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GRAIN GROWTH OF UO_2
PART II

H. HAUSNER

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VALLECITOS ATOMIC LABORATORY

GENERAL ELECTRIC

ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

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October 1965

GRAIN GROWTH OF UO_2

PART II

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FOREWORD

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CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. PREVIOUS INVESTIGATIONS	2
3. EXPERIMENTAL	3
4. RESULTS	10
5. DISCUSSION.	20
CONCLUSIONS	21
ACKNOWLEDGMENT	21
REFERENCES.	22

ILLUSTRATIONS

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Impurity Content of UO_2 Samples	7
2.	Microstructure of UO_2 Pellets	9
3.	Accuracy of Grain Size Determination	12
4.	Effect of Time and Temperature on Grain Size for Pellet Type A	16
5.	Effect of Time and Temperature on Grain Size for Pellet Type B	17
6.	Effect of Time and Temperature on Grain Size for Pellet Type C	18
7.	Effect of Time and Temperature on Grain Size for Pellet Type G	19

GRAIN GROWTH OF UO_2

Part II

H. Hausner

ABSTRACT

The influence of different fabrication procedures on the grain growth of UO_2 was studied between 1900 and 2300°C. The various methods of fabrication produced different initial grain sizes and different initial densities in the sintered pellets under study.

A decreasing time constant, n , was found when impurities were introduced during fabrication by ball milling.

The activation energy for grain growth showed different values when different fabrication procedures were applied to the same batch of UO_2 . However, the differences are rather small, so that the uncertainty associated with each value makes it difficult to establish the trend in the temperature dependence with increasing amount of impurities.

Large differences in the time constant, n , and the activation energy Q were observed when different batches of powder and different fabrication procedures were used.

1. INTRODUCTION

The experiments described in this report supplement the results published previously¹ under the High Performance UO_2 Program. In the earlier investigations the grain growth in UO_2 pellets was studied in the temperature range between 1900 and 2600°C. The grain size-time relationship could be expressed by

$$D^2 - D_0^2 = K \cdot t^n = K_0 e^{-Q/RT} \cdot t^n$$

where

D_0 = Average grain growth before heat treatment,

D = Average grain size after heat treatment,

t = Time at temperature,

T = Temperature ($^{\circ}\text{K}$),

Q = Activation energy,

R = Gas constant, and

K, K_0, n = Constants.

A low value for the exponent, $n \sim 0.33$, was found in these experiments, and an activation energy of 65 Kcal/mole was obtained for the grain growth process. The unexpected low time

constant, n , was believed to be related to the type of UO_2 investigated. Since these data were obtained from a single batch of UO_2 , it was important to investigate the effect of different lots of UO_2 in these studies. Furthermore, the experiments described in this report are directed toward the investigation of the influence of different fabrication procedures on grain growth. These different procedures resulted in different starting grain sizes and different initial densities in the sintered pellets.

2. PREVIOUS INVESTIGATIONS

The continuing interest in the dependence of the microstructure of ceramic materials on temperature is reflected in the increasing number of publications on this subject. The theoretical considerations have been summarized briefly in the previous report in this series,¹ and references about previous work are listed there, but several investigations about grain growth in ceramic systems have been published in the meantime. Daniels, et. al.,² studied grain growth behavior in magnesia and calcia. Their results could be expressed by an equation of the form $D^2 - D_0^2 = K \cdot t$, where D_0 and D are the grain diameters in the material before and after the heat treatment, t , is the time at temperature, and K is a constant. The rate of grain growth appeared to be independent of porosity in the range zero to 15%.

Tien and Subbarao³ investigated the composition $\text{Ca}_{0.16}\text{Zr}_{0.84}\text{O}_{1.84}$ and found that grain growth followed the equation $D = (k \cdot t)^n$ with n approximately 0.4. Their observed decrease in n with increasing temperature was explained by the change in porosity. A strong influence of the atmosphere on the grain growth rate was also observed.

