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DIFFUSION IN THE STABILIZED ZIRCONIA-URANIA SYSTEM

D. R. Mash and K. K. Ikeuye
Reese S. Kern, Editor

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DIFFUSION IN THE STABILIZED ZIRCONIA-URANIA SYSTEM

by

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ADVANCED MATERIALS AND PROCESSES

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ABSTRACT

Diffusion in the stabilized zirconia-urania system has been investigated by the "moving" boundary (metallographic) technique. The objective of the investigation was to measure penetration of zirconia cladding by urania at elevated temperatures.

Natural UO_2 cored pellets were coated by the plasma-spray technique. Uniform coatings of about 89 percent of theoretical density were applied using carefully controlled process conditions. Diffusion annealing treatments were carried out in the 2000°C to 2450°C range for 8-hour periods in helium. Diffusion zone characteristics, observed metallographically, provided evidence of relatively complicated interactions taking place in this ternary system at temperatures close to the melting point of the coating. The ZrO_2 - UO_2 interface region after diffusion included a void zone, a ternary solid solution zone, the "moving" boundary, and a high density zirconia-rich zone. The long term influence of each of these zones on the diffusion process, as well as a quantitative understanding of rate controlling factors associated with each zone, was beyond the scope of the current investigation.

A penetration coefficient, K , which is proportional to the diffusion coefficient, was measured as a function of temperature and the results were correlated by means of the usual rate equation to give the following expression:

$$K = K_0 \exp (-172,000/2RT)$$

$$\text{Where } K_0 = 1.6 \times 10^7 \text{ mil/hr}^{1/2}$$

$$T = \text{absolute temperature, } ^\circ\text{K.}$$

$$R = \text{gas constant} = 1.987 \text{ cal/mole/}^\circ\text{K.}$$

Based on these results, it can be concluded that diffusion in the stabilized ZrO_2 - UO_2 system is strongly temperature dependent; however, even at temperatures close to the melting point of zirconia, uranium would not completely penetrate a 0.050-inch coating after eight hours at temperature.

* * * *

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DIFFUSION IN THE STABILIZED ZIRCONIA-URANIA SYSTEM

I. INTRODUCTION

An experimental program was conducted in accordance with requirements of Part II, PPCS-255, dated May 20, 1963, entitled Fuel Fabrication and Testing, Power Burst Facility. The scope of the program included fabrication, diffusion testing, and reporting of test results on UO_2 pellets plasma-spray coated with reactor-grade, stabilized ZrO_2 . The experimental work involved 8-hour diffusion anneals at temperatures between 2000°C and 2450°C . Results were evaluated by metallographic methods using the "moving" boundary technique.

During the course of this investigation, a number of interesting phenomena were observed, which could not be studied extensively under the current program. These are covered briefly in the Discussion. Such observations could form the basis for further investigation of this important nuclear fuel system.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

1.1 UO₂

Natural urania cored pellets were obtained from General Electric Company's Atomic Products Division, San Jose, California. A total of 100 pellets was purchased in accordance with AMPRO Specification No. 11.04, which includes all requirements shown under PPCS-255, Part I, A5, and appropriate parts of C3. AMPRO Specification No. 11.04 is included in the Appendix. Chemical analysis of natural UO₂ is shown in Table I, both as furnished by the General Electric Company, and as checked by sampling a random pellet from the lot supplied. Both results are well within specification requirements.

TABLE I
CHEMICAL COMPOSITION OF NATURAL UO₂ PELLETS

<u>Element</u>	<u>G. E. Analysis</u>	<u>Check Analysis</u>
Aluminum	100 ppm	150
Beryllium	< 0.2	---
Boron	< 0.2	< 10
Calcium	50	20
Cadmium	< 1	< 1
Carbon	0.7	< 10
Chromium	20	10
Cobalt	2	< 20
Copper	5	1
Fluorine	10	---
Iron	125	100
Lead	< 1	5
Magnesium	10	10
Manganese	4	5
Molybdenum	< 3	< 100
Nickel	50	10
Silicon	60	60
Silver	< 0.1	0.2
Tin	< 1	3
Zinc	---	< 100
O/U Ratio	2.011	---

Note: Spectrographic analysis was used, except for special combustion analysis for carbon content.

