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STUDIES IN THE $\text{UO}_2\text{-ZrO}_2$ SYSTEM

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STUDIES IN THE UO_2 - ZrO_2 SYSTEM

Thomas R. Wright, Donald E. Kizer, and Donald L. Keller

Densification and homogenization of compacted ball-milled powders were accomplished by sintering from 10 to 15 hr at 1700 C or from 15 to 20 hr at 1600 C in flowing dry hydrogen. Homogeneous fuel pellets with densities in excess of 97 per cent of theoretical were obtained for property studies. The thermal-conductivity of the UO_2 -50 mole per cent ZrO_2 composition was found considerably lower than that of UO_2 but higher than that of ZrO_2 . The linear-thermal-expansion curve roughly paralleled that of pure UO_2 , at a slightly higher value, over the temperature range measured. Electrical resistivity decreased with increasing temperature, as is typical of a ceramic material. In tests of UO_2 -20 to 50 mole per cent ZrO_2 compositions, in general, both room-temperature and high-pressure hardness values increased as the ZrO_2 content increased. Homogeneous UO_2 -50 mole per cent ZrO_2 pellets were more resistant to cracking under thermal cycling than were inhomogeneous pellets of the same composition. Phase relationships in the UO_2 - ZrO_2 system up to 50 mole per cent ZrO_2 were evaluated to determine as a function of temperature the equilibrium phases present and the solubility limits of ZrO_2 in UO_2 . At 1000 C or above it was found that, at low ZrO_2 contents, a single-phase face-centered-cubic solid-solution region is present. At ZrO_2 contents greater than 13.5 mole per cent a two-phase face centered cubic-face centered tetragonal region exists at 1000 C. This two-phase region disappears above 1750 C.

INTRODUCTION

Fully enriched uranium dioxide fuel is currently being used in ML-1 reactor cores. In fuel pins located in high-flux positions, the UO_2 is diluted with about 30 volume per cent BeO in order to provide a uniform heat generation among all the fuel pins. At design burnups the UO_2 -BeO fuel has performed as satisfactorily as pure UO_2 fuel. At higher burnups, a solid-solution fuel such as UO_2 - ZrO_2 may have better irradiation resistance than a mixed oxide fuel of the UO_2 -BeO type. At the present time these two types of fuels, as well as pure UO_2 , are being evaluated in-pile. Results are expected early in 1965.

Prior to preparing and evaluating UO_2 - ZrO_2 irradiation specimens, a study was undertaken to determine the fabrication characteristics and properties of UO_2 - ZrO_2 compositions containing up to 50 mole per cent ZrO_2 , the range of particular interest to ML-1 applications. The result of these studies are reported herein.

FABRICATION STUDIES

The initial work on the program was devoted to developing the techniques required for the fabrication of high-density UO_2 -50 mole per cent ZrO_2 fuel materials. A four-part experimental study was undertaken in which UO_2 - ZrO_2 blends and compacts were prepared and evaluated with respect to:

- (1) Fabrication behavior of as-received materials
- (2) Optimization of materials achieved by comminution
- (3) Effect of compaction pressure on density
- (4) Homogenization of compacts attainable by heat treatment.

Standard techniques for the comminution of ceramic material by ball milling were followed. Particle sizes were determined by Coulter Counter measurements. The impurity levels of the powders were determined by emission spectroscopy.

Previously developed sintering conditions and apparatus were used during preparation of all specimens. Sintering temperatures were chosen as 1600 or 1700 C as determined from the work of Alexander and Shevlin^{(1)*} on the UO_2 -oxygen system. Temperatures in this range were chosen as those necessary to maintain the oxygen content of the UO_2 at near stoichiometric proportions under a dry-hydrogen atmosphere.

All sintering and homogenization treatments, except where noted, were carried out in a molybdenum-wound furnace with an alumina muffle and a dry-hydrogen atmosphere. Temperatures were measured optically except where noted.

Evaluations of both green-pressed and sintered compacts were accomplished by direct-measurement density determinations and metallographic examinations. The evaluation of specimen homogeneity was accomplished through the use of X-ray diffraction techniques.

Fabrication Behavior of As-Received Material

Initially it was believed that the UO_2 -50 mole per cent ZrO_2 specimens could be fabricated by simple blending of the as-received powders, compacting, and sintering.

Chemical-grade ZrO_2 and depleted ceramic-grade UO_2 were mixed in the correct proportions by blending 2 hr in a laboratory V-blender. The resulting mixture was then compacted in a hardened steel die under a 40-tsi pressure. Sintering was accomplished by a 2-hr treatment at 1600 C in flowing dry hydrogen or by vacuum heat treatments at both 1700 and 1800 C.

Measurements indicated a density of only 75 per cent of theoretical had been achieved by the hydrogen sintering treatment. The subsequent vacuum heat treatments at 1700 and 1800 C also failed to produce an appreciable change in the density. The results of these experiments are summarized in Table 1. From this study it was obvious that suitable bodies could not be fabricated from blends of the as-received powders. Special treatments were required in order to render the powder more sinterable.

*References are at the end of this report.

TABLE 1. FABRICATION BEHAVIOR OF AS-RECEIVED MATERIAL

Sintering Temperature, C	Sintering Time, hr	Atmosphere	Density, per cent of theoretical	
			Green	Sintered
1600	2	Hydrogen	56.5	75.3
1700	2	Vacuum	56.5	77.4
1800	3	Vacuum	56.5	82.3

Optimization of Materials by Comminution

In an attempt to reduce the particle size of the starting materials and therefore increase the driving force for densification, a comminution study was conducted on the UO_2 -50 mole per cent ZrO_2 mixture. A wet-milling technique was adopted because it is more efficient than dry milling in reducing the particle size, thereby increasing sinterability.