Spriggs, et. al.,⁴ studied grain growth in hot-pressed, fully dense magnesia. The data obtained agreed very closely to the theoretical equation $D^2 - D_0^2 = K \cdot t$. The authors postulate that porosity decreases the grain growth rate, limits the grain size, and decreases the time exponent, compared to the experimental results obtained by Daniels² on magnesia. The rate constant in Spriggs' studies was always higher and also showed a stronger temperature dependence. Nicholson⁵ studied grain growth in zinc oxide and found that the data followed the equation $D = (K \cdot t)^n$ with $n = 0.33$, similar to the value reported by Coble⁶ for alumina. This author also found the same exponent value in his investigations of magnesia systems.⁷ In summarizing these results it can be said that in all these investigations the grain growth behavior followed the equation $D = K \cdot t^n$ with n varying between 0.3 to 0.5. The exact reason for the differences in the time dependence and also in the temperature dependence, even in the same system, is not yet established, but may be caused by a different composition (e. g., impurities and porosity) of the different materials. The quantitative influence of these differences is not known to any significant extent and much more work is needed in this area.

In addition to the studies on the above-mentioned oxides, several investigations have been performed on UO_2 . Amato, et. al.,⁸ studied the grain growth of nonstoichiometric UO_2 ($\text{O}:\text{U} > 2.00$).

This group applied the equation $D^2 - D_0^2 = K \cdot t^n$ and reported that n had a value of 0.93 ± 0.15 for sintering in CO_2 . The activation energy was approximately 50 Kcal/mole. This value for the activation energy is about 30 Kcal lower than that reported for stoichiometric UO_2 by other investigators.

Mansour and White⁹ studied grain growth of UO_2 during sintering. By applying the grain size-time relationship $\frac{dD}{dt} = \frac{K}{D}$ a time constant of 0.67 was obtained.

Amato and Colombo¹⁰ proposed that the binder (or probably its residue) produced the observed difference in the grain growth in their experiments.

Lyons, et. al.,¹¹ correlated published results on UO_2 grain growth and fitted all data to form $D^3 - D_0^3 = K \cdot t$, which they considered to represent the "normal" grain growth in UO_2 . If one considered the varying results obtained in different investigations of oxides other than UO_2 and takes into consideration the possible and unknown variations within different batches of the same material fabricated by the same operational procedures,¹² this representation of the grain growth process would appear to be an oversimplification of the problem.

3. EXPERIMENTAL

Five groups of pellets, A, B, C, G, and H, were investigated at temperatures of 1900, 2100 and 2300°C, with a maximum time of 100 hours at temperature.

FABRICATION OF PELLETS

Different fabrication procedures were used to obtain differences in grain size and porosity in the starting material. The pellets in groups A through C consisted of 1.5% enriched UO_2 powder and the pellets for Group H were fabricated from 2.2% enriched UO_2 . The chemical and physical analysis of the starting powders are given in Table 1.

The fabrication procedures that were applied to produce the various groups of pellets are given in Table 2.

The particle size of the as-received powder used for the fabrication of pellet type A, and the wet ball-milled powder used for type C was essentially the same, as confirmed by electron micrographs. The particle size of this type ceramic grade powder is so small, that it is not further decreased significantly by milling. The surface area of both the as-received and the milled powder was found to be $2.5 \text{ m}^2/\text{gm}$.

The chemical, spectrographic and microscopic analysis of the pellets of each group are shown in Table 3. It can be seen that the O:U ratio in these pellets is constant (2.002) within the limits of accuracy of the determination, and that the UO_2 in all pellets can be considered essentially stoichiometric. Therefore, the influence of differences in the O:U ratios on the grain

