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ACTIVATION OF SOME UO_2 POWDERS
BY MILLING AND OXIDATION-REDUCTION^(a)

M. J. Barr

September 1970

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ERRATA

Page 21 (Table 6)

Columns marked 20,000 and 40,000 psi should have the following title above them:

Sintered Density, (a)
% TD

Color photo in this report should be identified as Page 10, Figure 4.

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ACTIVATION OF SOME UO_2 POWDERS
BY MILLING AND OXIDATION-REDUCTION

M. J. Barr

ABSTRACT

The effect of varying the activity of some UO_2 powders by various material treatments was evaluated by calcining small portions of ceramic grade normal UO_2 in nitrogen and in air to 400, 600, and 800°C. Portions of 93.15% enriched UO_2 powder were activated using the oxidation-reduction technique. Powder characteristics determined on as-received and activated powders included particle size distribution, O/U ratio, B.E.T. surface area, tap density and scanning electron micrographs. Pellet characteristics obtained from sinterability specimens included green and sintered pellet theoretical density, and sintered pellet microstructure. The particle characteristics determined were evaluated against changes in density and sintered pellet microstructure.

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ACTIVATION OF SOME UO_2 POWDERS
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M. J. Barr

INTRODUCTION

As UO_2 powder is the major constituent in mixed U-Pu oxide fuel pellets, its sinterability is an important characteristic. Factors influencing the sinterability of UO_2 powders were investigated by measuring particulate properties and the sinterability of portions of powder removed at key points in the activation process. The powders evaluated were ceramic grade, normal UO_2 produced from ammonium diuranate, and 93.15% enriched $^{235}\text{UO}_2$ produced through conversion of UF_6 . Characterization of each included spectroscopic analysis of impurities and measurement of O/U ratio, surface area, and moisture contents. Scanning electron micrographs of as-received and modified powders were also obtained. Characterization of modified powders (in addition to scanning electron micrograph) included O/U ratio, tap density, surface area and green and sintered pellet densities.

UO_2 sinterability studies made by other investigators have produced conflicting data, however, it is generally conceded that preparation history influences the reactivity of UO_2 powder.^(1,2) Attempts to relate sinterability to physical or chemical properties, preparation history, calcining temperature and sintering atmosphere have yielded controversial results. Variations in UO_2 preparation history, pellet fabrication techniques, and sintering conditions have confused the data. Work by J. Williams et al.⁽³⁾ showed a major increase in sintered density occurring as the O/U ratio was changed from $\text{UO}_{2.00}$ to $\text{UO}_{2.02}$ and only a slight

increase with higher O/U ratios. Low temperature sintering studies (1200°C) by Fuhrman, Hower, and Holden⁽⁴⁾ showed that higher sintered densities were obtained by sintering powder having an initial O/U ratio of 2.23. The same paper also showed that a preliminary oxidation-reduction cycle activated less sinterable oxides such that sintered densities of 95% of theoretical could be consistently produced. The majority of data published was obtained from pellets sintered in inert gas or CO₂ with small amounts of moisture added to produce hyperstoichiometric sintered pellets. There was also general agreement with the observation that small amounts of hydrogen in the sintering atmosphere adversely affected low temperature sinterability (<1400°C).

The work discussed herein investigated the effect of activation on particle properties and on sinterability in a dry, reducing atmosphere (argon-8% H₂) at relatively high sintering temperatures (1675°C). The experiments were also designed to:

- Show the effect of O/U ratio on sinterability using conditions similar to those used for fabrication of FTR fuel pellets.
- Reveal the change in particulate properties occurring from point-to-point in the activation process.
- Statistically evaluate the characterization data versus sinterability results to determine key particle characteristics or combinations influencing UO₂ sinterability.

SUMMARY

The achievable sintered density of ceramic grade normal UO₂ and 93% ²³⁵U enriched UO₂ was increased 2 to 3% by oxidation of the powder to an O/U ratio of approximately 2.65.