The first step in the study was to determine the time of milling versus particle size obtained. This was established with a 1-qt stainless steel mill approximately half filled with 1/2-in. stainless steel balls. Four hundred grams of the blended mix was added along with 180 cm^3 of distilled water. The loaded mill was then rotated at 75 rpm. The mixture was sampled after 0, 8, 16, and 24 hr of total milling time, and the particle-size distribution was determined by Coulter Counter analysis. The results are illustrated in Figure 1. A 16-hr milling time was necessary to achieve optimum particle-size reduction.

Avoiding the introduction of significant amounts of impurities during the comminution process was of concern in the study. To determine the combination of starting materials and grinding method that would provide powder mixtures having the optimum particle size at the lowest impurity pickup, various combinations of mills and grinding media were used with blends of ceramic-grade UO_2 , chemical-grade ZrO_2 , and reactor-grade ZrO_2 . All mill loading was done in the previously described manner, and the milling time was 16 hr in all cases.

Table 2 gives the impurity contents and median particle sizes achieved by the different comminution methods and also that of the as-received starting materials. It will be noticed that the combination of UO_2 and reactor-grade ZrO_2 that was milled 16 hr in a stainless steel mill using stainless steel balls as a grinding medium exhibited the maximum particle-size reduction; however, the total impurity content approached 5000 ppm. It was believed that the use of reactor-grade ZrO_2 and the rubber-lined mill with uranium rods gave the best combination of both low particle size and impurity content.

Following milling, the slurries were removed from the mills by washing with distilled water, placed in a Pyrex dish, and air dried at 350 F for 15 hr. The dried powder was then granulated by forcing it through a 100-mesh sieve.

This step after comminution served the dual purpose of raising the oxygen-to-uranium ratio to approximately 2.40 and agglomerating the fine particles so as to minimize dusting during subsequent die pressing.

FIGURE 1. EFFECT OF MILLING TIME ON PARTICLE SIZE FOR THE UO_2 -50 MOLE PER CENT ZrO_2 MIXTURE

TABLE 2. IMPURITY CONTENT AND MEDIAN PARTICLE SIZE OF AS-RECEIVED MATERIALS AND AFTER COMMINATION FOR 16 HR

Material Composition, mole per cent	Comminution Method	Impurity Content, ppm		Median Particle Size, μ
		Total	Comminution Pickup	
100 ceramic-grade $\text{UO}_2^{(a)}$	As-received	783	--	7
100 chemical-grade ZrO_2	As-received	6,610	--	4.5
100 reactor-grade ZrO_2	As-received	731	--	3
UO_2 -50 chemical-grade ZrO_2	Stainless mill, stainless balls	6,250	3,720	0.5
	Steel mill, steel balls	12,075	9,550	2
UO_2 -50 reactor-grade ZrO_2	Stainless mill, stainless balls	4,975	4,200	0.3
	Rubber-lined mill, uranium rods	1,095	330	0.8
	Stainless mill ^(b) , uranium rods	8,039	5,510	0.8

(a) All UO_2 employed was depleted ceramic grade.

(b) Milled 24 hr.

Effect of Compaction Pressure

In order to establish the optimum pressing pressure in compact preparation, it was necessary to conduct a compaction experiment to determine the effect of pressure on both the green and sintered densities.

This experiment was conducted by compacting powder blends prepared in the previously determined optimum manner in a 0.33-in.-diameter hardened-steel die at pressures ranging from 10 to 60 tsi.

After the green density of the pellets was measured, the specimens were sintered for 2 hr at 1600 C in flowing dry hydrogen. Upon cooling to room temperature under hydrogen, the sintered densities were measured. The results of measurements of the green and sintered compacts are shown in Figure 2.

Green density measurements could not be made on the 10- and 60-tsi specimen groups because of the extremely poor green strength of the 10-tsi group and the appearance of pressure cracks in the 60-tsi group. Sintered densities were measured in these two cases by immersion in CCl_4 .

From Figure 2, it may be seen that pressing at pressures in the range of from 30 to 50 tsi results in compacts of relatively high green density which upon sintering are capable of achieving densities of from 97 to 99 per cent of theoretical.

FIGURE 2. COMPACTION TEST FOR UO_2 -50 MOLE PER CENT ZrO_2

Homogenization of Compacts

X-ray diffraction examination of sintered and then resintered pellets reveal that 2 hr at 1600 C was insufficient to achieve equilibrium. To determine the conditions necessary to establish equilibrium it was necessary to conduct a homogenization study in which the lattice constant, a_0 , of the UO_2 rich face-centered-cubic phase was measured after heating various times at a constant temperature. The temperatures chosen for investigation were 1600 and 1700 C.

Presintered UO_2 -50 mole per cent ZrO_2 pellets prepared from ceramic-grade UO_2 and reactor-grade ZrO_2 were encapsulated in massive molybdenum cans and sealed by electron-beam welding. A short presintering treatment of 2 hr in hydrogen at 1600 or 1700 C, depending on the isotherm under investigation, was necessary in order to achieve a stoichiometric oxygen content in the UO_2 -rich component.

The sealed presintered specimens were heat treated in a vacuum of 1×10^{-5} mm of mercury for the desired time and then quenched by dropping into molten tin. The specimens were immediately removed from the tin and cooled in water.

The pellets were removed from the capsules and examined by X-ray diffraction using NiK_α radiation. The changes in the lattice parameter of the face-centered-cubic phase in the two-phase region as a function of time at 1600 and 1700 C are illustrated in Figure 3. The difference in lattice parameters at 1600 and 1700 C is due to the change in ZrO_2 solubility with temperature.

It was concluded that equilibrium between ZrO_2 and UO_2 was achieved in 15 to 20 hr at 1600 C and from 10 to 15 hr at 1700 C. These results are in good agreement with those obtained by Gebhardt and Elssner⁽²⁾.