TABLE 1. Composition of UO_2 Powders

		Powder I (natural)	Powder II * (1.5% enriched)	Powder III* (2.2% enriched)
O:U Ratio		2.09	2.07	2.07
Spectrographic Analysis (ppm)	Al	<10	2	<7
	Sb	<2	n. d. **	n. d.
	B	0.8	0.2	<0.20
	Bi	5	n. d.	n. d.
	Cd	<1	<0.1	<0.10
	Ca	25	26	33
	Cr	<10	3	12
	Co	<2	<5	<5
	Cu	2	21	32
	Fe	25	10	12
	Pb	<1	n. d.	n. d.
	Mg	<1	n. d.	n. d.
	Mn	3	3	<1
	Mo	<3	n. d. <1	n. d. <1
	Ni	<10	10	<10
	Si	50	4	13
	Ag	<0.1	<0.1	0.15
	Na	<35	n. d.	n. d.
	Sn	2	n. d.	n. d.
	Ti	n. d.	n. d. <100	n. d. <100
	V	15	n. d. <10	n. d. <10
	Zn	<10	n. d.	n. d.
	C	n. d.	43	55
	F	n. d.	49	50
	Cl	n. d.	<25	<25
	N	n. d.	<10	<10
Particle Size (Fisher sub-sieve)		n. d.	0.93 μ	1.04 μ
Bulk Density (Scott volumeter)		n. d.	1.14 gm/cm ³	1.15 gm/cm ³
Surface Area		2.5 m ² /gm	n. d.	n. d.

*Analysis obtained from vendor.

**Not determined.

TABLE 2. Pellet Fabrication

Group	A	B	C	G	H
Type of Powder	I	I	I	II	III
Ball Mill	-	Alumina	Alumina	Aluminum Mill + Stainless Steel Balls	Aluminum Mill + Stainless Steel Balls
Milling Time	-	2 Hours (dry)	8 Hours (wet)	10 min dry	10 min dry
Binder (Added Before Milling)	-	3% Carbowax	No Binder	1.5% Carbowax	1.5% Carbowax
Lubricant for Pressing	3% H ₂ O	-	3% H ₂ O	0.2% Sterotex	0.2% Sterotex
Green Density after Pressing, gm/cm ³	5.5	5.5	5.5	5.9	5.9
Removal of Binder	-	In H ₂ at 450°C for 4 Hours	-	In H ₂ at 450°C	In H ₂ at 450°C
Sintering	In H ₂ at 1750°C for 5 Hours	In H ₂ at 1750°C for 4 Hours	In H ₂ at 1750°C for 5 Hours	In H ₂ at 1650°C	In H ₂ at 1650°C

growth behavior should be negligible for these groups of pellets. In Table 3, the impurity content of the pellets is shown. The relative distribution of the main impurities in the pellets of the various groups can be compared in Figure 1. It should be realized that the determination of these small impurity concentrations gives rise in some cases to a wide range of probable error. In Table 4, the analysis of different pellets from the same group is listed. It is not evident whether the differences can be attributed to actual differences in the amounts of impurities in one pellet compared to another, or to the very limited accuracy of the spectrographic determinations. In pellets of Group H the grain growth behavior was quite variable. This variation in grain growth may have been caused by differences in composition among the pellets, especially in the Fe content.

Some general statements can be related to the fabrication procedures. The main impurity in almost all pellets is Si, based on the analytical results covered in Table 3. The Al content increases from Group A to Group C as would be expected from the increased milling time in the Al₂O₃ ball mill.

In the pellets from Group G and H, the Fe and Ni contents are higher than in pellets from Group A to C. This could be expected from the fabrication procedure. The Cr content shows a trend similar to that for Fe and Ni. The nitrogen content does not show any particular trend between the Groups.

TABLE 4. Main Impurities in pellets G and H (ppm)

No.	Group G				Group H		
	1	2	3*	4*	1	2*	3*
Al	50	24	100	20	50	200	100
Cr	25	44	25	25	25	20	20
Cu	30	50	65	65	30	100	100
Fe	75	200	500	200	150	1000	500
Ni	25	25	100	50	100	200	100
Si	60	20	30	30	200	300	60
N	84	n. d.	160	390	34	-	-

* Analysis published in GEAP-4264 (1963) p. 37
Pellets of group G and H come from these batches.

The microstructure of the pellets in the as-sintered condition are shown in Figure 2. Besides the difference in the grain size, a significant difference can be seen in the form and the distribution of the porosity among the different groups of pellets. Pellets from Group B showed areas with high and low porosity, probably caused by an inhomogeneous distribution of the binder before sintering.

