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MASTER

GRAIN GROWTH OF UO_2 PART I

BY
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✓ EUROPEAN ATOMIC ENERGY COMMUNITY

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European Atomic Energy Community

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PREFACE

The United States and the European Atomic Energy Community (Euratom), on May 29, and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U. S. -Euratom research and development program which is aimed at reactors to be constructed in Europe under the Joint Program.

The work described in this report represents the Joint U. S. -Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

ABSTRACT

1. Grain growth in UO_2 pellets was studied between 1900 C and 2600 C. The pellets were encapsulated in small vacuum-tight tungsten containers in an argon atmosphere.
2. The grain size-time relationship could be expressed by an equation:

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

A low exponent, $m \cong 1/3$, was found in these experiments and is related to the type of UO_2 investigated. An activation energy of 65 kcal/mole was obtained for the grain growth process.

The time exponent, m , increased with increasing temperature if the pellets were not contained in closed capsules but heated under an argon pressure of 1.5 atm.

3. An interaction between tungsten and UO_2 could be observed at a temperature of 2600 C after prolonged heat treatment.

SECTION I

INTRODUCTION

In the High Performance UO_2 Program⁽¹⁾ sponsored by the AEC and EURATOM, pelletized and powder-compacted fuels are being irradiated in the PWL of the GETR under conditions which cause significant changes in the UO_2 microstructure. It is not possible to use thermocouples inside the fuel for temperature measurements at the high heat ratings used in these experiments. Grain size measurements in the irradiated fuel have been used therefore to obtain information about the temperature distribution⁽²⁾ within the fuel. This technique is based upon the rate of grain growth at different temperatures as determined in out-of-pile studies. It was assumed that radiation has little or no effect on grain growth at the temperatures concerned.

In ceramic materials, grain size and grain growth are not only temperature and time dependent but are also influenced by the preparation of the starting powder, the previous fabrication history, and also by the chemical composition and the presence of impurities. There is only limited information available about the development of grain structure in UO_2 bodies as a result of a heat treatment at high temperatures over an extended period of time. Therefore, a study of microstructural changes of UO_2 after high temperature treatment was performed to obtain basis for correlation with the in-pile tests.

In this report consideration is given to the portion of the work which was concerned with the grain growth behavior of UO_2 under isothermal conditions between 1800 and 2600 C.

SECTION II

THEORETICAL CONSIDERATIONS2.1 Grain Boundaries

Most studies concerned with the structure and the movement of grain boundaries have been performed on metallic systems. At the present time several theories are available to account for the presence and movement of grain boundaries, but none of them fits the experimental results and observations completely.

A grain boundary is normally described as a border which separates grains or crystallites with different orientation or sometimes different composition. The dislocation theory is widely used today to explain grain boundary structure. Burgers⁽³⁾ and Bragg⁽⁴⁾ discussed the means whereby the transition zone between two crystallites may be brought about by a system of dislocation lines. Shockley and Read⁽⁵⁾ developed the models in considerable detail and calculated the energy of a grain boundary. If a grain boundary is considered as a transition zone between two crystallites of different orientations, two cases require attention:

- a. The small angle grain boundary (for a difference in the orientation between the two crystals of < 5 degrees).
- b. The large angle grain boundary (for a difference in orientation between the two grains of > 15 degrees).

The dislocation model should only be applied to small angle grain boundaries, because of the difficulty of analysis in the case of the large-angle grain boundaries at the present time. The dislocations in large-angle boundaries are so close together that their individual character is lost. The difference between these two types of grain boundaries arises from the movement of these boundaries and in the diffusion along them.

To circumvent these difficulties, Mott⁽⁶⁾ considered a grain boundary to consist of alternating regions of good matching and poor matching between the two crystal lattices. Mott assumed that during migration of a grain boundary a group of n atoms at the edge of one crystal disorders, or melts, and then crystallizes on the adjoining crystal.

On the other hand, Ke⁽⁷⁾ assumed that the grain boundary consisted of lattice vacancies, or a certain region of disordered structure, which are responsible for diffusion.

Smoluchowski⁽⁸⁾ combined to a certain extent the dislocation theory model with those from other theories. He assumed that a grain boundary with an angle less than 15 degrees consists primarily of dislocations. When the angle of the orientation increases, increasing groups of dislocations form and eventually a continuous misfit region will exist between the two crystal-lites when the angle of the grain boundary exceeds 35 degrees.