Dimensional and weight measurements for each pellet used in this investigation are included in Table I, Appendix. As shown in this tabulation, density of pellets ranged from 10.36 to 10.48 g/cc, as determined by direct measurement. Dimensions and densities were within specification requirements, except as noted in Table I, Appendix.

Processing history of the UO_2 pellets was summarized by the supplier as follows [1]:

- (1) Material received as natural ceramic-grade uranium dioxide, United Nuclear Corp. Lot No. MO2-WA,
- (2) powder pressed into pellets, including center hole, by standard General Electric process,
- (3) green pellets fired at 1600°C ,
- (4) outside of pellets centerless-ground to correct diameter, and
- (5) samples for chemical analysis taken from completed pellets.

1.2 Stabilized Zirconia

Reactor-grade zirconia powder, stabilized in the face-centered cubic phase by addition of 15 to 17 mole% CaO , was employed for plasma-spray coating of the UO_2 pellets. This material was obtained from the Wah Chang Corporation, Albany Division, Albany, Oregon, and met all requirements of PPCS-255, Part 1, C4.

The following purchasing specification was used in connection with this procurement:

Hafnium-free, reactor-grade ZrO_2 powder, stabilized with 15 mole% - 17 mole% CaO (7.4 w/o - 8.3 w/o CaO).

Particle size range: -325 mesh, +10 micron with less than 2% outside of this range.

Please furnish:

- (1) Chemical analysis
- (2) Screen analysis
- (3) Brief processing history

All materials should be from one lot, if possible.

Chemical analysis and particle size distribution are shown in Table II. In addition, the following processing history has been reported^[2]:

- (1) Starting material reactor-grade zirconium oxide and commercial grade calcium oxide,
- (2) raw materials in proper portions are intimately mixed and blended,

TABLE II

CHEMICAL COMPOSITION OF STABILIZED ZrO₂ POWDER

<u>Element</u>	<u>Wah Chang Analysis</u>	<u>Check Analysis</u>
Al	300 ppm	----
Cr	50	----
Fe	500	----
Hf	< 40	----
Mg	300	----
Mn	30	----
Ni	20	----
S	560	----
Si	180	----
Ti	100	----
C	< 200	----
CaO	8.24% by wt.	8.3%

<u>Screen Analysis</u>	
<u>Microns</u>	<u>Weight %</u>
-10	2.89
10 to 15	2.81
15 to 20	33.30
20 to 44	61.00

- (3) material is milled by hammer mill,
- (4) material is heated to 1600°C for 1 to 4 hours,
- (5) cooled to room temperature,
- (6) crushed,
- (7) ball milled,
- (8) screened to remove oversize,
- (9) -325 material is then air classified to remove less than 10 micron particles,

- (10) product sampled for chemistry and particle size,
- (11) product tested and inspected for shipment, and
- (12) shipped.

Qualitative X-ray diffraction analysis of the stabilized zirconia was carried out to determine whether the various experimental treatments produced modifications in the FCC (fluorite) structure. The following results were obtained:

As-received powder	--face-centered cubic lines only
Plasma-sprayed coating	--face-centered cubic lines only
Coating annealed 8 hours at 2000°C	--face-centered cubic lines only.

Additional carbon analyses were carried out after diffusion annealing treatments to determine whether contamination problems existed as a result of furnace construction or other experimental factors. No carbon pick up was found in the zirconia coatings after diffusion runs had been completed.