Reduction of oxidized powder to low O/U ratios (2.10 to 2.15) may not be necessary provided the greater volume shrinkage obtained when sintering highly oxidized powder can be tolerated.

Analysis of the particle properties determined (O/U, surface area, etc.) shows that none of the properties measured can be used as a unique indicator to predict sinterability. A 2 to 3% increase in sintered density can be obtained through ball milling of less sinterable 93% enriched UO_2 . Milling of highly sinterable ceramic grade UO_2 produced inconclusive data.

EXPERIMENTAL PROCEDURE

CERAMIC GRADE NORMAL UO_2

After complete characterization, a master batch of ceramic grade UO_2 powder was subdivided and portions were calcined in a quartz crucible to 400, 600, and 800°C in air and in nitrogen. After calcination, samples were characterized and the remaining powder was pressed into approximately 0.250 in. diameter pellets. Test groups were sintered 2 hr in argon-8% hydrogen at 1675°C. Green and sintered densities were calculated from geometric measurements. Diametral variation and microstructure were also obtained.

ENRICHED UO_2

A master batch of 93.15% enriched UO_2 powder was subdivided and portions subjected to the following treatments.

- Wet ball milled with a 2/1 weight ratio of Al_2O_3 media to powder.
- Wet ball milled with a 3/1 weight ratio of WC media to powder.

- Oxidized in air with samples removed after 1 hr at 140°C and after 1 hr at 500°C.
- Oxidized Powder (500°C) reduced in argon-8% hydrogen with samples removed after 1 hr at 400°C and after 4 hr at 500°C.

After each modification operation samples were characterized and a portion pressed into approximately 0.250 in. diameter pellets. Green pellet characteristics were determined and the pellets subsequently sintered 4 hr in argon-8% hydrogen to 1675°C. Sintered densities, diametral variation, and microstructure were determined on the pellets.

DISCUSSION OF RESULTS

CERAMIC GRADE NORMAL UO₂

Spectroscopic impurities, fluorine, chlorine, and carbon in as-received ceramic grade UO₂ are presented in Table 1.

TABLE 1. Normal UO₂ Impurity Levels

<u>Impurity</u>	<u>As-Received UO₂</u>	<u>After Calcination in Nitrogen to 800°C</u>
Ag	<0.1	<0.1
Al	100	100
Ca	100	100
Cr	<25	<25
Cu	5	2
Fe	20	20
Mg	<5	<5
Mn	<1	2
Mo	<5	5
Na	<2	<2
Ni	<10	<10
P	<50	<50
Pb	2	10
Si	5	5
Sn	<5	<5
V	<20	<20
Zn	<50	<50
Cl	<10	NA
Fl	<5	NA
C	125	NA

NA -- Not Available

Scanning electron micrographs of the as-received powder are shown in Figure 1. The scanning micrographs show the powder to consist of agglomerates of very small particles or crystallites. Magnification to 10,000 diameters still failed to resolve individual particles. The effect of calcination on surface area, moisture content, O/U ratio, and tap density is presented in Table 2. In addition, the effect of calcination on particle size distribution is shown in Figures 2 and 3. The particle size distribution curves indicate little change in particle size with calcination to 800°C. The gradual decrease in surface area and moisture content with higher calcining temperature and the increase in O/U content with calcination to 400°C in air are consistent with theory. The slight increase in O/U ratio with calcination in nitrogen is believed due to residual moisture and oxygen present in the glovebox atmosphere. Data in Table 1 indicate that calcination to 800°C in nitrogen does not measurably affect impurity levels. The color variation as a result of calcination temperature and atmosphere is shown in Figure 4. The code letters ELD in Figure 4 represent air calcination and ELDN represents nitrogen calcination. The calcine temperature follows the code letters.