2.2 Migration of Grain Boundaries

In view of the different concepts of the structure of a grain boundary, different theories about the migration of these boundaries are found in the literature. On the basis that the elementary step in grain boundary migration is closely related to grain boundary diffusion, Turnbull^(9, 10) has applied the absolute reaction rate theory to derive the equation

$$G = e \cdot \lambda (kT/h) (\Delta F/RT) e^{\Delta S_A/R} \cdot e^{-Q_G/RT} \quad (1)$$

in which

- G = rate of grain boundary migration
- e = Naperian base
- kT/h = frequency factor for atomic jumps (k = Boltzmann's constant, h = Planck's constant)
- λ = distance of jumps (thickness of grain boundary)
- ΔS_A = entropy of activation per g-atom
- ΔF = driving energy
- Q_G = measured activation energy per g-atom
- T = absolute temperature
- R = universal gas constant

If the driving force for grain boundary migration is assumed to be the interface energy between two grains and the energy difference across a curved boundary, one can write

$$\Delta F = \frac{K \sigma V}{r} \quad (2)$$

in which,

- K = geometric factor
- σ = surface energy
- V = g-atomic volume
- r = radius

then by substituting (2) in (1),

$$G = e \cdot \lambda (kT/h) (K\sigma V/r \cdot RT) e^{\Delta S_A/R} \cdot e^{-Q_G/RT} \quad (3)$$

If the radius of curvature of the grain boundary is replaced by the grain diameter, one can obtain the equation

$$\frac{dD}{dt} = \frac{K_0 \sigma V}{D} e^{-Q/RT} \quad (4)$$

in which D = grain diameter
 t = time

and K_0 includes the frequency factor and the entropy of activation term.

After integration one obtains

$$D^2 - D_0^2 = K_0 v \cdot e^{-Q/RT} \cdot t \quad (5)$$

where D_0 = grain diameter at $t = 0$

Equation (5) can be expressed in the more general form

$$D^2 - D_0^2 = K v \cdot t \quad (6)$$

where $K = K_0 \cdot e^{-Q/RT}$

G. F. Bolling and W. C. Wingard⁽¹¹⁾ stated that an equation of the general form

$$D^2 - D_0^2 = K \cdot t \quad (7)$$

was not found to hold experimentally in many cases. They preferred the equation in the form

$$D = C \cdot t^n = (K \cdot t)^n \quad (8)$$

Equation (8), which was used by Beck et al⁽¹²⁾, is derived from equation (7) for the case $D_0 = 0$ and $n = 1/2$. In several other investigations of grain growth in metals and alloys⁽¹³⁾ the exponent, n , did not have the expected value of $1/2$ but a smaller one which increased with increasing temperature.

Application of the principles found applicable for metals to ceramic systems is limited. A review of the subject is given in references^(14,15,16). The relations for grain size development in ceramics can be expected to be more complicated than in metals because of the porosity and the higher amount of impurities which are normally found in ceramic systems. Furthermore, interactions between the material and its environment are more likely in ceramics because of the higher temperatures required for grain growth in these nonmetallic systems.

2.3 Previous Investigations on UO_2

Belle⁽¹⁷⁾ studied the sintering behavior of wet ball-milled oxide compacts at 1500 and 1700 C. The initial sintering behavior could be described by the relation $D = K \cdot t^n$, where $n = 0.67$. At longer sintering times at 1700 C the value of n decreased to about 0.33.

Kisiel⁽¹⁸⁾ has obtained data for UO_2 grain growth in sintered pellets at temperatures between 2000 and 2300 C for a holding time of 15 minutes. He then calculated values for longer holding times by using the equation $D = K \cdot t^{0.1}$ (D = mean grain diameter, t = time).

MacEwan⁽¹⁹⁾ investigated grain growth in sintered UO_2 in the temperature range 1555 to 2440 C. His results could be expressed by the relation:

$$D^2 - D_0^2 = K_0 \cdot t^{0.8} e^{-87,000/RT} \quad (9)$$

Recently, H. Stehle⁽²⁰⁾ described his experimental results on grain growth in sintered UO_2 between 1550 and 2100 C, with a cubic equation of the form:

$$D^3 - D_0^3 = K_0 \cdot e^{-87,000/RT} \cdot t. \quad (10)$$

The value for the activation energy for grain boundary migration is only about 2/3 of the value found by MacEwan, if the experimental data are expressed in a D^2 relationship as in equation (9).