1.3 High-Fired Zirconium Dioxide Tubes

Diffusion specimens were packed for protection in ZrO₂ tubes, 3/4 in. ID x 10 in. length x 1/8-in. wall. These standard, high-fired, ZrO₂ tubes were purchased from Leco, St. Joseph, Michigan.

2. PLASMA-SPRAY COATING PROCEDURE

Uranium dioxide pellets were lightly grit blasted with 24-grit aluminum oxide, using a pressure of 40 psi, at a distance of eight to ten inches. Grit blasting was performed with pellets rotating at 450 rpm.

Surface-prepared pellets were dried overnight under an infrared lamp to remove moisture that may have collected during the blasting operations. Each pellet was then remeasured for outside diameter dimension and reweighed.

Twelve pellets were placed on a specially designed mandrel for plasma-spraying. The pellets were separated by means of steel spacers. The loaded mandrel was rotated at 450 rpm and preheated to 250 to 300°F, using the plasma flame. Heating time was regulated so that spray temperature was achieved in 15 to 20 minutes.

The zirconia was plasma-sprayed using the following conditions:

Plasma gas:	Argon with 10% hydrogen
Carrier gas:	Argon, 10 cfh
Current:	400 amperes
Voltage:	45 volts
Gun traverse:	90 in./min.
Spray Distance:	5-1/2 inches.

The plasma-spray coating procedure is shown in Figure 1.

Air cooling was required once the spraying operation commenced. Approximately 45 minutes spray time was required to coat a mandrel of 12 samples to a thickness of 0.050 to 0.055 inch. After coating, the specimen cooling rate was controlled by gradually decreasing the power over a period of two minutes. Typical appearance of pellets at each stage of the coating process is shown in Figure 2.

Fig. 1 Plasma-spray coating of UO_2 pellets with CaO-stabilized zirconia.

Fig. 2 Steps in plasma-spray coating of UO_2 pellets.

Left: UO_2 cored pellet as sintered and ground.

Center: Surface prepared for spraying by pressure grit blasting with alumina abrasive.

Right: As-sprayed 0.050 in. stabilized zirconia coating.

Ends of the specimen were lapped lightly to remove zirconia over-spray. Visual inspection and final measurements were then carried out.

Density of the coating was determined by calculating the volume of coating from measured dimensions and by obtaining the weight gain of the coated pellets. Values of the coating density are shown in Column 12 of Table I, Appendix. The average density of the as-sprayed coating was 89.3 percent of theoretical density.

3. DIFFUSION TREATMENTS

A graphite resistance-heated furnace having a constant temperature zone two inches in diameter and seven inches high was used for all diffusion annealing treatments.

Ten pellets for a diffusion experiment were inserted in a protective zirconia tube, packing zirconia powder above and below. The loaded zirconia tube was then centrally located in the graphite furnace and evacuated overnight to remove all absorbed gases. Each diffusion annealing run was preceded by a temperature cycle control run using one coated pellet embedded at midpoint of the zirconia tube. Such a loading is shown in Figure 3.

Fig. 3 High temperature furnace and specimen loading details used in diffusion annealing treatments.

The furnace temperature was increased steadily, up to about 1100°C, evacuating at all times. Beyond this point, the vacuum line was closed off, helium gas admitted, and the furnace pressurized at 3 psi. The higher temperature anneals required a constant flow of gas across the inner surface of the sight windows to prevent fogging; therefore, annealing runs for temperatures of 2200°C, 2350°C, and 2450°C had a continuous flow of helium at a positive pressure of 3 to 5 psi. Diffusion runs were terminated by slowly cutting back the power, approximating the conditions of the control sample.

Temperature measurements were made by sighting through quartz windows located appropriately, using a calibrated L & N optical pyrometer. Correction of apparent temperature was required to determine true specimen temperature because of attenuation by the quartz windows. The required correction in the 2000 to 2650°C range was found to be 200°C. This correction was added to the apparent temperature to give the true temperature of the diffusion specimens. Once established, the furnace settings (power input) remained relatively constant throughout the 8-hour diffusion annealing period. Temperature was maintained within $\pm 10^\circ\text{C}$.