HEAT TREATMENT

For each heat treatment condition, one pellet from each group, with an outside diameter of 1 cm and a height of 0.35 to 0.40 cm, was placed into a single tungsten capsule (1.15 cm o. d., 1.05 cm i. d., and 3 cm high) which was then welded leaktight under an argon atmosphere. The different pellets were separated by 0.1-cm-thick tungsten spacers. Before seal welding, all the tungsten parts were cleaned thoroughly by chemical treatment and by heating in vacuum to $\sim 1500^{\circ}\text{C}$. For the grain growth anneal the capsules were heat treated in vacuum at 1900 and 2100°C in a tantalum resistance furnace and at 2300°C in an induction concentrator furnace. Capsule temperatures during heat treatment were measured with a W - W/25 Re thermocouple or with an optical pyrometer. The capsules were leak-checked after treatment. In some cases, leaks had developed after the long-term heat treatments at 2100°C ; and a few leaks were also found after the treatments at 2300°C .

GRAIN SIZE DETERMINATION

The heat-treated samples were rough ground with a series of metallographic papers and then polished with diamond and alumina (Linde B). A mixture of 90% H_2O_2 and 10% H_2SO_4 was used as the etchant to develop the grain structure. The average grain size of the heat-treated

FIGURE 1. IMPURITY CONTENT OF UO_2 SAMPLES

VAL 5926

TABLE 4. Main Impurities in pellets G and H (ppm)

No.	Group G				Group H		
	1	2	3*	4*	1	2*	3*
Al	50	24	100	20	50	200	100
Cr	25	44	25	25	25	20	20
Cu	30	50	65	65	30	100	100
Fe	75	200	500	200	150	1000	500
Ni	25	25	100	50	100	200	100
Si	60	20	30	30	200	300	60
N	84	n. d.	160	390	34	-	-

* Analysis published in GEAP-4264 (1963) p. 37
Pellets of group G and H come from these batches.

The microstructure of the pellets in the as-sintered condition are shown in Figure 2. Besides the difference in the grain size, a significant difference can be seen in the form and the distribution of the porosity among the different groups of pellets. Pellets from Group B showed areas with high and low porosity, probably caused by an inhomogeneous distribution of the binder before sintering.

HEAT TREATMENT

For each heat treatment condition, one pellet from each group, with an outside diameter of 1 cm and a height of 0.35 to 0.40 cm, was placed into a single tungsten capsule (1.15 cm o.d., 1.05 cm i.d., and 3 cm high) which was then welded leaktight under an argon atmosphere. The different pellets were separated by 0.1-cm-thick tungsten spacers. Before seal welding, all the tungsten parts were cleaned thoroughly by chemical treatment and by heating in vacuum to $\sim 1500^{\circ}\text{C}$. For the grain growth anneal the capsules were heat treated in vacuum at 1900 and 2100 $^{\circ}\text{C}$ in a tantalum resistance furnace and at 2300 $^{\circ}\text{C}$ in an induction concentrator furnace. Capsule temperatures during heat treatment were measured with a W - W/25 Re thermocouple or with an optical pyrometer. The capsules were leak-checked after treatment. In some cases, leaks had developed after the long-term heat treatments at 2100 $^{\circ}\text{C}$; and a few leaks were also found after the treatments at 2300 $^{\circ}\text{C}$.

GRAIN SIZE DETERMINATION

The heat-treated samples were rough ground with a series of metallographic papers and then polished with diamond and alumina (Linde B). A mixture of 90% H_2O_2 and 10% H_2SO_4 was used as the etchant to develop the grain structure. The average grain size of the heat-treated

FIGURE 2. MICROSTRUCTURE OF UO_2 PELLETS. PRODUCED BY VARIATION IN PROCESS AND POWDERS

samples was determined by a linear intercept method in which 200 to 300 grains in different areas of the pellets were counted.

DATA ANALYSIS

The data were analyzed with statistical techniques. Values for the time constant, n , and the activation energy for the different types of pellet were calculated by a generalized regression analysis. The computer program used was GEORGE, a FORTRAN program written for IBM-7090 and converted for compatibility with the PHILCO-2000.