Ross and Whitton⁽²¹⁾ utilized electron microscopy to study the sintering of UO_2 powder compacts between 790 and 1655 C. The results could be expressed by

$$D^2 - D_0^2 = K_0 \cdot t^{0.8} e^{-Q/RT} \quad (11)$$

in which $Q = 75 \pm 5$ Kcal/mole.

SECTION III

EXPERIMENTAL

3.1 Induction Concentrator Furnace

Induction heating was used to obtain the high temperatures required for the experiments. In Figure 1 is shown the experimental setup. The equipment consists of a Vycor tube (60 cm long, 9 cm in diameter) which carried the induction coil. The tube was sealed at both ends by rubber gaskets to water-cooled copper plates. Radiation shields protected the gaskets from direct radiation. Forced air cooling was used at the highest temperatures to avoid extreme heating of the top end of the Vycor tube.

The tube was connected to a high vacuum pump so that the whole assembly could be maintained at a pressure of 10^{-4} to 10^{-5} mm Hg. It was also possible to apply a moderate pressure of inert gas to the system.

The power source was a 20 KW induction unit which operated at a frequency of 450 Kc/sec. A concentrator (Figure 1) was designed whereby the magnetic field of the induction coil could be "concentrated" in a small area to get a high energy input into the susceptor.⁽²²⁻²⁴⁾ It was possible to obtain temperatures to 2900 C within this induction furnace with the special heating assembly to be described in the following section.

3.2 Heating Assembly

The first part of the experimental program was done with the heating assembly shown in Figure 2. An argon pressure of 1.5 atm was maintained throughout these heat treatments. Because of the high vapor pressure⁽²⁵⁾ of UO_2 (Figure 4) significant vaporization of the UO_2 was found to occur when the UO_2 pellets were heat-treated for some hours at temperatures above 2000 C. Large crystals of UO_2 were present at the surface of the pellets.

It might be assumed that this high vaporization rate had some influence on the appearance of the UO_2 after a high temperature treatment. An improved heating assembly (Figure 3) was therefore designed in which vaporization of the UO_2 could be suppressed more efficiently. In addition the pressure of the inert gas above the UO_2 changed with temperature in a way similar to that occurring within an operating fuel rod.

The UO_2 pellets (1.02 cm OD, 0.705 and 0.350 cm long), which were used in this assembly, were encapsulated in small tungsten containers (1.15 cm OD, 1.27 cm long). The tube was then sealed on both ends under an A-He mixture by welding end caps to it. Space was provided within

Figure 1. INDUCTION CONCENTRATOR FURNACE

Figure 2. HEATING ASSEMBLY A

Figure 3. HEATING ASSEMBLY "B"

Figure 4. VAPOR PRESSURE OF UO_2

the capsule to accommodate the expansion of the UO_2 at temperatures to its melting point. The pressure buildup within the capsule at the highest temperatures has been calculated to be approximately 20 Kg/cm^2 (300 psi). This pressure in the filler gas reduces the vaporization of UO_2 that occurs. It was also possible to heat the welded tungsten capsule in vacuum and thereby avoid higher heat losses from the assembly which occur when it was heated in argon.

Prior to welding the end caps to the tubing, the tungsten tube (made by vapor deposition) and the end caps were thoroughly cleaned in hydrochloric acid, sodium hydroxide, water and acetone. After the chemical treatment, all items were heated in vacuum to approximately 1300°C to remove traces of oxygen. The welded capsules were pressurized in a bomb with He and then checked with a mass spectrometer type leak detector for possible leaks. This leak check was repeated after the heat treatment had been completed to see if the capsule had remained tight during the experiment.

The small capsule containing the UO_2 specimen was placed on a tungsten pedestal and centered within a larger tungsten tube of 1.9 cm ID and 3.5 cm long. The larger tube acted as the main susceptor within the induction concentrator furnace and brought the inner capsule to the desired temperature by radiant heating. The arrangement of this heating assembly within the concentrator is shown in Figure 3. The experiments conducted for 30, 100, and 400 hours at 1900°C and 2140°C were performed in a resistance heated vacuum furnace.

The experiments with encapsulated pellets will be reported as heat treatment in the "closed system", those which were performed under 1.5 atm of argon as heat treatment in the "open system".

