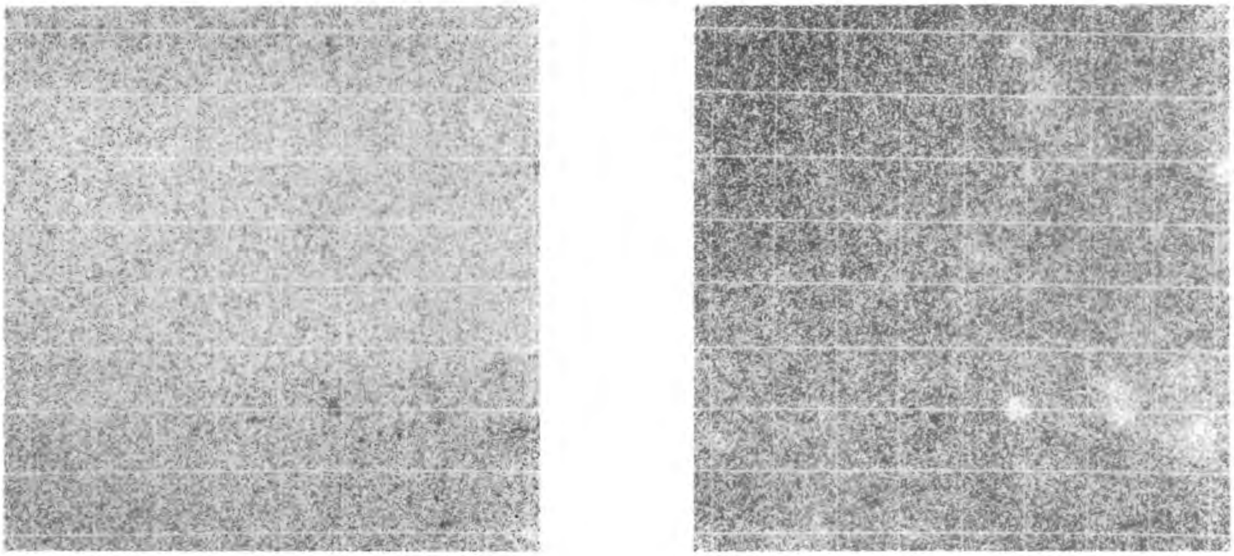


FIGURE 10. Microstructure of a Sintered ThO_2-20 wt% UO_2 Pellet Made From Powders Separately Milled for 12 h Then Co-Milled for 4 h, 96% TD



ThO_2 - 20 wt% UO_2



THORIUM MAP

URANIUM MAP

FIGURE 11. Microprobe Analysis of ThO_2-20 wt% UO_2 Sintered Pellets Prepared by Co-Milling the Powders