4. RESULTS

ACCURACY OF GRAIN SIZE DETERMINATION

To obtain a measure of the accuracy of the experiments, the grain size of six different pellets (Group G) was determined in the as-fabricated condition and then after a heat treatment of 2300°C for 1 hour. Vertical and horizontal sections were also compared. The results of this investigation can be summarized as follows:

1. The average grain diameter in the as-fabricated pellets was 9.2μ with a range of $\pm 10\%$. Only one pellet contained larger size grains (12.6μ).
2. No difference in the mean grain size was found between vertical and horizontal sections, such a difference might be caused by preferred arrangements of particles during the pressing operation.
3. After the 1-hour heat treatment, the mean grain size of the five pellets with an initial grain size of 9.2μ was found to be 68μ . Fourteen of sixteen grain size measurements fell within a range of $\pm 10\%$. The pellet with a starting grain size of 12.6μ showed a larger mean grain size than the other pellets only in one area (96μ); all other areas examined fell within $\pm 10\%$ of 68μ .
4. From these experiments, it can be concluded that the grain size determination is accurate to about $\pm 10\%$ (Figure 3).

TIME AND TEMPERATURE DEPENDENCE OF GRAIN GROWTH

In Table 5 the average grain diameters of the pellets are shown after heat treatments for varying time intervals at different temperatures.

In general, the data for pellets A through G are similar, i. e., the grain size increases with time and temperature with a few exceptions. On the other hand, the pellets in Group H show quite an irregular grain growth behavior. As discussed previously, these erratic results may be caused by differences in the amount of impurities from pellet to pellet. For this reason the pellets in H have not been included in the statistical analysis of the results.

TABLE 5. Grain Size of Pellets After Heat Treatment

		<u>A</u>	<u>B</u>	<u>C</u>	<u>G</u>	<u>H</u>
1900°C	2 h	24	34	49	37*	47*
	5 h	36	40	62	40	29
	12 h	54	-	74	53	43
	30 h	72	71	80	62	57
	100 h	82	91	109	81	85
2100°C	2 h	68	68	96	48	52
	5 h	85	93	118	58	70
	12 h	109	101	157	59	65
	30 h	155	140	183	73	75
	100 h	254	146	177	69	121
2300°C	2 h	93	109	176	63	59
	5 h	113	93	213	74	125
	10 h	135	113	275	77	52
	20 h	173	181	329	89	119

* 2.5 hours at temperature

FIGURE 3. ACCURACY OF GRAIN SIZE DETERMINATION

STATISTICAL ANALYSIS OF GRAIN GROWTH DATA

The dependence of grain growth on time and temperature will be described by the equation

$$D^2 - D_0^2 = K \cdot t^n$$

where

$$K = K_0 \cdot [\exp(-Q/RT)]$$

and

D_0 = Average grain size before heat treatment,

D = Average grain size after heat treatment,

t = Time at temperature,

T = Temperature ($^{\circ}\text{K}$),

Q = Activation Energy,

R = Gas law constant, and

K, K_0, n = Constants

As the first step in the analysis, the data obtained for one pellet group at a specific temperature were used to obtain estimates of n and K . Next, estimates of the residual variance (the sum of the squared distances from the observed points to those predicted by the fitted curve divided by the number of points less two) were found. These steps were performed to:

1. Check the adequacy of the model by determining whether the residual variance was consistent with the known variability associated with each datum point. This variability was estimated from the observed variability in D values for as-received pellets and for pellets heat treated for 1 hour at 2300°C .
2. Determine whether the parameter n is dependent on pellet type and (or) temperature.

An estimate was first made of the variation in D values between nominally identical pellets. In the as-received pellets, ten determinations of D were used and for pellets heat treated for 1 hour at 2300°C , seventeen determinations were used. The following values were obtained:

	<u>As-Received</u>	<u>Sintered</u>
Average D	9.2μ	68.2μ
Standard Deviation (δ)	0.548μ	5.17μ
$\delta/\text{Average}$	0.0593	0.0758
$(\delta/\text{Average})^2$	0.00352	0.00574

$$\text{Average Value of } (\delta/\text{Average})^2 = 0.00463$$

This value is then compared with the residual variance for each fit. The mathematical grain growth model is made linear by taking the logarithm at both sides of Equation (1) to give:

$$\log (D^2 - D_o^2) = \log K + n \cdot \log t.$$

Next, the variance of $\log (D^2 - D_o^2)$ is found, given that the variance of D is 0.00463 times D^2 . From the standard statistical approach to find the variance of a function:

$$\text{var} \left[\log (D^2 - D_o^2) \right] = 0.434^2 \text{var} \ln \left[(D^2 - D_o^2) \right] \quad (4)$$

$$\text{var} \left[\ln (D^2 - D_o^2) \right] \cong \frac{1}{(D^2 - D_o^2)^2} \left[4D^2 \text{var} D + 4D_o^2 \text{var} D_o \right] \quad (5)$$