3.3 Temperature Measurements

The temperature distribution along the length of the tungsten heater (assembly B) was determined at two different temperatures with (W-5 Re) (W-26 Re) thermocouple. The temperature variation along the heater tube is shown in Figure 5. The spatial position of the capsule containing UO_2 within the heater is also shown. It can be readily seen that the UO_2 specimen is situated in a constant temperature zone. Observation of the melting point of small platinum fuses at different places within the capsule confirmed the constant temperature distribution.

During the experiments the temperature of the capsule which contained the UO_2 was measured by means of a calibrated, optical (disappearing filament) pyrometer. The black-body behavior of the sample capsule had been thoroughly investigated prior its use. The emissivity of the capsule was determined at various temperatures because small deviations from black-body conditions may cause a significant error in temperature measurements at 2500 - 2600°C . The necessary corrections for the measured temperatures are shown in Figure 6.

Corrections were also made for the absorption of the sighting glass and prism in the optical system between 1000 and 2800°C . By use of Wien's equation for the black body radiation at temperature T

$$I = C_1 \cdot \lambda^{-5} \cdot e^{-C_2/\lambda T} \quad (12)$$

Figure 5. TEMPERATURE DISTRIBUTION IN HEATER ASSEMBLY

Figure 6. EMISSIVITY CORRECTION

and the absorption law

$$I = I_0 \cdot e^{-ax} \quad (13)$$

one obtains

$$1/T - 1/T_{app} = \frac{-\lambda(ax)}{C_2} \quad (14)$$

in which T = true temperature ($^{\circ}\text{K}$)
 T_{app} = apparent temperature
 λ = wave length
 a = Absorption coefficient
 x = thickness of absorber
 C_1, C_2 = constants

Because the right side of the equation is essentially constant, it is possible to calculate the necessary corrections due to absorption over an extended temperature region after the constant has been evaluated at one temperature. The necessary corrections at the different temperatures have been plotted in Figure 7. In order to check the calculated values, several measurements of T_{true} and $T_{apparent}$ were made over a wide temperature range by using a Sylvania RF-lamp as a temperature source. The agreement between measured and calculated data can be seen from Figure 7 to be very good.

The temperature measurements of the heater assembly were checked by comparison with the melting points obtained for several materials heated in the system. Excellent agreement was obtained between the measured value for the melting point and the literature value as shown in Table I.

TABLE I
CALIBRATION OF HEATER ASSEMBLY

<u>Material</u>	<u>Melting Point ($^{\circ}\text{C}$)</u>	
	<u>Actual</u>	<u>Measured</u>
Pt	1773.5	1780
Al_2O_3 (sapphire)	2050	2041
Y_2O_3	2410	2414
Nb	2415	2404
Mo	2620	2623

On the basis of these measurements it can be concluded that the temperature of the heater assembly could be measured at least with an accuracy of $\pm 20^{\circ}\text{C}$.

Figure 7. CORRECTION FOR ABSORPTION

3.4 Grain Size Determination

The heat-treated samples were rough ground wet with a series of metallographic papers with kerosene as a lubricant, and then polished with diamond and alumina (Linde B). A mixture of 90 percent H_2O_2 and 10 percent H_2SO_4 was used as the etchant. The grain size of the heat treated pellets was determined by the linear-intercept method. (26,27) About 200 to 300 grains were counted to determine the average grain diameter. Because of inhomogeneities within each sample, the use of different magnifications, and differences from sample to sample, the accuracy of the grain size determination is about ± 10 percent.

3.5 Materials

The following composition was obtained for the UO_2 by chemical and spectrographic analysis:

O:U ratio	2.013	
U-235	0.79 percent	
<u>Impurities</u>		
<u>ppm</u>	<u>ppm</u>	<u>ppm</u>
Al < 4	Pb < 1	An < 10
Bi < 1	Mg 2	Ni 15
B < 0.2	Mn 2	Sb < 2
Cd < 1	Mo < 3	
Ca < 10	Si 60	C 10
Cr 25	Ag 0.1	Cl 23
Co < 2	Na < 35	F 5
Cu 2	Sn < 1	N < 10
Fe 100		

The total impurity content in the UO_2 is about 340 ppm; the main impurities (about 50 percent of the total amount) are Fe and Si.

The density of sintered UO_2 body was 94 percent of theoretical. The grain size of the sintered pellet was 5.5μ , as determined by the linear-intercept method.