The furnace correction was verified by a simple melting point determination experiment wherein the 17 mole% CaO-stabilized zirconia and high purity alumina were melted in air and temperatures measured by the optical pyrometer. Results obtained were as follows:

<u>Material</u>	<u>Optical Pyrometer Readings ($^\circ\text{C}$)</u>	<u>Handbook Value of Melting Point ($^\circ\text{C}$)</u>
17 mole% CaO-ZrO ₂ in air	2530 - 2570	2550
High purity Al ₂ O ₃ in air	2030 - 2060	2050
17 mole% CaO-ZrO ₂ in furnace	2350	2550

As a result of these measurements, it was concluded that 17 mole% CaO-ZrO₂ melts at about 2550°C and that the required correction due to the furnace was 200°C. The air melting point determination procedure was confirmed by the Al₂O₃ standard of known melting point.

Measurements were carried out on all specimens after diffusion annealing to ascertain the degree of shrinkage which might have occurred in the pellet and coating. The central hole in the UO₂ pellet was measured as a criterion of shrinkage. A slight expansion was noted as a result of the annealing treatments which ranged from one percent at 2350°C to three percent at 2450°C. These slight changes in diameter did not influence diffusion zone measurements because a difference method was used in which diffusion-annealed specimens were measured with reference to the original interface as the zero point.

4. EVALUATION METHODS

4.1 Metallographic Examination

Specimens were removed from the furnace and, in some cases, extracted pellet by pellet from the zirconia-tube container. Higher temperature runs caused the pellets, zirconia powder, and the tube to be sintered as a unit, and the pellets were not readily removed. In this case, the zirconia tube and the specimen were sliced through with a diamond cutoff wheel. Each sectioned pellet was mounted in Shell Epon 828. Whenever possible, the pellets were mounted first, then sectioned to minimize mechanical breakage and cracking from cutting and preliminary polishing operations.

Mounted specimens were polished on silicon carbide papers from 240 grit through 600 grit, and on alumina papers down through 3/0. Final polishing was performed on nylon cloth wheels in 3 steps with 9-micron and 1-micron diamond polishing compounds and, finally, with Beuhler's No. 3 alumina.

Several etches were used to bring out grain boundaries and diffusion zone in urania and zirconia. The etchant developed by Cain[3] was useful in etching the uranium dioxide to develop grain boundaries. Specimens were immersed for various times from 1/2 to 3 minutes in a solution consisting of 10 cc H_2SO_4 - 90 cc H_2O_2 (30 v/o concentration). This etchant had no effect on the zirconia coating.

A second etchant used was that of Cohen and Schaner[4]. Polished specimens were immersed in a solution containing 50 g NH_4F in 50 cc of H_2O at 110°C . Nalgene beakers and tongs coated with Teflon were used to handle specimens in the above etchant. Etching time varied from 3 to 12 minutes, longer times being required to bring out grain boundaries in the zirconia. Generally, the UO_2 would be heavily over-etched by the time the zirconia grain boundaries were clearly shown.

A third etchant used was a mixture of 10 cc HF in 90 cc H_2O . This was useful in staining the zirconia-rich diffusion area.

Generally, all specimens were given a double etching, first with either H_2SO_4 - H_2O_2 or NH_4F - H_2O and, finally, in 10 percent HF aqueous solution. Effectiveness of the two-step treatment in revealing the extent of penetration of uranium into the ZrO_2 -rich region is shown in Figure 4. Results are compared for a typical microstructure etched by single and two-step procedures. The latter technique proved to be mandatory to permit direct measurement of the "moving" boundary.