Green and sintered pellet densities, percent diameter shrinkage, and sintered pellet diameter variation are shown in Table 3. Although green density was not corrected for O/M ratio, the densities obtained can be related to percent diameter shrinkage (Figure 5). Sintered densities were improved about 2% by calcination of starting powder in air at 400 and 600°C. Calcination in air at 800°C produced sintered densities equivalent to the as-received powder. Calcining in nitrogen at 400 and 600°C did not affect sinterability to a significant degree, however, 800°C calcination reduced the sintered density to about 91% theoretical.

3000X MICROGRAPH #M-6

629

10,000X MICROGRAPH #M-6

687

FIGURE 1. Normal Ceramic Grade UO_2 --As-Received

TABLE 2. Effect of Calcination on Normal UO_2 Powder Characteristics

Treatment	Color	Surface Area, m^2/g	Moisture Content, ppm		O/U Ratio	Tap Density, g/cm^3
			At 200°C	At 800°C		
Normal As-Received	Dark Green	9.0	4070	4530	2.17	1.37
Air Calcination, °C						
400	Light Olive	5.6	3200	3600	2.66	0.88
600	Dark Olive	4.2	2100	2300	2.65	1.00
800	Brown	1.0	700	800	2.62	1.43
Nitrogen Calcination, °C						
400	Navy Blue	5.7	2200	2500	2.22	0.90
600	Dark Navy Blue	2.3	1900	2000	2.18	0.90
800	Blue-Black	1.6	530	580	2.23	2.00

FIGURE 2. Particle Size Distribution of Normal UO_2 Calcined in Air

FIGURE 3. Particle Size Distribution of Normal UO_2 Calcined in Nitrogen

(1)	2.16	2.661	2.646	2.620	2.219	2.18	2.231
(2)	.252"	.252"	.252"	.2515"	.2525"	.2524"	.2515"
(3)	.200"	.183"	.187"	.195"	.201"	.203"	.214"
(4)	47.14%	39.29%	41.47%	45.62%	47.40%	49.40%	57.96%
(5)	95.62%	97.55%	97.66%	95.54%	95.86%	96.06%	91.22%

- (1) Powder 0/M
- (2) Green diameter
- (3) Sintered diameter
- (4) Green density
- (5) Sintered Density

TABLE 3. Normal UO_2 ; Green and Sintered Pellet Properties

<u>Treatment</u>	<u>Green Density (30,000 psi), % Theoretical</u>	<u>Sintered Density, % Theoretical</u>	<u>Diameter Shrinkage, %</u>	<u>Diametral Variation, mils</u>
Normal As-Received	47.14	95.62	20.6	2.0
Air Calcination, %				
400	39.29	97.55	27.2	2.0
600	41.47	97.66	25.8	2.0
800	45.62	95.54	22.5	1.0
Nitrogen Calcination, °C				
400	47.40	95.86	20.1	2.2
600	49.40	96.06	19.5	2.0
800	57.96	91.22	14.9	2.0

a. Green density is based on 10.97 g/cm^3 and has not been corrected for O/U ratio.

FIGURE 5. Green Density Versus Diameter Shrinkage for UO_{2+x} (Normal)

The 500X micrographs shown in Figure 6 indicate that air calcining affects sintered pellet grain size. The as-received powder yielded sintered grains of 40 to 50 μ diameter and air calcination at 400, 600, and 800°C reduced the diameter of sintered grains to about 10 μ . Calcination in nitrogen at 400°C also produced powder which sintered to an average grain size of 10 μ . Calcination to higher temperatures in nitrogen did not further reduce the grain size to a significant degree. All micrographs shown in Figures 6 and 7 show the center portion of the pellet. All test groups were sintered at the same time.

Some conclusions that may be drawn from an analysis of the normal UO_2 calcination data are:

- Calcination to 800°C in nitrogen or air does not significantly affect powder particle size distribution.
- Variations in O/U ratio, surface area, moisture content or tap density have little apparent effect on sinterability.
- The powder characteristics measured do not adequately explain variations in sinterability (within the characteristics limits evaluated).