Some experiments were performed with enriched UO_2 that had the following composition:

Impurities:

	ppm		ppm
Al	15	Ni	75
Sb	< 2	Si	35
B	< 0.2	Ag	< 0.1
Bi	< 1	Na	< 35
Cd	< 2	Sn	< 1
Ca	10	V	< 15
Cr	20	Zn	< 50
Co	< 2	C	21
Cu	5	F	9
Fe	500	Cl	< 5
Pb	< 1	N	< 10
Mg	10		
Mn	4		
Mo	< 3		
		O:U ratio	1.989
		U-235	20.09 percent

The sum of the impurities is about 840 ppm: the main impurity is again Fe with 500 ppm compared with the 100 ppm in the first type of UO_2 . This is a rather impure material. The density of the pellets was 91.5 percent of theoretical. The average grain size was about 11μ .

The tungsten tubing was fabricated by vapor deposition and had the following composition:

<u>Element</u>	<u>ppm</u>
Al	5
Cu	10
Sn	10
Fe	10
Cr	1
Si	100
Mg	2
Mn	< 1
W	Balance

The high Si content is probably due to contamination during cutting of the tubing with a SiC wheel.

SECTION IV

RESULTS AND DISCUSSION4.1 Microstructure of Pellets in the "As-Received" Condition

The natural UO_2 investigated showed a uniformly distributed porosity in the specimen (Figure 8). Some large voids were present, and small metallic inclusions can also be observed. Prolonged contact with water did not change the appearance of the inclusions and nitric acid did not appear to affect them. It can therefore be concluded that these small inclusions are not uranium metal.

One can observe certain areas in the pellets which show a much higher porosity and also other regions with a higher density than the surroundings. Examples of high porosity and high density regions are readily apparent in Figure 8. The high density regions also have a larger grain size than the adjacent areas.

In contrast to the natural UO_2 , the enriched UO_2 samples showed much larger voids, irregularly distributed porosity and more extensive regions of higher density (Figure 9). These factors resulted in a microstructure after heat treatment which showed areas with very different grain sizes in some samples. The difference in appearance is, of course, not intrinsically related to the enrichment. It is of interest, however, to note the extent of the differences from one batch of UO_2 to another.

4.2 The Effect of Heat Treatment on Grain Size

The average grain size obtained after the heat treatment of natural and enriched UO_2 specimens at different temperatures and for different lengths of time is given in Table II. The data in this table are discussed in detail in the following sections.

4.3 Types of Systems for Heat Treatment

It was possible to extend the heat treatment of the encapsulated pellets (closed system) to a much longer holding time at temperature because vaporization was effectively suppressed. From the results obtained with the closed system (Figure 18), it was concluded that the previous results using the open system (1.5 atm A) were influenced to a large degree by vaporization (Figure 17) of the oxide. Crystals of UO_2 , which appear to grow out of the surface of the UO_2 pellet, could be observed after the specimen had been maintained for only two hours at a temperature of 2140 C in the open system. This crystal formation at the surface of the UO_2 became more and more pronounced with longer heating time and higher temperatures.

As Polished. 250X
Typical appearance showing
small metallic inclusions.

As Polished. 250X
High porosity area.

Etched 250X
High density area.

Figure 8. MICROSTRUCTURE OF NATURAL UO_2 PELLETS

Etched 100X
Area with different grain sizes. (20 min. at 2200°C)

As Polished 250X
Typical appearance as fabricated. (sintered at 1650°C)

Figure 9. MICROSTRUCTURE OF ENRICHED UO_2 PELLETS

TABLE II

GRAIN SIZE (MICRONS) AFTER HEAT TREATMENT AT VARIOUS TEMPERATURES

Time (Hrs.)	Temperature (°C)										
	1775	1900	1950	2000	2140	2200	2325	2400	2450	2500	2600
<u>Natural UO₂ (Open System)</u>											
0.33	14		22		29			42			118
2			28		57			100			400*
4			29		65			190*			400-600*
8			33		66			900*			500-1000*
<u>Natural UO₂ (Closed System)</u>											
0.33		19			38			69			108
2		29			52			94			157(122-190)
5		34			64			122			
11.66		41			72						
30		44									
100		54			96**						
400					117						
<u>Enriched UO₂ (Closed System)</u>											
0.33				20		26	42	55	57	65	104

* Exact determination is difficult because the large grain size gives poor counting statistics.