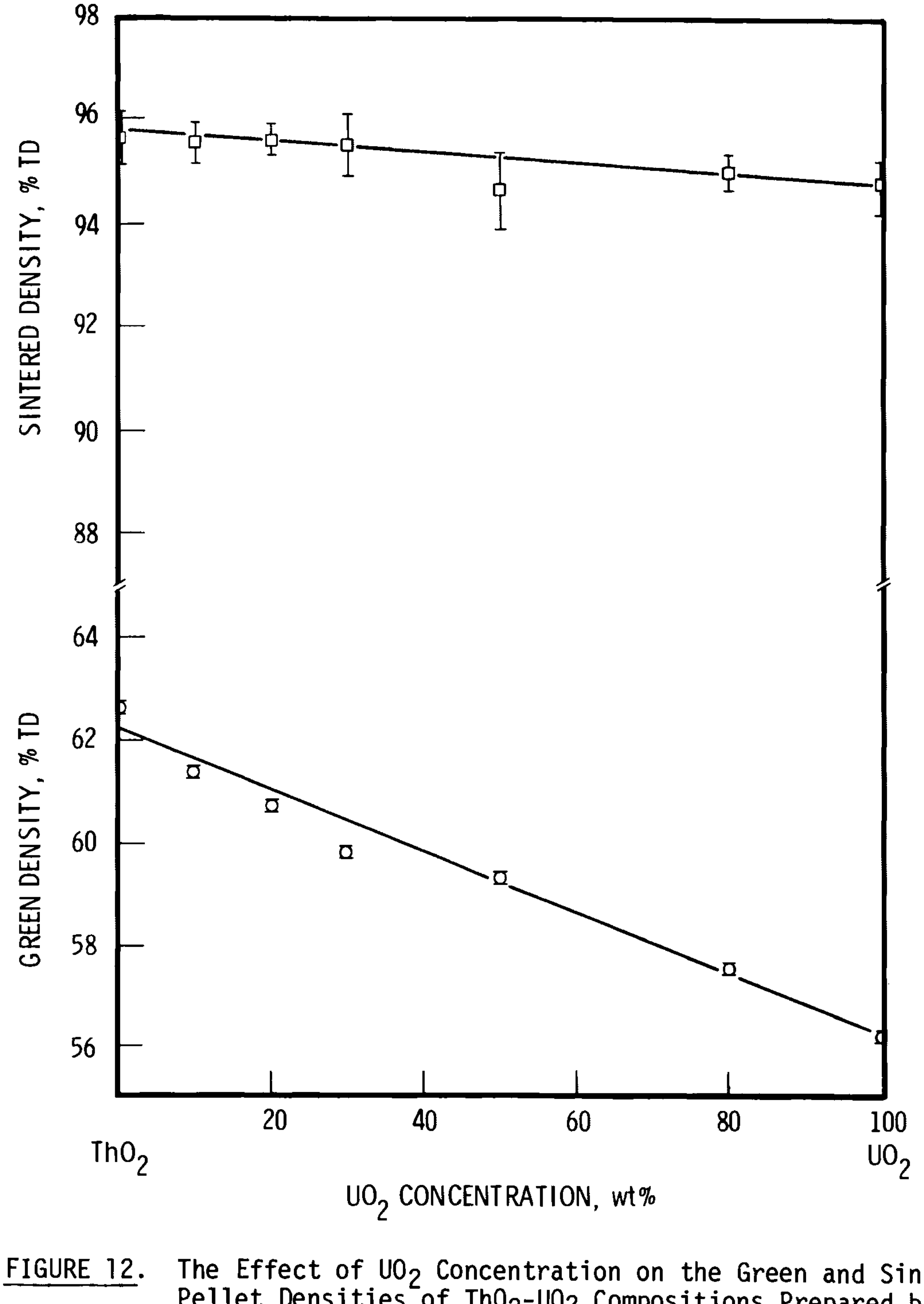


FIGURE 12. The Effect of UO_2 Concentration on the Green and Sintered Pellet Densities of ThO_2-UO_2 Compositions Prepared by Co-Milling the Powders

X-ray lattice parameters measured on the ThO_2-UO_2 pellets indicated that the components were in complete solid solution. No extraneous diffraction lines were found over the entire composition range, and the plot of lattice parameter versus composition in Figure 13 shows the Vegard's law is closely followed.

EFFECTS OF CaO ADDITIONS

One of the objectives of this development program was to establish a process for fabrication of ThO_2-UO_2 pellets for irradiation testing and subsequent reprocessing studies. In a complete fuel cycle, the irradiated fuel must be compatible with reprocessing steps and therefore readily dissolved in nitric acid solutions. Additions of MgO, ZnO and CaO to ThO_2 sol-gel particles improve the dissolution rates of sintered particles in nitric acid.(11) A series of fabrication experiments were done to assess the effect of CaO additions on ThO_2-20 wt% UO_2 pellets to be used for cold dissolution studies at Savannah River Laboratory.