Conclusions from Fabrication Studies

In these fabrication studies, sintering of the as-received powder blends was demonstrated to be an infeasible method of producing high-density UO_2 -50 mole per cent ZrO_2 compacts. However, a comminution treatment of the powders prior to compaction and sintering resulted in densities of 97 per cent of theoretical. It was determined experimentally that, by wet ball milling the powder blend 16 hr in a rubber-lined mill using uranium slugs as a grinding medium and then drying the resultant slurry in air at 350 F for 15 hr, a readily sinterable powder could be obtained.

Green-pressed densities around 65 per cent of theoretical could be obtained by cold compacting the powders at pressures in the range of 30 to 50 tsi.

Although high densities could be achieved after 2 hr at 1600 C in dry hydrogen, sintering treatments of from 15 to 20 hr were required at 1600 C and from 10 to 15 hr at 1700 C in order to achieve chemical homogeneity.

Figure 4a is a microstructure of a high-density homogeneous pellet of the UO_2 -50 mole per cent ZrO_2 composition prepared in the preceding manner from ceramic-grade UO_2 and reactor-grade ZrO_2 . Sintering was carried out for 15 hr at 1700 C. The

FIGURE 3. THE CHANGE IN LATTICE PARAMETER WITH SINTERING TIME FOR UO_2 -50 MOLE PER CENT ZrO_2

oxygen-to-uranium ratio was 2.009 after sintering. The specimen contained only 1110 ppm total impurities of which 740 were in the starting material.

A microstructure of UO_2 , prepared in an identical manner and sintered along with the specimen shown in Figure 4a, is illustrated in Figure 4b. The UO_2 - ZrO_2 specimen exhibited little grain growth as compared to the UO_2 shown in Figure 4b.

These evaluations established that high-density, homogeneous UO_2 -50 mole per cent ZrO_2 fuels can be fabricated using the processes outlined.

PROPERTY STUDIES

The objective of this part of the study was to investigate various physical properties concerned with the heat-transfer behavior, phase stability, and strength of the UO_2 -50 mole per cent ZrO_2 composition to temperatures of 1000 to 1200 C in an attempt to form a reasonable appraisal of the fuel short of irradiation testing. Abnormalities in the property measurements which could indicate structural changes were also of particular interest. In order to accomplish the objective, five types of property tests were carried out:

<u>Test</u>	<u>Temperature, C</u>
Thermal conductivity	20-1000
Thermal expansion	20-1000
Electrical resistivity	20-900
Hardness	20-1500
Thermal cycling	20-1000

All specimens were prepared in the optimum manner developed in the initial phase of this investigation. The specimens were compacted by either cold die pressing or cold isostatic pressing. Specimens having a large length-to-diameter ratio, such as the thermal-conductivity and thermal-expansion specimens, required the use of cold isostatic pressing during fabrication. The specimens were sintered in flowing dry hydrogen for 20 hr at 1700 C to insure homogeneity.

The thermal-conductivity and thermal-expansion specimens were ground to their final size and shape with a diamond grinding wheel, using undiluted cutting oil as a coolant. These specimens were then cleaned in ethyl alcohol and outgassed in vacuum at room temperature before testing.

The compositions, densities, and sizes of the test specimens are given in Table 3.

Thermal Conductivity

Method of Testing

Initial thermal-conductivity measurements were made by the steady-state longitudinal-heat-flow method described by Van Dusen and Shelton⁽³⁾. The method, in brief, consisted of heating one end of a specimen, measuring the temperature gradient

250X

RM29810

a. UO_2 -50 Mole Per Cent ZrO_2 Compact

150X

RM29809

b. UO_2 Compact

FIGURE 4. STRUCTURES OF UO_2 -50 MOLE PER CENT ZrO_2 AND UO_2 COMPACTS SINTERED 15 HR AT 1700 C

Both specimens exhibited densities 97 per cent of theoretical. Note the finer grain size of the UO_2 -50 mole per cent ZrO_2 specimen.

TABLE 3. COMPOSITIONS, DENSITIES, AND DIMENSIONS OF PHYSICAL-PROPERTY SPECIMENS

Measured Property	Composition, mole per cent	Density, per cent of theoretical	Dimensions of Test Specimen, in.	
			Diameter	Length or Thickness
Thermal conductivity ^(a)	UO ₂ -50 ZrO ₂	97.6	0.75	3
Thermal expansion	UO ₂ -50 ZrO ₂	98.5	0.25	3
Electrical resistivity	UO ₂ -50 ZrO ₂	97.6	0.75	3
Hardness	UO ₂	95.3	1.5	0.25
	UO ₂ -20 ZrO ₂	92.4	1.5	0.25
	UO ₂ -30 ZrO ₂	96.1	1.5	0.25
	UO ₂ -40 ZrO ₂	97.5	1.5	0.25
	UO ₂ -50 ZrO ₂	98.2	1.5	0.25
Thermal-cycling behavior	UO ₂	98.5	0.25	0.50
	UO ₂ -50 ZrO ₂	97.4	0.25	0.50
	UO ₂ -50 ZrO ₂ ^(b)	96.2	0.25	0.50

(a) Later thermal-conductivity measurements by the thermal-diffusivity technique used disk-shaped specimens cut from 0.25-in. -diameter rods.

(b) Inhomogeneous UO₂-50 mole per cent ZrO₂ specimen.

along the specimen, and determining the rate of heat flow through the specimen by means of a metal standard of known thermal conductivity attached to its cold end. Radial heat flow into, or away from, the specimen was minimized by thermal insulation and an encircling guard tube in which temperatures were adjusted, as nearly as possible, to match those of the specimen and standard at corresponding levels. The thermal insulation used consisted of bubbled alumina which was poured into the annular space between the specimen and the guard cylinder. The specimen was protected by a vacuum of approximately 2×10^{-5} mm of mercury during the measurements.

The temperature gradient along the specimen was measured by three calibrated Chromel-Alumel thermocouples wedged in holes spaced along the length of the specimen. Similar thermocouples were also placed in the Type 347 stainless steel used as a standard. This permitted the calculation of two thermal-conductivity values at a different mean temperature.