** 97.3 hours at temperature.

In the preparation of the metallographic samples it was therefore difficult to decide how much of the sample surface should be removed to obtain corresponding samples from every experiment. Furthermore, the grain size of the remaining UO_2 was in any case probably influenced by this vaporization effect. It is therefore believed that the increasing slope observed with increasing temperature in Figure 17 is at least in part caused by the effect of vaporization. It can also be seen that the experiments in the closed system gave a much clearer picture for interpretation because the scatter in the data is much smaller. At the lower temperatures the agreement in the experimental data between the open and closed systems is fairly good. This is to be expected because the degree of UO_2 vaporization is low. MacEwan⁽¹⁹⁾ has observed also that a lack of experimental reproducibility becomes manifest above 2000 C in an open system. The maximum annealing time in his experiments had to be limited to 12.5, 2.33 and 0.75 hours at temperatures of 2000, 2200 and 2440 C, respectively, in order to prevent more than 10 percent of the specimen from being volatilized.

4.4 Grain Growth of Different Types of UO_2

The relation between average grain size and temperature is shown in Figure 10 for a heat treatment of 20 minutes for two different types of UO_2 . The data lie reasonably close to the curve. The density, starting grain size, impurities, and O:U ratio for the two types of UO_2 can be compared in Table III.

TABLE III
INITIAL UO_2 DATA

	<u>O:U Ratio</u>	<u>Density</u>	<u>Grain Size</u>	<u>Total Impurities</u>	<u>Fe</u>
Natural UO_2	2.013	94.0% T.D.	5.5 μ	340 ppm	100
20% Enriched UO_2	1.989	91.5% T.D.	11 μ	840 ppm	500

There is no strong indication that these two types of UO_2 showed a significant difference in the final grain size developed during these short heat treatments. If only the data obtained with the encapsulated pellets is considered, there is evidence that the final grain size in the enriched UO_2 is smaller than in the normal oxide. This can be explained either by the presence of a larger amount of inclusions (porosity and impurities) or by the difference in stoichiometry of the oxides.

4.5 Microstructure Between 1800 and 2800 C

In Figures 11 and 12, examples of the microstructures in the as-polished and etched conditions are shown for natural UO_2 (open system) after a heat treatment of 20 minutes. There is no significant difference in the amount of porosity and in pore size between the original material and the samples maintained for twenty minutes at 1775 C. After a further increase in temperature a small, but distinct decrease in porosity can be observed with the resultant formation of pores of larger size. At a temperature of about 2600 C, the small pores have almost completely disappeared

Figure 10. EFFECT OF TEMPERATURE ON GRAIN SIZE

As Polished

250 X

20 min. at 2140°C

As Polished

250 X

20 min. at 2580°C

As Polished

250 X

5 min. at 2850°C

Figure 11. EFFECT OF TEMPERATURE ON SIZE AND DISTRIBUTION OF PORES IN SINTERED UO_2

GEAP-4315

Etched

250 X

20 min. at 2140°C

Etched

250 X

20 min. at 2580°C

Etched

250 X

5 min. at 2850°C

Figure 12. EFFECT OF TEMPERATURE ON GRAIN SIZE OF SINTERED UO_2

GEAP-4315

and only large spherical voids are present. These large voids are not restricted to the grain boundaries but are found also within the grains. These specimens had a density of about 98 percent of theoretical after the heat treatment. The porosity disappears nearly completely after the melting point has been exceeded.

As can be expected, the spherical pores develop at a lower temperature during a longer heating time. This is evident in the samples which have been heat treated at 1900 C and 2140 C for 100 hours (Figures 13 and 14). It is interesting to note that the region near the grain boundary is free of porosity. No marked difference was observed in the pore size development of natural UO_2 and enriched UO_2 pellets, when both are heat treated in a closed system. Both showed the same general pattern which has just been described.

4.6 Grain Size Distribution

In Figure 15, the relative grain size distribution of the natural UO_2 specimens is shown after a heat treatment of 20 minutes in an open system. The average grain diameter is given for each temperature. The original material shows a size distribution with a narrow range. The grain size range broadens with increasing temperature with a uniform distribution throughout the entire range at the higher temperatures. In the treatment used the average grain size was used for D ; this was done independent of the form of the grain size distribution curve.