Preliminary sinterability tests were done by following the procedures established for ThO_2-UO_2 powders. Lot DF-1 UO_2 powder was separately milled for 8 h then blended with 8 h ball-milled lot TB-3 ThO_2 powder and CaO powder. This blend was co-milled for 4 h, pressed and sintered into pellets. Table 7 lists the pellet fabrication data for ThO_2-20wt% UO_2 sintered pellets containing 0.33 and 0.66 wt% CaO; Figure 14 shows the etched microstructures of these pellets. Sintered density dropped only slightly with increasing CaO addition, but microstructure was notably altered by the presence of CaO. Apparently the CaO causes areas of discontinuous grain growth which show up as clusters of 10 to 20 μm grains surrounded by small grains. The clusters are frequently centered around spherical pores. Microprobe analysis of these samples showed homogeneous distribution of Ca and no evidence of Ca associated with grain boundaries or pores. Continued sintering (16 h at 1700°C) had no effect on density or microstructure.

The cracking problem mentioned in the previous section became more apparent when CaO was present. The data in Table 7 show that the percentage of cracked pellets decreased with increasing CaO concentration. Since

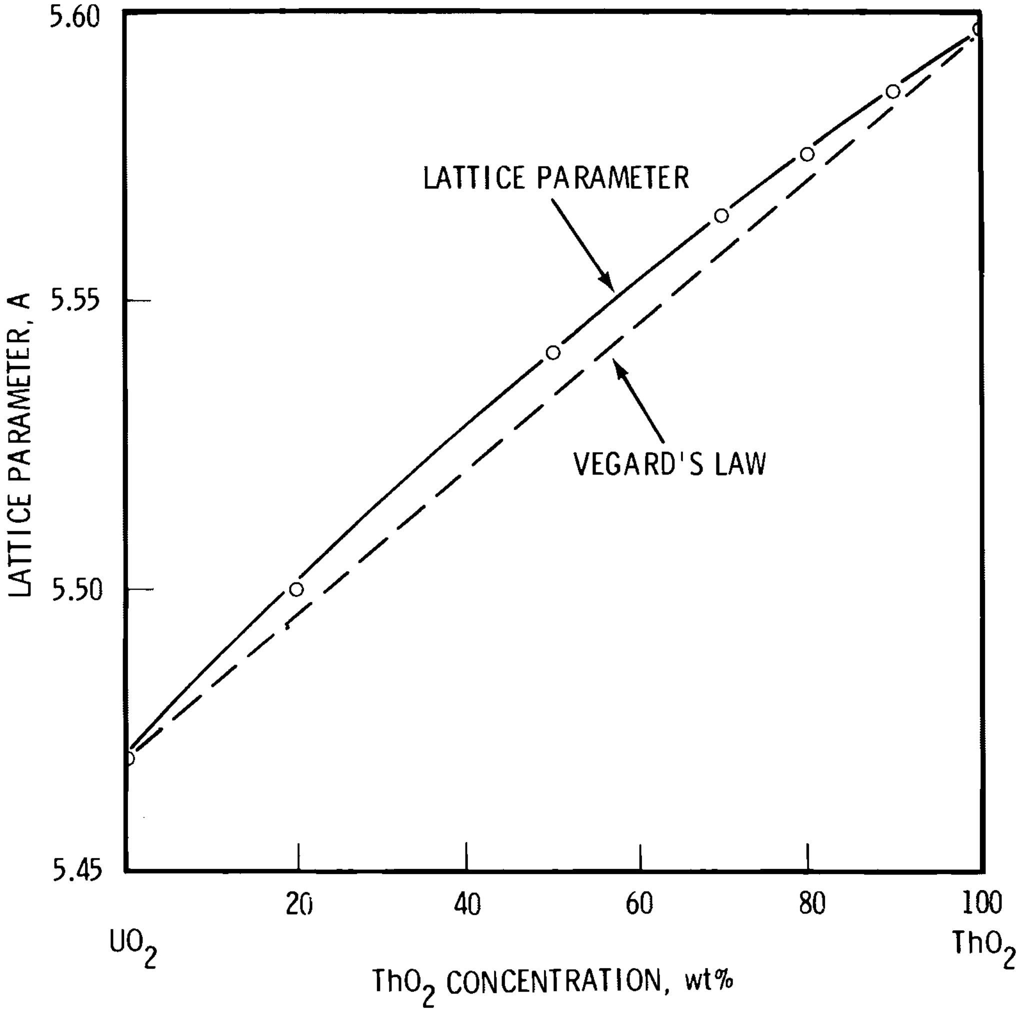


FIGURE 13. Lattice Parameters of ThO_2-UO_2 Solid Solutions

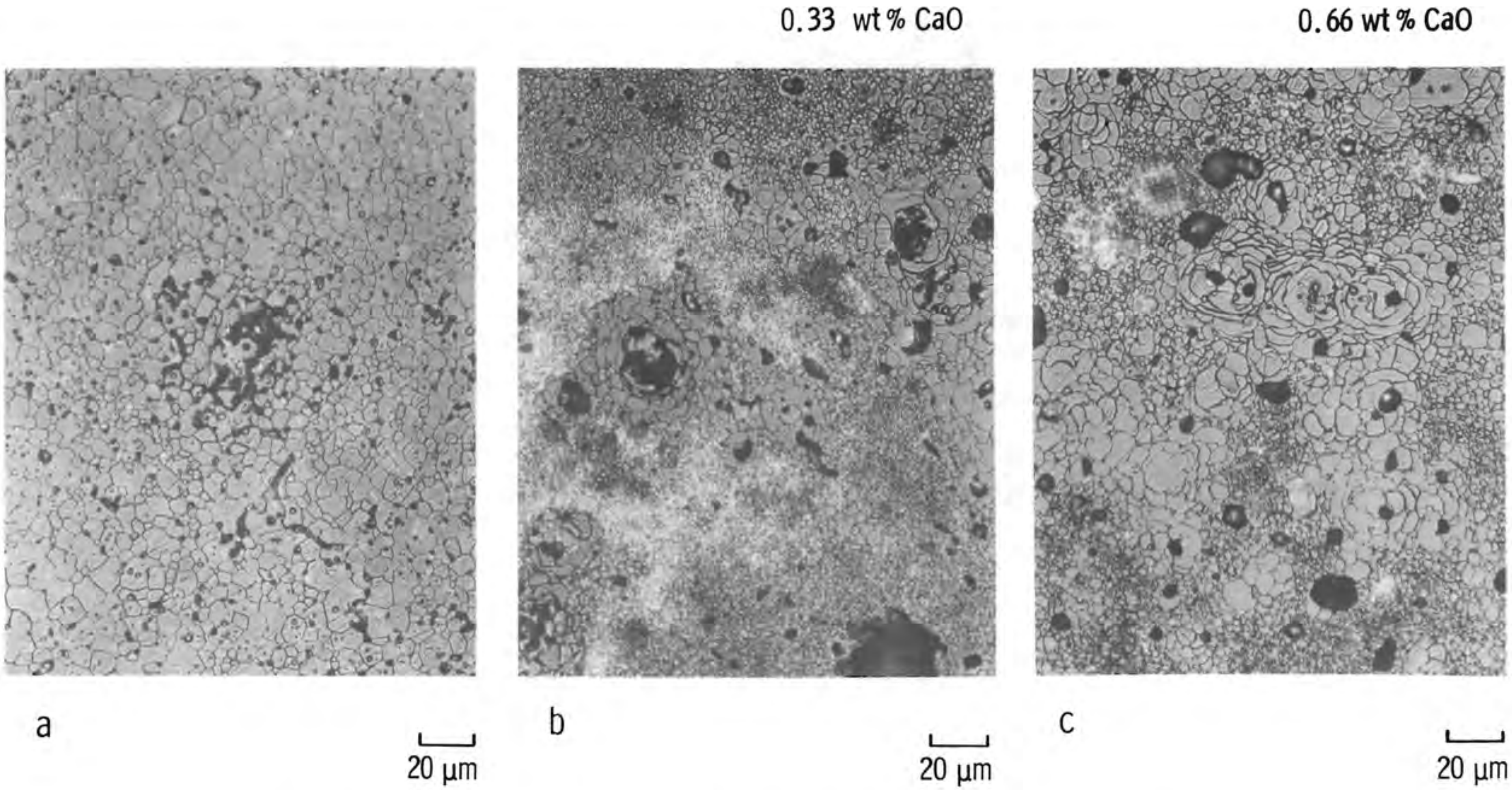


FIGURE 14. Microstructures of ThO_2-20 wt% UO_2 Sintered Pellets, (a) Containing No CaO, 96% TD, (b) Containing 0.33 wt% CaO, 96% TD and (c) Containing 0.66 wt% CaO, 93% TD

TABLE 7. Properties of ThO_2-20 wt% UO_2 Containing CaO

CaO, wt%	Tap Density, Mg/m^3	Green Density, % TD±2σ	Sintered Density, % TD±2σ[a]	Open Porosity, wt%[a]	Cracked Pellets, %
0	3.56	60.0±0.6	95.9±0.4	0.14	30
0.33	3.52	59.7±0.6	95.7±0.4	0.03	38
0.66	3.45	58.8±0.5	94.9±1.0	0.10	48

(a) Sintered pellet densities and open porosities were measured with a water immersion technique.

cracking will affect dissolution rates, methods to eliminate it were evaluated. Three types of cracks were noted: 1) edge chips and end caps which were caused by faults in the punches and excessive compaction pressures, 2) microcracks and surface crazes which occurred in pellets with the 0.66 wt% CaO addition, and 3) gross diagonal pellet cracks. The third type of crack occured during pressing and showed up on the sintered pellet as a large surface crack which goes through the pellet (Figure 15a and b). Attempts to eliminate the cracking by varying die lubricant additions and powder properties had no effect. For example, cracking occurred whether the die lubricant was sprayed directly on the die or blended with the powders. Powders which were preslugged and granulated prior to pressing behaved similarly to those which were pressed directly after ball milling. In summary, the coarse diagonal cracks appeared to be inherent to the powders. Since cracking did not appear on the pure ThO_2 pellets, the UO_2 powder became suspect. A similar batch of ThO_2-UO_2 containing 0.5 wt% CaO was prepared using lot DF-2 UO_2. The powder mix was prepared by the co-milling technique, and pellets were pressed and sintered using the standard conditions. No cracking was observed in these pellets; they had an average immersion density of 95.1±0.2% TD and 0.03 volume % open porosity, but the discontinuous grain growth was still present. Apparently, the cracking problems were caused by the properties of Lot DF-1 UO_2. No further investigation of this powder was done.