Measurements were made in steps of increasing temperature to the maximum after which one or more equilibria were obtained at lower temperatures. This duplication of measurements was used as a check on the thermocouples and changes which may have taken place in the specimen. The thermal-conductivity measuring process is a week-long heat treatment which is different for each section of the specimen.

Thermal-conductivity measurements were made to 1000 C. The data obtained by this steady-state method are shown in Figure 5. The data suggest a curve with a slightly positive slope as the best fit. The apparatus used for these measurements was designed for materials which have a relatively high thermal conductivity. Low-conductivity materials, such as the specimen in this case, present difficulties in balancing temperatures at corresponding levels on the specimen and the guard. In these measurements a satisfactory balance could not be obtained above 400 C. For this reason, values up to 400 C are believed to be accurate within ± 5 per cent while those above 400 C are not believed to be accurate within the limits of allowable experimental error, and no confidence can be placed in these values.

Because of these difficulties, specimens were prepared for measurement by the thermal-diffusivity method. A single pulse or flash from a laser was used to obtain the heat pulse incident on the front face of the specimen. The thermal response of the back face was obtained using a lead-sulfide detector, bridge circuit, and oscilloscope.

The thermal-conductivity values for the UO_2 -50 mole per cent ZrO_2 specimen were then calculated at temperatures to 1000 C from the measured thermal diffusivity, calculated density, and literature values for the specific heat. The thermal-conductivity values obtained by this method are also shown in Figure 5, along with the literature values for UO_2 ⁽⁴⁾ and ZrO_2 ⁽⁵⁾.

Results

As noted above, the thermal-conductivity values obtained by the thermal-diffusivity method of measurement are believed to be more accurate than those obtained by the steady-state heat-flow method. The thermal conductivity obtained by the thermal-diffusivity method is calculated to be 0.0216 w/(cm)(C) at 1000 C. This value is approximately the same as the value reported for ZrO_2 , but the negative slope of the curve reflects the negative slope of the thermal-conductivity curve for UO_2 , as may be seen in Figure 5.

FIGURE 5. THERMAL CONDUCTIVITY UO₂-50 MOLE PER CENT ZrO₂, UO₂, AND ZrO₂

Although the values obtained by the diffusivity method more closely resembled the expected values for this material, some doubt existed as to the possible partial transparency of the thin specimen (0.25 in. in diameter by 0.030 in. thick) to the wavelengths involved at the higher temperatures. It was believed that this transparency might have given values for diffusivity somewhat above the correct values. In order to determine this effect, the specimen was coated on both faces with iron by vacuum deposition. Although the coating was soft and did not bond well to the specimen, it was thought to be opaque. The thermal-diffusivity values of both the uncoated and coated specimens as a function of temperature are shown in Figure 6.

It was observed that all data for the coated specimen fell approximately 7 to 10 per cent below the values obtained for the uncoated specimen. The data at the low temperatures should not have been different from those obtained with the uncoated specimen if the only effect of the coating was to make the specimen more opaque. This suggested that the poor bond between the coating and the specimen surface resulted in a high thermal resistance and gave values for diffusivity considerably below the correct values. Consequently, it is believed that the true values for diffusivity are best represented by the curve for the uncoated specimen. The calculated thermal conductivity data shown in Figure 5 for the thermal-diffusivity method are believed to be correct and are expected to be in error by no more than ± 7 per cent. Table 4 gives the interpolated thermal-conductivity values for all specimens.

TABLE 4. INTERPOLATED THERMAL-CONDUCTIVITY VALUES
FOR UO_2 -50 MOLE PER CENT ZrO_2 SPECIMENS

Temperature, C	Thermal Conductivity, w/(cm)(C)		
	Steady-State Method	Thermal-Diffusivity Method	
		Uncoated Specimen	Coated Specimen
100	0.0225	--	--
200	0.0230	0.0228	0.0207
300	0.0234	0.0226	0.0206
400	0.0238	0.0224	0.0206
500	0.0244	0.0223	0.0205
600	0.0256	0.0222	0.0205
700	0.0271	0.0220	0.0204
800	0.0286	0.0218	0.0203
900	0.0300	0.0217	0.0202
1000	0.0315	0.0216	0.0200
1100	--	0.0214	--

Thermal Expansion

Method of Testing

Linear-thermal-expansion measurements were made on two UO_2 -50 mole per cent ZrO_2 specimens. One, LE-188, was prepared expressly for the measurements; the other, TC-215, had been used earlier in the thermal-conductivity measurements.

The linear-thermal-expansion measurements were made in a vertical quartz-tube recording dilatometer with the specimen protected by a vacuum of approximately

FIGURE 6. THERMAL DIFFUSIVITY AS A FUNCTION OF TEMPERATURE FOR UO_2 -50 MOLE PER CENT ZrO_2

2×10^{-5} mm of mercury. The specimens were given two thermal cycles from room temperature to 1000 C and back to room temperature at a maximum heating and cooling rate of 3 C per min.

Elongation-versus-temperature curves were automatically plotted by an x-y recorder. The x-axis movement corresponded to the temperature and the y-axis to the elongation. The error in the expansion measurements was estimated not to exceed ± 2 per cent.

Results

Tables 5 and 6 show the percentage expansion and the mean thermal-expansion coefficient, respectively, for Specimens LE-188 and TC-215. Also included in Table 5 are literature values for UO_2 and ZrO_2 .