ENRICHED UO_2

The enriched UO_2 (93.12% ^{235}U) was produced through conversion of uranium hexafluoride. Cationic impurities, fluorine, chlorine, moisture and carbon content are presented in Table 4. Particle size distribution of as-received powder is shown in Figure 8. Scanning electron micrographs (5000 and 20,000X) are shown in Figure 9. The difference in particle morphology between ceramic grade normal UO_2 (ammonium diuranate process) and enriched UO_2 (uranium hexafluoride conversion) is readily apparent when Figure 1 is compared with Figure 9.

500X 9315D
NORMAL UO_2 - 400°C NITROGEN

500X 9315E
NORMAL UO_2 - 600°C NITROGEN

500X 9315F
NORMAL UO_2 - 800°C NITROGEN

FIGURE 6. Microstructure of Sintered Normal UO_2 Pellets
As-Received and After Calcine

500X 9235B
NORMAL UO_2 - AS-RECEIVED

500X 9314D
NORMAL UO_2 - 400°C AIR CALCINE

500X 9314E
NORMAL UO_2 - 600°C AIR CALCINE

500X 9314F
NORMAL UO_2 - 800°C AIR CALCINE

FIGURE 7. Microstructure of Sintered Normal UO_2 Pellets After Nitrogen Calcine

TABLE 4. Enriched UO_2 Impurity Content

<u>Impurity</u>	<u>Level, ppm</u>
Ag	<0.1
Al	20 to 50
B	<0.1
Ca	<1
Cr	<25
Cu	2
Fe	20
Mg	<5
Mn	1
Mo	<5
Na	<2
Ni	10
P	<50
Pb	<1
Si	<5
Sn	<5
W	0
F	22
Cl	6
H_2O	1000
C	100
After Al_2O_3 Milling	Al-200
After WC Milling	W-0.55%

FIGURE 8. Particle Size Distribution of Enriched UO_2

5000X MICROGRAPH

#3677

20,000X MICROGRAPH

#3678

FIGURE 9. Scanning Electron Micrographs of As-Received Enriched UO_2

Table 5 contains O/U ratio, surface area, tap density and green density data. Data in Table 5 indicate that both wet milling and oxidation-reduction are effective in changing particle properties. The decrease in green density caused by 500°C oxidation is the result of U_3O_8 formation. Green densities were based on 10.84 g/cm³ theoretical density for comparison purposes. The increase in the O/U ratio of wet milled powder (2.15) is believed the result of oxygen pickup from water during milling.

Sintered pellet densities, percent diameter shrinkage, and diameter variation are presented in Table 6. Sintering was accomplished in dry argon-8% hydrogen for 4 hr at 1675°C. The O/U ratio of sintered pellets was approximately 2.0. It can be seen from Table 6 that the change occurring during the transition from $UO_{2.08}$ to $UO_{2.65}$ allowed the greatest improvement in sintered density (compare Group 3 with Group 1). The addition of oxygen alone had little effect on sintered density as evidenced by: (1) material heated to 140°C in air (Group 2) sintered to approximately the same density as as-received material (Group 1), and (2) reducing the O/U ratio to 2.17 (Group 4) produced essentially the same densities as Group 3. Hard reduction at 500°C for 4 hr produced densities only about 1/2% less than Group 3 but still 2% or more higher than the starting material having an equivalent (approximately) O/U ratio.

Green density (based on TD of 10.84 g/cm³ and percent diameter shrinkage are plotted in Figure 10. The green densities used in Figure 10 were not corrected for O/U or binder content. However, the curve indicated a reasonably good relationship between green density and percent shrinkage.