For the data under discussion, $(D^2 - D_o^2)^2 \cong D^2$ especially at the higher temperatures and heat treatments for longer times. Under these conditions Equation (5) may be written in the following approximate form:

$$\begin{aligned} \text{var} \left[\ln (D^2 - D_o^2) \right] &\cong 4D^2 \text{var} D/D^4 \\ &\cong 4 (0.00463) \cong 0.0185 \end{aligned}$$

From (4) and (6) follows:

$$\text{var} \left[\log (D^2 - D_o^2) \right] \cong 0.00348$$

This is the value that should be observed for the residual variance if the variation between the observed and predicted points is consistent with that observed between nominally identical pellets.

Actual estimates of the residual variances are shown below. No estimate is given for pellet type B at 2300°C because the two intermediate data points were considered unreliable. These points, therefore, were not included in the analysis:

	A	B	C	G
1900°C	0.0203	0.0042	0.0025	0.0017
2100°C	0.0033	0.0041	0.0010	0.0035
2300°C	0.0012	-	0.0012	0.0012

With the exception of pellet type A at 1900°C these residual variances are consistent from a statistical point of view with the 0.00348 value given by Equation (7). This consistency indicates that the model chosen provides an adequate fit through the data.

Analysis of the individual estimates of the n parameter showed that there is no effect of temperature on the values of n . Over-all estimates, by type, are:

Estimates of n Parameter

<u>Pellet Type</u>	<u>n</u>	<u>Standard Deviation</u>
A	0.675	0.029
B	0.610	0.034
C	0.481	0.034
G	0.387	0.034

Thus these pellet types differ in their values for n , with the possible exception of types A and B.

Since n is not temperature dependent, Equations (1) and (2) can be combined into a single equation to provide simultaneous estimation of K_0 , n and Q/R by the methods of multiple regression. The combined equation for the model may be written:

$$\log (D^2 - D_0^2) = \log K_0 - \frac{0.434 Q}{R} \left(\frac{1}{T} \right) + n \cdot \log t$$

To calculate the different parameters, the computer program GEORGE was used. For type A all 14 points were included; for type B the 100-hour, 2011°C observation and the 5- and 10-hour observations at 2300°C were not used; the 100-hour, 2100°C points for type C and G are also excluded. All these points are inconsistent with the fact that, in general, grain size increases with time and temperature. Estimates of the parameters after eliminating these points are:

	<u>$\log K_0$</u>	<u>$0.434 Q/R$</u>	<u>Q (Kcal/mole)</u>	<u>n</u>	<u>Residual Variance</u>
A	9.66 ± 0.62	1.529 ± 0.148	70 ± 6.8	0.698 ± 0.076	0.0239
B	10.45 ± 0.60	1.687 ± 0.141	77 ± 6.5	0.600 ± 0.067	0.0138
C	11.14 ± 0.18	1.741 ± 0.043	80 ± 2.0	0.478 ± 0.025	0.0020
G	5.78 ± 0.24	0.609 ± 0.058	28 ± 2.7	0.383 ± 0.035	0.0035

The values in the last column indicate the model provides an excellent fit for types C and G since this value should be 0.00348 from Equation (7) for a perfect fit. Plots of the experimental data, which are shown in Figures 4 through 7, suggest that the difficulty is in the 2300°C data for pellet types A and B. If the data at this temperature are not included, the following estimates of the parameters are obtained for Types A and B.