TABLE 5. MEASURED LINEAR THERMAL EXPANSION OF UO_2 -50 MOLE PER CENT ZrO_2

Temperature, C	Linear Thermal Expansion, per cent			
	Test Specimens		Literature Values	
	LE-188	TC-215	$\text{ZrO}_2^{(6)}$	$\text{UO}_2^{(7)}$
20	0	0	0	0
100	0.075	0.075	0.06	0.06
200	0.170	0.170	0.14	0.15
300	0.275	0.275	0.22	0.26
400	0.380	0.380	0.31	0.35
500	0.494	0.494	0.38	0.46
600	0.608	0.608	0.47	0.55
700	0.723	0.723	0.57	0.67
800	0.843	0.843	0.66	0.78
900	0.965	0.965	0.75	0.89
1000	1.093	1.093	0.82	1.02

TABLE 6. MEAN LINEAR-THERMAL-EXPANSION COEFFICIENT FOR UO_2 -50 MOLE PER CENT ZrO_2

Temperature Range, C	Mean Linear-Thermal-Expansion Coefficient, 10^{-6} per C	
	LE-188	TC-215
20 - 100	9.4	9.4
20 - 200	9.7	9.7
20 - 300	9.8	9.8
20 - 400	10.0	10.0
20 - 500	10.3	10.3
20 - 600	10.5	10.5
20 - 700	10.6	10.6
20 - 800	10.8	10.8
20 - 900	11.0	11.0
20 - 1000	11.2	11.2

A plot of percentage expansion as a function of temperature is illustrated in Figure 7. It will be noted that the UO_2 -50 mole per cent ZrO_2 material has a higher expansion than either UO_2 or ZrO_2 .

FIGURE 7. PER CENT LINEAR THERMAL EXPANSION OF UO_2 -50 MOLE PER CENT ZrO_2

It will also be interesting to note in Table 5 that the expansion of the thermal-conductivity specimen, TC-215, was identical with that of Specimen LE-188. Apparently, there were no structural changes in this specimen during the week-long thermal-conductivity test.

During the cooling cycle a hysteresis effect was not observed in either specimen after heating to 1000 C, nor was any variation noted during the two measurement cycles.

Electrical Resistivity

Method of Testing

Electrical-resistivity measurements were made on the UO_2 -50 mole per cent ZrO_2 specimen in the temperature range of 20 to 1000 C using the voltage-drop method. Potential drops were measured across the specimen and across a series-connected resistor. Potential drops were measured with the current flowing both normally and reversed, and the values were averaged to reduce the effects of thermal and induced voltages. The specimen was protected by a vacuum of 5×10^{-4} mm of mercury during the measurements.

The error in the electrical-resistivity data is estimated to not exceed ± 2 per cent. The relatively high estimated error results mainly from the high electrical resistance of the specimen and the difficulty of measuring voltage and current.

Results

Figure 8 shows the electrical resistivity-versus-temperature curve, while Table 7 gives the interpolated measured data for the UO_2 -50 mole per cent ZrO_2

TABLE 7. INTERPOLATED ELECTRICAL RESISTIVITY FOR
 UO_2 -50 MOLE PER CENT ZrO_2

Temperature, C	Electrical Resistivity, ohm-cm
50	4.8×10^7
100	7.5×10^6
150	0.5×10^6
200	4.0×10^5
250	7.7×10^4
300	2.3×10^4
350	7.5×10^3
400	3.0×10^3
450	9.4×10^2
500	6.1×10^2
550	3.9×10^2
600	1.8×10^2
650	1.0×10^2
700	8.2×10^1
750	6.8×10^1
800	5.5×10^1
850	4.2×10^1
900	3.2×10^1

FIGURE 8. ELECTRICAL-RESISTIVITY OF UO_2 -50 MOLE PER CENT ZrO_2

composition. The results shown are typical for a ceramic composition in that the resistivity decreases as a function of increasing temperature.

Hardness Testing

Method of Testing

Room-temperature hardnesses were obtained on specimens of the UO_2 and UO_2 -20, -30, -40, and -50 mole per cent ZrO_2 compositions. Hardness values at room temperature were obtained with a Vickers hardness tester using a 10-kg load.

Hardnesses in the range of 800 to 1500 C were determined by means of a vacuum hot-hardness apparatus. The machine consisted of a dead-weight hardness device with the specimen supported within a tantalum strip furnace. All testing was conducted in a vacuum of 1×10^{-3} mm of mercury or better. The indenter system consisted of a 1-in. -diameter rod supported vertically by two guide plates.

The indenter rod weighed 1.13 kg and was raised and lowered by a yoke arrangement that could be operated from outside the vacuum chamber. The lower end of the rod was entirely within the hot zone of the furnace and was provided with a hard carbide tip.

This tip was cut and polished to form a standard 136-deg square-based pyramid, so that all results obtained were in conventional Vickers units. The apparatus was calibrated at room temperature and found to produce hardness numbers equivalent to those obtained on a standard Vickers machine.

The experimental procedures employed were to make four indentations at each temperature on a metallographically polished surface using the 1.13-kg dead-weight load. Temperatures were measured optically and are believed to be accurate within 50 C.

Results

Values for both room-temperature and hot hardness are given in Table 8. A Vickers hardness-versus-composition plot at room temperature is shown in Figure 9

TABLE 8. HARDNESS VALUES OF UO_2 - ZrO_2 COMPOSITIONS

Temperature, C	Hardness Value for Sample of Composition Shown, kg per mm ²				
	UO ₂ -20 Mole		UO ₂ -30 Mole	UO ₂ -40 Mole	UO ₂ -50 Mole
	UO ₂	Per Cent ZrO ₂	Per Cent ZrO ₂	Per Cent ZrO ₂	Per Cent ZrO ₂
Room	608	806	950	1066	1101
800	72	360	381	388	411
900	94	387	382	396	416
1000	79	353	381	402	420
1100	77	338	384	404	381
1200	71	300	383	391	352
1300	73	257	342	290	277
1400	52	205	236	212	217
1500	--	152	152	169	173

while Figure 10 illustrates the hardness of each composition as a function of temperature.