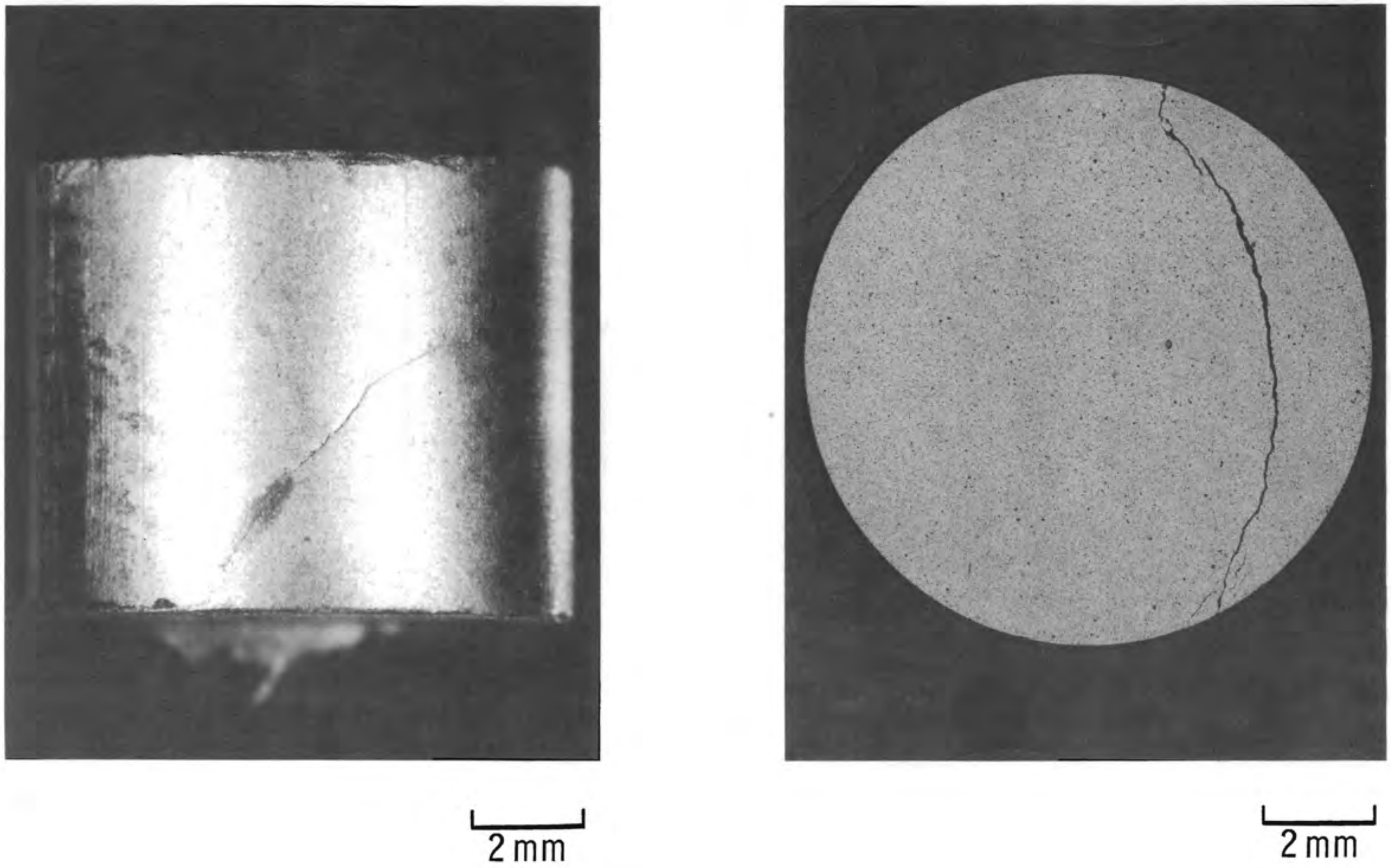


FIGURE 15. (a) ThO_2-20 wt% UO_2 Pellet Showing Cracked Surface
(b) Cross-Section Through Pellet Showing Internal Crack

CONCLUSIONS

Based on the results of this study the following conclusions were reached:

- Extensive ball milling (12 to 16 h) was needed to enhance the pressing and sintering characteristics of as-received ThO_2 powders to fabricate 95% TD pellets.
- A reference process for producing ThO_2-UO_2 was established.
- Fabrication of 95% TD ThO_2-UO_2 pellets containing up to 80 wt% UO_2 was achieved by separate milling of the single oxide powders followed by co-milling of the mixtures.
- Microstructures of the ThO_2-UO_2 pellets were homogeneous with random small pores and uniform grains. Single phase solid solution of the components occurred during sintering.
- Additions of CaO to ThO_2-20 wt% UO_2 had little or no effect on sintered pellet density but caused areas of discontinuous grain growth.

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ACKNOWLEDGMENTS

The authors are indebted to several co-workers at the Pacific Northwest Laboratory who performed much of the work reported in this document. Personal acknowledgment, identified with areas of major performance, are noted below. Special thanks are extended to the contributors.

- P. E. Hart, Program Management
- E. H. Shade, J. E. Lester, J. E. Spasoff, D. Smith, Process Development Technicians
- D. H. Parks, Metallography
- C. W. Griffin, Attrition Study and Analysis

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