	<u>$\log K_0$</u>	<u>$0.434 Q/R$</u>	<u>Q (Kcal/mole)</u>	<u>n</u>	<u>Residual Variance</u>
A	12.15 ± 0.72	2.082 ± 0.163	95 ± 7.5	0.690 ± 0.054	0.0101
B	11.89 ± 0.67	2.015 ± 0.153	92 ± 7.0	0.635 ± 0.2	0.00685

FIGURE 4. EFFECT OF TIME AND TEMPERATURE ON GRAIN SIZE (Pellet Type A)

FIGURE 5. EFFECT OF TIME AND TEMPERATURE ON GRAIN SIZE (Pellet Type B)

FIGURE 6. EFFECT OF TIME AND TEMPERATURE ON GRAIN SIZE (Pellet Type C)

FIGURE 7. EFFECT OF TIME AND TEMPERATURE ON GRAIN SIZE (Pellet Type G)

The agreement with the value from Equation (7) still leaves something to be desired. There is, however, considerable improvement over the results found with the 2300°C data included.

5. DISCUSSION

The results obtained with the pellet types A, B, and C represent the influence of different fabrication procedures on the time and temperature dependence of grain growth in UO_2 pellets made from the same batch of powder. Type A pellets were fabricated with the as-received powder. Type B pellets were dry ball-milled for 2 hours with the addition of 3% Carbowax, and type C pellets were wet ball-milled for 8 hours. As expected, these procedures resulted in an increase in the amount of impurities in types B and C (not considering the nitrogen content). The density of type B was 90% of theoretical density as compared to 95 and 96% for type A and C. The as-sintered grain sizes in type B and C were 24 and 23 μ , respectively, as compared for 11 μ for type A.

If comparing the time dependencies for grain growth, as given by the time constant n , it is evident that the constant decreases steadily from types A through C. The difference in the n -values for types A and B is small, so that the values with associated deviations overlap. These results lead to the following conclusions:

1. The density difference between types A and B does not have a very significant effect on the time constant n . The porosity in type B was present in the form of large pores; a different behavior might be expected, if the porosity were very finely divided.
2. The difference in grain size between pellet type A and B does not cause a significant difference in the time constant n . It can be concluded furthermore, that some other mechanism must be responsible for the difference in n between type B and C.
3. The major influence on the different grain behavior is probably the introduction of impurities by the ball milling process. Very small amounts of impurities seem to have a pronounced effect in this regard. It should be pointed out, that the situation may be more complex than that described. The grain size in the as-sintered pellets B and C was originally larger than in type A. This difference suggests an enhancement in grain growth by the introduction of impurities. However, it must be realized that different conditions are present during the initial sintering of the pellets from those used during the grain growth investigations, notably the temperature level and the atmosphere. This difference may markedly affect the rate of grain growth.

Considering the temperature dependence of the grain growth process as expressed by the activation energy, Q , the values seem to increase from types A through C. This increase would be in agreement with theories, that grain boundary movement is impeded by impurities, and that an increase in the amount of impurities results in a higher activation energy.¹³ However, the differences between types A, B, and C are actually so small that the uncertainty associated with each value makes it difficult to draw any definite conclusions. This is especially true, if the data at 2300°C are excluded.

When compared to pellet types A, B, and C the grain growth of type G pellets is quite different. The type G pellets were prepared from another type of powder by a different fabrication procedure. A rather low time constant value of 0.38 was found as well as a small temperature.

dependence for grain growth that leads to an activation energy of only 28 Kcal/mole. This behavior may be caused by either the difference in the preparation of the two powders or by the different fabrication procedure used to make the pellets. Either of these differences may introduce different amounts and/or different kinds of impurities into the powder. When compared to the results reported in Part I of these studies, (GEAP-4315) where pellets were fabricated using the same procedure as for the type G pellets in the present study, the time constant was almost identical in both cases. The activation energy for type G pellets, however, is only 28 Kcal/mole as compared to 65 Kcal/mole for the pellets described in Part I. No explanation is apparent for this large difference in the temperature dependence of type G pellets compared to the pellets prepared by the same procedure reported previously.

CONCLUSIONS

Grain growth in UO_2 is affected not only by the type of powder which is used for the fabrication of the sintered pellets, but also by differences in the fabrication procedures applied to the same batch of powder. Very small amounts of impurities introduced during fabrication may change the time and temperature dependence for grain growth considerably. Very large differences in grain growth characteristics may be found when different batches of powder are used.

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