The reported results are the average room-temperature micrometer measurements of four indentations made at each temperature. In general, the integrity of the indentations was excellent, the only exception being that slight cracking was noted around the edges of some of the room-temperature and 800 C indentations.

It may be seen in Figure 9 that the room-temperature hardness increases as the ZrO_2 content increases. This is also generally true for the hot hardness at temperatures below 1000 C as may be seen in Figure 10. However, all compositions containing ZrO_2 exhibit a rapid decrease in hardness at temperatures above 1000 C. It may also be noticed that this decrease in hardness is more rapid for the high- ZrO_2 -content materials in this temperature range, indicating that it may be the ZrO_2 -rich phase which is softening.

Although not shown in the curve, data obtained from Mr. John Pottinger⁽⁸⁾ indicate a gradual softening of UO_2 from a hardness of 600 to 700 DPH at room temperature to the values shown in Figure 10.

Thermal-Cycling Behavior

Method of Testing

Three specimens, homogeneous UO_2 -50 mole per cent ZrO_2 , inhomogeneous UO_2 -50 mole per cent ZrO_2 , and UO_2 were thermally cycled 25 times between 1000 C and room temperature to test the effect of thermal cycling on the core integrity.

The homogeneous UO_2 -50 mole per cent ZrO_2 pellet was prepared by sintering the powder mixture 20 hr at 1700 C in hydrogen. The inhomogeneous UO_2 -50 mole per cent ZrO_2 and UO_2 pellets were sintered at 1600 C for 2 hr.

The specimens were individually wrapped in molybdenum foil and sealed in a single Type 347 stainless steel tube by electron-beam welding. The tube was heated in air in a SiC resistance furnace to 1000 C and held for 24 hr.

The specimens were then thermal cycled 25 times between room temperature and 1000 C, after which the tube was cut open and the specimens were examined metallographically. Specimens were cooled by removal from the furnace. They were allowed to cool to room temperature. Heating was accomplished by placing the specimens in a furnace operating at 1000 C.

Results

Upon examination of the specimens, it was found that the UO_2 and the homogeneous UO_2 -50 mole per cent ZrO_2 cores had developed internal cracks while still retaining their integrity. The inhomogeneous UO_2 -50 mole per cent ZrO_2 specimen was cracked severely. It is apparent that the homogenization treatment during sintering will render the UO_2 -50 mole per cent ZrO_2 composition more resistant to cracking when subjected to a thermal cycle in a reactor.

Representative photomicrographs of the specimens are shown in Figure 11.

FIGURE 9. ROOM-TEMPERATURE HARDNESS OF $\text{UO}_2\text{-ZrO}_2$ COMPOSITIONS

FIGURE 10. HOT HARDNESS OF $\text{UO}_2\text{-ZrO}_2$ COMPOSITIONS

100X

RM27319

a. UO_2

100X

RM28125

b. Homogeneous UO_2 -50 Mole
Per Cent ZrO_2

100X

RM28124

c. Inhomogeneous UO_2 -50
Mole Per Cent ZrO_2

FIGURE 11. THERMAL-CYCLED HOMOGENEOUS UO_2 - ZrO_2 , INHOMOGENEOUS UO_2 - ZrO_2 , AND UO_2

Conclusions from Property Studies

These major conclusions can be drawn from the results of the property studies:

- (1) The thermal conductivity of the UO_2 -50 mole per cent ZrO_2 composition is considerably lower than that exhibited by UO_2 but higher than that of ZrO_2 up to 700 C. The thermal-conductivity curve exhibits a slight negative slope which is possibly a result of the dominance of UO_2 .
- (2) The linear thermal expansion measured on the UO_2 -50 mole per cent ZrO_2 composition is roughly parallel to that of pure UO_2 , at a slightly higher value, over the temperature range measured. No inflections in the expansion curve are observed either on heating or cooling.
- (3) The electrical resistivity exhibited by the UO_2 -50 mole per cent ZrO_2 composition is typical of a ceramic material in that it decreases as a function of increasing temperature. No inflections were noted in this property, which is extremely structure sensitive.
- (4) In general, both room-temperature measurements and measurements made in the 800 to 1000 C temperature range show a hardening effect with increasing ZrO_2 additions to 50 mole per cent.
- (5) All ZrO_2 -containing specimens exhibited a marked decrease in hardness at temperatures above 1000 C. The fact that the most rapid decreases in hardness at the higher test temperatures were exhibited by the specimens containing the greatest ZrO_2 content, demonstrated that the ZrO_2 -rich phase is the softer of the two phases present at temperatures above 1200 C.
- (6) Homogeneous UO_2 -50 mole per cent ZrO_2 and pure UO_2 demonstrated better structural integrity during thermal cycling from room temperature to 1000 C than did inhomogeneous UO_2 -50 mole per cent ZrO_2 . This fact is important from the standpoint of the fuel cracking during the thermal cycling experienced during reactor shut down.
- (7) With the exception of the low thermal conductivity, all property values and measurements indicate that the homogeneous UO_2 -50 mole per cent ZrO_2 composition would make a suitable reactor fuel for use up to 1000 C.

PHASE-RELATIONSHIP STUDIES

The UO_2 - ZrO_2 system has been investigated by a number of people. The available phase diagrams prepared by these investigators are shown in Figure 12. Although most of the controversy concerned with this system appears to involve the ZrO_2 -rich portion of the diagram, there also appears to be some doubt as to the location of the solubility limits of ZrO_2 in UO_2 . This area holds a great deal of interest from a fuels standpoint in that it is the region of the highest uranium content.

a. UO_2 - ZrO_2 Phase Diagram According to Lambertson and Mueller (9)

b. UO_2 - ZrO_2 Phase Diagram According to Wolten (10, 11)

c. UO_2 - ZrO_2 Phase Diagram According to Voronov, et al. (12)

d. UO_2 - ZrO_2 Phase Diagram According to Evans (13, 14)

e. UO_2 - ZrO_2 Phase Diagram According to Cohen and Schaner (15)

FIGURE 12. UO_2 - ZrO_2 PHASE DIAGRAMS PREVIOUSLY REPORTED

The earliest data, those of Lambertson and Mueller⁽⁹⁾, indicate a solubility of 40 mole per cent ZrO_2 in UO_2 at 1000 C, while Voronov, et al.⁽¹²⁾ and most of the other authors indicate a solubility of between 10 and 20 mole per cent ZrO_2 in UO_2 at 1000 C.