4.7 Density-Temperature Relationship

In Figure 16 the change in density is shown as a function of temperature for a twenty minute holding time at temperature (natural UO_2 , open system). The density of the starting material was between 93.4 and 94.1 percent of theoretical. At 1775 C, no difference was observed between the density of the original material and the sample after a heat treatment of 20 minutes. A steady increase in density with increasing temperature is observed until a density of 98 percent is obtained when the specimen is held at 2600 C for 20 minutes. The increase in density with time at temperature was not very large, but the fractional decrease in porosity was significant. After 100 hours at 1900 C, the density had increased from 94 to 96.5 percent, and after 97 hours at 2140 C, from 94 to 97 percent. This fact is in agreement with the general observation that grain growth is influenced to a greater extent by an increase in temperature than by an increase in time at a given temperature.

4.8 Grain Size-Time Relationship

In Figures 17 and 18, the effect of the heating time on grain size of the natural UO_2 pellets is shown. As already mentioned, the results in the closed system give a much clearer picture for interpretation because vaporization was suppressed more effectively than in the open system. The difference in the slopes of the curves in Figure 17 may be in part the result of the influence of vaporization which caused crystal formation on the surface of the pellets. It is well known that large crystals of UO_2 can be grown from the vapor phase. An example of vapor-deposited UO_2

As Polished. 250X

As Fabricated.
(sintered at 1650°C)

As Polished. 250X

(1900°C - 100 hours)

As Polished. 250X

(2140°C - 97 hours)

Figure 13. EFFECT OF TEMPERATURE ON SIZE AND DISTRIBUTION OF PORES IN SINTERED UO_2

Etched

250X

As Fabricated.
(sintered at 1650°C)

Etched

250X

(1900°C - 100 hours)

Etched

250X

(2140°C - 97 hours)

Figure 14. EFFECT OF TEMPERATURE ON GRAIN SIZE OF SINTERED UO_2

Figure 15. GRAIN SIZE DISTRIBUTION

Figure 16. EFFECT OF TEMPERATURE ON DENSITY

Figure 17. EFFECT OF HEATING TIME ON GRAIN SIZE (Open system)

Figure 18. EFFECT OF HEATING TIME ON GRAIN SIZE (Closed system)

(2300 C, vacuum) is shown in Figure 19. Furthermore, vaporization of impurities with a change in the composition of the UO_2 may also contribute to the observed results.

From the data in Figure 18, the grain size-time relationship may be expressed by the expression

$$D^2 - D_0^2 = K \cdot t^{0.35} \quad (15)$$

where

D = average grain diameter after heat treatment
 D_0 = average grain diameter of the starting material
 K = constant
 t = time at temperature

The data can be fitted by an equation of the form $D = C \cdot t^m$, if it is assumed that the initial grain size is negligibly small. Actually the standard deviation in the constant C is smaller, when this equation is utilized, than for K when equation (15) is used.

In comparison with other investigations on grain growth in UO_2 ^(19,20), much smaller values of m (slope of the $\log D$ vs. $\log t$ curves) have been obtained in this work.

In grain growth studies in metals it was found that the factor " m " was equal to 1 if interfering effects were negligible. If inclusions are present in the metal, the value of " m " was found to decrease. ⁽²⁸⁾ Therefore, it may be possible that in the UO_2 , grain growth is also hindered by inclusions, i. e. porosity and/or impurities. The influence of porosity in preventing grain growth in ceramics is well known. The role of impurities in grain growth studies have generally been investigated more from a qualitative standpoint than in a quantitative way. Impurities may act in two ways, either accelerating or slowing down grain growth. C. A. Bruch ⁽²⁹⁾ observed during quantitative grain growth studies of alumina with small additions of magnesium oxide, that the rate of grain growth was higher at the surface than in the interior of the samples. He suspected that the higher rate of surface grain growth was caused by evaporation of MgO from the surface of the sample. Therefore the presence of the MgO appeared to reduce the rate of grain growth.

If we compare the density of the UO_2 used in this investigation with that of UO_2 used by MacEwan ⁽¹⁹⁾ and with one type investigated by Stehle ⁽²⁰⁾, no significant difference can be seen. The amount of impurities (300 ppm) which were present in MacEwan's UO_2 ⁽¹⁹⁾ does not differ very much from that (340 ppm) found in our UO_2 . It may be that a higher amount of a particular impurity and/or the distribution of inclusions (porosity) are responsible for the lower rate of grain growth observed in the present investigation. A different size or shape of pores may also be responsible for the different grain growth behaviour. Variations in the preparation of the starting UO_2 powder and in the fabrication of the pellets are known to have a significant influence on the final properties of sintered UO_2 pellets. ⁽³⁰⁾ It is conceivable that these influences persist

Figure 19. VAPOR DEPOSITED UO_2
CRYSTALS WITH 111 ORIENTATION

and affect the structure attained after subsequent heat treatment. This type of phenomenon has been observed with other ceramic materials.