TABLE 5. Powder and Green Pellet Properties of 93% Enriched UO_2

Group	Material Treatment	O/M Ratio	B.E.T. Surface Area, m^2/g	Tap Density, g/cm^3	Green Density, (a) % TD		Green Pellet Ejection Pressure at Press Pressures	
					20,000 psi	40,000 psi	20,000 psi	40,000 psi
1	As-Received	2.08	2.0 - 2.15	2.08	52.51	56.59	1400	3300
2	140°C Roast in Air	2.23	1.8	2.11	52.62	57.39	1400	3300
3	500°C Roast in Air	2.65	3.5	1.30	42.56	46.26	2200	5000
4	1 hr Reduction at 400°C in Ar-8% H_2	2.17	3.4	1.27	43.07	47.05	3300	7000
5	4 hr Reduction at 500°C in Ar-8% H_2	2.10	1.9	1.67	49.73	54.68	1600	3300
6	Wet Mill, 2:1 Ratio of Al_2O_3 Media to Powder	2.15	1.7	2.08	52.73	57.21	1400	3300
7	Wet Mill, 3:1 Ratio of WC Media to Powder	2.15	2.6	2.14	53.95	58.47	1400	3300
8	Blend--70% As-received + 30% 500°C Roast	NA	NA	1.88	48.47	53.43	1900	3900

NA--Not Available

a. Based on $10.84 \text{ g}/\text{cm}^3$ theoretical

TABLE 6. Properties of 93% Enriched UO_2 Sintered Pellets

Group	Material Treatment	20,000 psi	40,000 psi	% Diameter Shrinkage, psi		Diametral Variation, psi	
				20,000	40,000	20,000	40,000
1	As-Received	93.06	94.48	17.73	15.90	1.0	1.0
2	140°C Roast in Air	92.85	94.89	17.65	15.97	1.4	1.0
3	500°C Roast in Air	96.20	97.00	25.37	23.09	1.5	1.5
4	1 hr Reduction at 400°C in Ar-8% H_2	96.03	96.25	24.83	22.67	1.3	1.7
5	4 hr Reduction at 500°C in Ar-8% H_2	95.78	96.34	20.44	18.22	1.0	1.0
6	Wet Mill, 2:1 Ratio of Al_2O_3 Media to Powder	94.77	95.09	18.41	16.32	1.1	1.4
7	Wet Mill, 3:1 Ratio of WC Media to Powder	96.07	96.89	18.13	16.30	1.0	1.0
8	Blend--70% As-Received + 30% 500°C Roast	93.38	94.45	20.28	18.06	1.0	1.0

a. Based on $10.84/\text{g}/\text{cm}^3$ theoretical

FIGURE 10. Green Density Versus Diameter Shrinkage for 93% Enriched UO_2

The effect of adding activated powder to less sinterable powder was evaluated by Group 8. Comparison of the sintered pellet densities from Groups 1 and 8 shows that there was no significant increase in sintered density when activated powder was added to as-received powder.

Scanning electron micrographs (5,000 and 20,000X magnifications) of samples from powder Groups 1 (Figure 9, as-received) and 3 (Figure 11, 500°C air calcined) show that a pronounced change in particle morphology does not occur with oxidation. Comparison of Figures 9 and 11 does, however, indicate a hazing of the particle surface after air oxidation with no obvious change in shape. Particle size analysis (not shown) of as-received and oxidized powders also produced essentially identical curves. Work by Clayton and Aronson⁽²⁾ indicated that the original microstructure characteristics were recovered when UO_2 powders were oxidized to U_3O_8 and reconverted to UO_2 by reduction.

Micrographs of sintered pellets are shown in Figure 12. The 10X micrographs show surface texture differences among pellets produced from as-received, 500°C oxidized, and oxidized then reduced powders. The difference in surface porosity between the Group 1 pellet and Groups 3 and 5 pellets is attributed to a lower sintered density (approximately 2 to 3%) in the Group 1 pellet. The 500X micrographs show an increase in grain size with oxidation of powder (compare the Group 3 pellet with the Group 1 pellet). The quantity of microcracks in the Group 3 micrograph confuse grain size analysis. However, undisturbed areas show larger grains similar to those in the Group 5 micrograph. The Group 5 micrograph indicates that reduction from an O/U of 2.65 to 2.10 in the powder did not reduce the sintered grain size. These micrographs indicate that O/U content does not, by itself, significantly influence sintered pellet grain size.