In addition to the question of the solubility limit of ZrO_2 in UO_2 , there is also the question of the existence of a monoclinic ZrO_2 -rich phase which all authors, except Wolten^(10,11), indicate below 100 C. Evans^(13,14) shows the existence of this phase at temperatures as high as 400 C.

Eorgan⁽¹⁶⁾, et al., are currently investigating the UO_2 - ZrO_2 system in the temperature range of 600 to 700 C by equilibrating UO_2 and ZrO_2 in a fused-salt solution. Present results indicate that only cubic UO_2 and monoclinic ZrO_2 are the stable phase in this temperature range. The investigators believe this inconsistency with the existing phase diagram is a result of the difficulty of attaining equilibrium in the conventional phase studies of such refractory oxide solids. This work is currently being continued at temperatures above 700 C to determine the lower limit of solid-solution formation. However, it is believed that this will not affect the phase relationship existing above 1000 C, as will be discussed.

The purpose of this investigation was to determine the exact solubility limits of ZrO_2 in UO_2 at temperatures greater than 1000 C and to determine the likelihood of the formation of the monoclinic phase from a homogeneous fuel at low temperatures in a typical reactor cycle. A temperature of 590 C was chosen as typical for the ML-1 applications.

Experimental Procedures

Sample Preparation

The materials used in this investigation were 6- μ depleted ceramic-grade UO_2 and hafnium-free (<50 ppm) reactor-grade ZrO_2 . The dry powders were first blended for 1 hr in a laboratory V-blender and then wet mixed with distilled water for 2 hr in a laboratory jar mill. After drying at 350 F for 15 hr in air, the powders were compacted by hydrostatically pressing at 50 tsi. The compacted powder blends were then homogenized in a molybdenum-wound resistance furnace for 20 hr in flowing dry hydrogen at 1700 C.

Following the homogenizing treatment, the pellets were crushed to minus 325 mesh with a hardened-steel mortar and pestle. The crushed powders then were compacted into 0.125-in.-diameter by 0.250-in.-long pellets and encapsulated.

A sample of each specimen was analyzed for composition and oxygen-to-uranium ratio. The chemical analysis is shown in Table 9. The compositions had an average oxygen-to-uranium ratio of 2.007, as determined by polarographic techniques, before the annealing treatments.

TABLE 9. CHEMICAL ANALYSIS OF $\text{UO}_2\text{-ZrO}_2$
COMPOSITIONS USED IN PHASE-
RELATIONSHIP STUDIES

Nominal UO_2 Content, mole per cent	Measured Chemical Compositions		
	UO_2 , w/o	ZrO_2 , w/o	UO_2 , mole per cent
100	100	--	100
97	98.4	1.6	97
85	92.7	7.3	85
80	89.8	10.2	80
70	83.9	16.1	70
60	77.2	22.8	60.5
50	68.6	31.4	50.7

Annealing Conditions

Annealing conditions are summarized in Table 10. The compacts for the 1000 and 1200 C anneals were electron-beam sealed in tantalum, and a capsule of each composition was then electron-beam sealed in a massive Inconel capsule. This double-encapsulation technique was necessary so that these 200-hr anneals could be conducted in air. Quenching of these specimens was accomplished by plunging the entire Inconel capsule into water.

TABLE 10. SUMMARY OF ANNEALING CONDITIONS IN
PHASE-RELATIONSHIP STUDIES

Temperature, C	Time, hr	Atmosphere	Quench
590	1500	Air	Water
1000	200	Air	Water
1200	200	Air	Water
1400	20	Vacuum	Molten tin
1500	10	Vacuum	Molten tin
1600	5	Vacuum	Molten tin
1700	2	Vacuum	Molten tin
1800	1	Vacuum	Molten tin

The specimens for the high-temperature anneals were electron-beam sealed in molybdenum capsules. High-temperature heat treatments were conducted in a tantalum-resistance furnace under a vacuum of approximately 10^{-5} mm of mercury. Quenching was accomplished by dropping the specimens into a molten tin bath through the use of a special quenching apparatus in the vacuum chamber of the furnace.

Temperatures were measured where possible by both a platinum-platinum 30 w/o rhodium thermocouple and a calibrated optical pyrometer and are believed to be accurate to within ± 20 C.

X-Ray Procedure

The annealed and quenched pellets were crushed with a hardened-steel mortar and pestle to minus 200 mesh. The powder was attached to the end of a thin glass fiber, and the fiber was mounted in the film camera.

NiK_α radiation was used in all measurements. Lattice-parameter measurements were made from the back-reflection patterns in all cases.

Following the measuring of the cell dimensions of each composition, the lattice constant of the face-centered-cubic phase was plotted versus composition at a constant temperature. The solubility limits of ZrO_2 in UO_2 could then be determined from the location of the intercepts of the line constructed by the lattice constant of the face-centered-cubic phase in the single-phase region with the lines constructed by the lattice constants of the face-centered-cubic phase in the two-phase region. This assumes that Vegard's law approximates a straight line in this region of the system.

Results

The measurements of the lattice parameters of the phases in existence at a constant temperature are given in Table 11.

The Vegard's law application is illustrated in the upper section of Figure 13, while the intercepts are plotted as a function of temperature in the lower section. The latter graph is the diagram of state of the UO_2 , UO_2 -50 mole per cent ZrO_2 system.

The solubility limits, as derived from the Vegard's law intercepts, are listed in Table 12.