Diffusion zone measurements were made metallographically at 200 X magnification. A 0.0005-in. calibrated dial gauge was fixed to the microscope stage so that the distance traveled across the diffusion zone could be measured directly with an accuracy of better than 0.0002 in. The original interface was used as the zero reference for all measurements. At least 12 readings were made on each diffusion specimen. The results of ten specimens were then combined to provide an average penetration distance for each temperature of test.

Fig. 4 Effect of etching technique in revealing diffusion zone stabilized ZrO₂-UO₂ system.

Total penetration was corrected for diffusion occurring during temperature cycling, and the resulting penetration coefficient was used to develop the required temperature dependence. The activation energy term in the Arrhenius rate equation was calculated.

5. DATA ANALYSIS

Diffusion rate was determined by the "moving" boundary technique in which the growth or penetration of a diffusion zone is measured metallographically. This technique provides a direct, unambiguous penetration coefficient for use in calculating the extent of diffusion between urania and zirconia for any time and temperature. This technique has been used successfully in past investigations[5].

Procedure can be described briefly and related to classical diffusion experiments in a straightforward manner. The rate of advance of a boundary of fixed concentration is a simple function of the diffusion coefficient, D . Diffusion from a uniform solution into a solvent, across a sharp boundary at $x = 0$, is described by the following equation:

$$C(x, t) = \frac{C_0}{2} \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\omega^2} d\omega \right] \quad (1)$$

where

C_0 = Original concentration of solute at interface

x = Distance, mils

t = Time, hours

ω = Integration variable

It is desired to know the rate at which a boundary of fixed concentration moves away from the original interface in the "x" direction. If "x" is measured as a function of "t", a penetration coefficient is defined which includes the diffusion coefficient. Thus, to make both sides of equation (1) constant, the upper integration term must be a constant which gives:

$$\frac{x}{\sqrt{t}} = k\sqrt{D} = K \text{ (penetration coefficient)} \quad (2)$$

Measurement of "x" as a function of time provides all the data needed to compute "K" for a specific temperature. Conversely, once "K" is known, penetration from the original interface (diffusion zone growth) can be calculated for any diffusion time.

Temperature dependence of "K" can be shown to follow the typical Arrhenius relationship. Thus,

$$D = D_0 \exp (-Q/RT) \quad (3)$$

and, therefore,

$$K = K_0 \exp (-Q/2RT) \quad (4)$$

because $K \approx D^{1/2}$.

In equation (4),

Q = Activation energy, cal/mole

T = Absolute temperature, °K

R = Gas constant = 1.987 cal/mole/°K

K_0 = Constant, mil/hr^{1/2}

K = Penetration coefficient, mil/hr^{1/2}.

Thus, the results of diffusion measurements at a series of temperatures can be summarized in a single graph of $\log_e K$ versus $1/T$, in which the slope of the curve is equal to $(-Q/2R)$.

III. EXPERIMENTAL RESULTS

Diffusion treatments were conducted at the following temperatures:

Temperature (°C)	Number of Specimens			Comments
	8-hour anneal	Temp. cy- cling control	Reference control	
2560	--	1	---	melting occurred
2550	--	1	---	melting occurred
2450	10	1	1	good test
2350	10	1	1	good test
2200	10	1	1	good test
2000	10	1	1	good test

Dimensional and weight measurements of pellets used in the test program are listed in Table IV, Appendix. Pellet numbers used in the above tests are shown in Table V, Appendix. Detailed measurements of the diffusion zone by pellet number are included in Table VI, Appendix, for record purposes.

Average diffusion data are summarized in Table III and are correlated in Figures 5 and 6. The semi-log plot of K versus $1/T$ shows marked temperature dependence with an activation energy of 172,000 cal/mole, which is believed to be within ± 10 percent accuracy. Figure 6 provides a direct correlation of penetration distance x , with temperature for an 8-hour diffusion period.