The effect of a slightly higher O:U ratio in the sintered pellets on the slope of the $\log D$ vs. $\log t$ curve has not been studied. It may be expected that a steeper slope would be obtained by the introduction of excess oxygen into UO_2 ; this would lead to a higher sintering rate. A change in grain size distribution has also been proposed as reason for the deviation from the theoretical value of "m".⁽³¹⁾ Some observations obtained after long heat treatment at 2140 C in this investigation make it more likely that the decrease of grain growth was probably the result of some kind of defect locking mechanism. It is interesting to note that the first evidence of discontinuous grain growth could be observed in a specimen maintained at 2140 C for 25 hours (Figure 20). It is known that this type of secondary crystallization occurs especially when continuous grain growth is inhibited by the presence of impurities or pores.

The influence of mass redistribution due to the high vapor pressure of UO_2 causes regions of high density near cracks as a result of migration of pores and the subsequent formation of large grains (Figure 21). Again, in Figure 21 it can be seen that the region near the grain boundary is free of porosity. After the pellet was held for 120 minutes at 2600 C, very large grains were found in certain segregated areas. In Figure 18, the point at 120 minutes above the 2600 C curve refers to a region where very large grains have been formed. The point below the curve is representative of a region with considerably smaller grains.

The formation of specific areas of large grains is caused by both vaporization and by discontinuous grain growth. These phenomena are responsible for a sudden increase in average grain size in the temperature range above 2400 C. The crucible material may also influence grain growth behavior in this temperature range over an extended period of time. An interaction between tungsten and UO_2 has been observed in both the open and closed system. In Figure 22, it can be seen that after two hours at 2600 C in a closed system, a metallic layer was formed at the outer surface of the UO_2 pellet which was in contact with the container. X-ray diffraction analysis showed the presence of tungsten. Photomicrographs show the metallic phase is close to the surface from which the tungsten migrated into the UO_2 .

4.9 Activation Energy

In Figure 23, $\log K$ is plotted against the reciprocal of the absolute temperature following the equation

$$D^2 - D_0^2 = K \cdot t^m \quad (16)$$

$$\text{In which } K = K_0 \cdot e^{-Q/RT} \quad (17)$$

$$\text{Therefore } \log \frac{D^2 - D_0^2}{t^m} = \log K = \log K_0 - \left(\frac{0.434 Q}{R} \right) \left(\frac{1}{T} \right) \quad (18)$$

Etched

150X

Figure 20. DISCONTINUOUS GRAIN GROWTH

Etched

(2400°C - 5 hours)

150X

Figure 21. PORE MIGRATION IN UO_2

8X

As Polished

(2600°C - 2 hours)

250X

Figure 22. REACTION BETWEEN W AND UO_2

Figure 23. TEMPERATURE DEPENDENCE OF GRAIN GROWTH

A least squares treatment of the experimental data was used to obtain the best fitting linear relationship between $\log K$ and $(1/T)$. From the slope of the line in Figure 23, an activation energy of 65 Kcal/mole was calculated. In comparison with previous investigations this value is lower than that found by MacEwan (87 Kcal/mole) and is in fairly good agreement with the value given by Stehle (≈ 58 Kcal/mole).

4.10 Temperature Gradient in a Fuel Element

When used in the determination of the temperature profile in an irradiated fuel by application of the data obtained in this type of out-of-pile studies, it is necessary to be aware of the limits of the method. In Figure 24 the grain growth data obtained as a function of temperature in the experiments with a heating time of 20 minutes are plotted on a semi-logarithmic basis. It can be seen that it is not possible to get an accuracy better than $\pm 120^\circ\text{C}$ for the determination of temperature for a given grain size, because of the different types of UO_2 and different conditions investigated. The accuracy would be even lower if the results of other investigators are included. To obtain as high an accuracy as possible in this type of investigation, it is necessary to characterize the same batch of UO_2 in the out-of-pile studies that is used for the fuel in the in-pile work. The ideal case would be if the investigations could be performed by applying the same heating time and temperature gradient that obtains for the irradiation. For short time fuel irradiations this is possible without too much difficulty. Extrapolation of such data to very high temperatures or longer time at temperature involves a high degree of uncertainty.

Figure 24. EFFECT OF TEMPERATURE ON GRAIN SIZE

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