Conclusions from Phase Studies

The results are in good agreement with those of Voronov, et al.⁽¹²⁾, and Cohen and Schaner⁽¹⁵⁾ in the UO_2 -rich portion of the phase diagram. The existence of a metastable tetragonal phase reported by Cohen and Schaner could not be verified. The existence of such a phase was difficult to establish because, using the reported values, the tetragonality is very small ($c/a = 1.005$).

Lattice parameters of the tetragonal phase were difficult to obtain precisely because of the preponderance of the face-centered-cubic phase. The high-angle lines were, for this reason, very weak and not usable for lattice-parameter measurements. However, the cell dimensions of the tetragonal phase were measured in Specimen B-50 and yielded a c/a of 1.019, which was in extremely good agreement with those values reported by Cohen and Schaner.

This phase is reported as being face-centered tetragonal, which is not a Bravais lattice. Since the only reflections present are those with $h + k = 2n$, the lattice is actually a single tetragonal cell of a small parameter: $a = 3.64 \text{ \AA}$.

TABLE 11. RESULTS OF X-RAY DIFFRACTION EXAMINATIONS OF $\text{UO}_2\text{-ZrO}_2$ SPECIMENS

Specimen	UO_2 Content (Balance ZrO_2), mole per cent	Phase Identity	Lattice Parameter (a_0), Å
<u>1800 C Isotherm</u>			
DC-1	100	FCC	5.4707
DC-4	97	FCC	5.460
DC-5	85	FCC	5.423
A-80	80	FCC	5.406
A-70	70	FCC	5.385
A-60	60	FCC	5.355
A-50	50	FCC	5.323
<u>1700 C Isotherm</u>			
DC-1	100	FCC	5.4707
DC-4	97	FCC	5.460
DC-5	85	FCC	5.423
B-80	80	FCC	5.406
B-70	70	FCC	5.384
B-60	60	FCC	5.363
B-50	50	FCC	5.342
		Tetragonal	$a_0 = 5.25$ $c_0 = 5.15$
<u>1600 C Isotherm</u>			
DC-1	100	FCC	5.4707
DC-4	97	FCC	5.460
DC-5	85	FCC	5.423
C-80	80	FCC	5.408
C-70	70	FCC	5.404
		Tetragonal	--
C-60	60	FCC	5.405
		Tetragonal	--
C-50	50	FCC	5.382
		Tetragonal	--
<u>1400 C Isotherm</u>			
DC-1	100	FCC	5.4707
DC-4	97	FCC	5.460
DC-5	85	FCC	5.423
D-80	80	FCC	5.417
D-70	70	FCC	5.415
		Tetragonal	--
D-60	60	FCC	5.419
		Tetragonal	--
D-50	50	FCC	5.414
		Tetragonal	--
<u>1200 C Isotherm</u>			
DC-1	100	FCC	5.4707
DC-4	97	FCC	5.460

TABLE 11. (Continued)

Specimen	UO ₂ Content (Balance ZrO ₂), mole per cent	Phase Identity	Lattice Parameter (a ₀), Å
<u>1200 C Isotherm</u> (Continued)			
DC -5	85	FCC	5.423
F-80	80	FCC	5.423
F-70	70	FCC	5.427
F-60	60	FCC	5.429
F-50	50	Tetragonal	--
		FCC	5.443
		Tetragonal	--
<u>100 C Isotherm</u>			
DC -1	100	FCC	5.4797
DC -4	97	FCC	5.460
DC -5	85	FCC	5.423
G-80	80	FCC	5.411
G-70	70	FCC	5.392
G-60	60	FCC	5.384
G-50	50	Tetragonal	--
		FCC	5.435
		FCC	5.403
		Tetragonal	--
<u>590 C Isotherm</u>			
LT-1	50	FCC	5.408
		FCC	5.346
		Tetragonal	a ₀ = 5.157 c ₀ = 5.266

TABLE 12. SOLUBILITY LIMITS OF ZrO₂
IN UO₂

Temperature, C	ZrO ₂ Soluble in UO ₂ , mole per cent
1000	≈13.5
1200	15
1400	16.5
1600	23
1700	45
1800	>50

FIGURE 13. VEGARD'S LAW PLOT AND PHASE RELATIONSHIPS IN UO_2 -RICH PORTION OF THE UO_2 - ZrO_2 SYSTEM

The appearance of the tetragonal phase in Specimen B-50 indicated that the point lay in a two-phase field. The lattice parameter of the face-centered-cubic phase should, accordingly, be on a horizontal line. Since no points beyond 50 mole per cent UO_2 were obtained, a horizontal line was drawn through this value of the lattice parameter to obtain the solubility limit at this temperature.

It is interesting to note the presence of two face-centered-cubic phases in Specimens G-50 and LT-1. This "extra phase" was also observed in two additional homogeneous specimens which were heated to 1000 C and slow cooled. Phase separation on cooling would have been a reasonable explanation for the latter two specimens; however, G-50 and LT-1 were both subjected to extremely rapid quenches. A more probable explanation would be that an equilibrium situation was not achieved at this temperature during annealing.

It is also of considerable interest to note that monoclinic ZrO_2 was never observed in specimens subjected to slow cooling or in the 1500-hr anneal at 590 C.

From the standpoint of the ultimate use of the UO_2 -50 mole per cent ZrO_2 composition as a nuclear fuel, two phases will exist in the fuel, a UO_2 -rich face-centered-cubic phase and a ZrO_2 -rich face-centered-tetragonal phase. The degree of tetragonality of the face-centered-tetragonal phase is extremely small, $c/a = 1.019$, and a phase inversion would not be expected to be destructive should the tetragonal phase become cubic under irradiation. Therefore, on the basis of the phase diagram in the region under consideration, it is believed that these compositions would be readily adaptable for use as a nuclear fuel.

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TRW:DEK:DLK/slp