TABLE III
SUMMARY OF DIFFUSION MEASUREMENTS

Penetration (mils)	Temperature (°C)					
	2650 ^[a]	2550 ^[a]	2450	2350	2200	2000
Total, 8 hours test	--	--	7.1	3.8	1.2	nil
Total, cycling control test	--	--	1.5	0.9	nil	nil
True 8 hours penetration	--	--	5.6	2.9	1.2	nil
Penetration coefficient, K	--	--	2.0	1.0	0.4	--

[a] Melting of stabilized ZrO_2 occurred during preliminary temperature cycling test. Consequently, these anneals were eliminated from the program and the 2000°C anneal was added.

Fig. 5 Penetration coefficient-temperature relationship for diffusion in the stabilized $\text{ZrO}_2\text{-UO}_2$ system.

Equation of curve is: $K = 1.6 \times 10^7 \exp \left(\frac{-172,000}{2RT} \right)$

Fig. 6 Penetration distance-temperature relationship for 8-hour diffusion period in the stabilized $\text{ZrO}_2\text{-UO}_2$ system.

Features of diffusion behavior in stabilized $\text{ZrO}_2\text{-UO}_2$ are shown in the series of photomicrographs, Figures 7 to 14. As shown, the diffusion zone varies in extent and characteristics with increasing temperature and, thus, with increasing rate.

Fig. 7 Typical interface of plasma-spray coated control specimen prior to thermal treatment.

Fig. 8 Typical as-sprayed control specimen of UO_2 coated with stabilized ZrO_2 .

UO₂ DZ ZrO₂

200 X

(A)

S-480, 2450°C Control Specimen, Pellet
No. 39

Etch--Step 1: 10cc H₂SO₄
 90cc H₂O₂ (30 v/o conc)

Step 2: 10cc HF
 90cc H₂O

200 X

(B)

S-484, 2350°C Control Specimen, Pellet
No. 67

Etch--Same as above.

200 X

(C)

S-444, 2200°C Control Specimen, Pellet
No. 15

Etch--Same as above.

Fig. 9 Temperature cycle control specimens for diffusion experiments in the stabilized ZrO₂-UO₂ system.

Fig. 10 Typical diffusion results at 2450°C in the stabilized ZrO_2 - UO_2 system.
Etch: Double Etch Technique.

Figures 7 and 8 show typical interfaces between zirconia-urania after the plasma-spray coating process. A mechanical bond exists with a relatively clean boundary in evidence. No radial cracking in the cladding is observed; however, some evidence of superficial cracking or laps in the UO_2 pellet exists. It is not known whether this isolated effect was present before coating or was a result of the coating process. The former case is suspected, otherwise the surface effect would be more general in extent.

The heating-cooling cycle associated with each diffusion anneal permitted some diffusion to take place as shown in Figure 9. The extent of diffusion was a function of diffusion temperature and the time involved in establishing equilibrium at that temperature. Data obtained from the control specimens were used

Fig. 11 Typical diffusion results at 2350°C in the stabilized ZrO_2 - UO_2 system.
Etch: Double Etch Technique.

to correct the 8-hour measurements made on the diffusion specimens. This series of thermal cycling control specimens shows all of the essential characteristics noted in the interaction zone, ie, a porous or void zone marking the original interface, an alloy zone showing a new interface of "moving" boundary, and a pore-free region on the zirconia-rich side of the new boundary.

Maximum diffusion was evidenced at 2450°C with all metallographic aspects of the interaction exaggerated so as to be plainly observed (Figure 10). The "moving" boundary, revealed by the two-step etching process, is associated with a void zone, alloy zone, and pore-free zirconia-rich zone. The change in composition from the urania-zirconia-calcia ternary solid solution to the high zirconia phase forms the "moving" boundary which passes through existing zirconia-rich grains. On the urania-rich side of the diffusion zone, the structure