5000X MICROGRAPH

#3690

20,000X MICROGRAPH

#3691

FIGURE 11. Scanning Electron Micrographs of Enriched UO_2
Oxidized at 500°C

10X

0157A

500X

0157F

AS-RECEIVED ENRICHED UO_2 (GROUP 1)

10X

0159A

500X

0159J

ENRICHED UO_2 OXIDIZED AT 500°C 500X (GROUP 3)

10X

0160A

500X

0160

OXIDIZED UO_2 AFTER 4 HOUR REDUCTION (GROUP 5)

FIGURE 12. Enriched UO_2 Sintered Pellet Microstructure

The increase in grain size after oxidation of the enriched UO_2 (Figure 12) conflicts with the decrease in grain size after air calcination of ceramic grade normal UO_2 (Figure 6). Reasons for this difference are not understood, however, a comparison of pellet processing history and powder characterization data reveal the following:

- The temperature used in the ceramic grade normal UO_2 oxidation was higher (to 800°C) than those used for enriched UO_2 (500°C) and the greatest decrease in sintered grain size occurred at the higher temperatures.
- The enriched UO_2 was a less sinterable powder in the as-received condition.
- The enriched UO_2 used in this study was produced through conversion of uranium hexafluoride and the ceramic grade normal UO_2 through the uranium diuranate process.
- Examination of crystallite or particle morphology shows the powders to be significantly different.

STATISTICAL EVALUATION OF CHARACTERIZATION DATA

The purpose of the statistical evaluation was to express the sintered density of UO_2 as functions of surface area, O/U ratio, tap density, green density, moisture content, and pellet ejection pressure (data not included). An analysis of normal UO_2 data produced the following equation:

$$Y = 108.778 - 2.162 X_2 - 0.224 X_3$$

where Y = sintered density expressed as % TD

X_2 = tap density in g/cm^3

X_3 = green density expressed as % TD

The correlation between the model equation and data obtained was good with the model explaining 96% of the observed variation in sintered density of normal UO_2 . It is significant that particle properties such as surface area, O/U ratio and moisture content are not included in the equation and that the two variables that were included are performance tests.

Attempts to fit enriched UO_2 data to a model equation were disappointing. Model equations were developed using press pressure as constants; however, for enriched powder pressed at 20,000 psi the model explained only 56% of the observed variation, and for powder pressed at 40,000 psi, the only significant term in the model equation was the constant.

An attempt to fit all UO_2 data into a model equation showed that the only significant term was the constant.

Some conclusions drawn from the statistical evaluation of characterization data are:

- A sinterability test is the best performance indicator for the UO_2 powders evaluated.
- Characterization data such as surface area, O/U ratio, and moisture content are not useful as performance indicators.
- Green and tap density may be useful as performance indicators on powder from one source using a controlled sinterability test.
- None of the characteristics determined could be used as a performance indicator on more than one type of powder.

GENERAL CONCLUSIONS

Conclusions that may be drawn from the UO_2 activation experiments include:

- The sintered density of both ceramic grade normal UO_2 and 93% enriched UO_2 was increased 2 to 3% by oxidation of the powder to an O/U ratio of approximately 2.65.
- The oxygen-to-uranium ratio by itself does not have a significant affect on sinterability.
- Oxidation and/or calcination in air can affect sintered pellet grain size.

- Calcination to 800°C in nitrogen will adversely affect UO_2 sintered density.
- Sinterability of more than one UO_2 powder cannot be predicted from characterization data and the best performance test is a controlled sinterability test.

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