400 X, S-459, Pellet No. 9

200 X, S-459, Pellet No. 9

400 X, S-453, Pellet No. 5

200 X, S-456, Pellet No. 3

Fig. 12 Typical diffusion results at 2200°C in the stabilized ZrO_2 - UO_2 system.
Etch: Double Etch Technique.

conforms more closely to the existing UO_2 grain size and shape. The presence of the extensive void zone is extremely interesting and is treated in the Discussion in a speculative fashion. Similar characteristics are exhibited at 2350°C on a less exaggerated basis (Figure 11). The original interface is clearly identified by the discontinuous void region. The diffusion boundary exhibits a clear transition to the zirconia-rich phase. Interesting features of the diffusion zone include the presence of cubic etch-pit pattern and a few twins crossing the boundary.

Diffusion at 2200°C was rather minimal, as shown in Figure 12. The smooth diffusion boundary can be observed to be close to the original interface as marked by the void zone. The void zone appears related to both UO_2 and ZrO_2 phases, as discussed later.

Fig. 13 Typical diffusion results at 2000°C in the stabilized ZrO_2 - UO_2 system.
Etch: Double Etch Technique.

Results at 2000°C were compromised somewhat because of the separating tendency of the coating during cooling from the diffusion annealing temperature. Negligible diffusion had taken place (Figure 13). The principal evidence of interaction was associated with the void zone which showed some agglomerated pores in a semi-continuous pattern. None of the characteristics of the higher temperature treatments were very apparent at 2000°C. This result was expected because of the strong temperature dependence of the penetration curves shown in Figures 5 and 6.

As a visual summary of diffusion behavior, Figure 14 shows a comparison of typical boundary regions after 8-hour annealing treatments at temperatures of interest.

UO₂

ZrO₂

(A)

Zone (mils)

S-468
Pellet No. 20

7

2450°C--8 hours

(B)

S-494
Pellet No. 66

3.8

2350°C--8 hours

(C)

S-453
Pellet No. 5

1.2

2200°C--8 hours

(D)

S-499
Pellet No. 83

nil

2000°C--8 hours

Fig. 14 Comparison of typical diffusion zones in the stabilized ZrO₂-UO₂ system.
200 X, Etch: Double Etch Technique.

This comparison clearly shows the strong temperature dependence of the diffusion behavior. No preferred path for diffusion was exhibited; rather, volume and grain boundary diffusion appeared to proceed together. The boundary is remarkably smooth and straight in every case.

IV. DISCUSSION

The zone of interaction between urania and stabilized zirconia exhibits a number of interesting characteristics which merit brief discussion. Many aspects of the behavior of this system must be understood in qualitative terms only, because a complete description of all of the phenomena taking place during diffusion would require a much more comprehensive investigation than has been carried out in connection with the current study. All conclusions are drawn on the basis of metallographic evidence and, therefore, must be tentative until supported by more exhaustive analytic work and by additional experiments.

The progress of diffusion, as a function of temperature, has been shown metallographically to be accompanied by the following characteristics:

(1) The original mechanically bonded interface between stabilized zirconia and urania is replaced by a low-angle boundary exhibiting a sharp change in composition from urania-rich to zirconia-rich regions. This diffusion bond provides a relatively strong, coherent composite material. This effect is accompanied by an agglomeration of voids which are distributed along the original interface.

(2) It appears that uranium diffuses into the zirconia phase more rapidly than vice-versa. Metallographic evidence of this includes:

(a) The direction of boundary motion is into the zirconia phase.

(b) Void formation and agglomeration accompany the growth of the diffusion zone.

(c) Apparent densification of the zirconia phase accompanies diffusion in the region of the diffusion zone.

(d) Etching procedures reveal only that the urania-containing phase has extended further in the diffusion direction at the expense of the zirconia phase.

(3) Void formation accompanies the diffusion process and appears to be the result of several processes:

(a) The inter-diffusion of uranium and zirconium ions can be considered to occur with respect to a fixed oxygen lattice. A vacancy mechanism can be postulated, since uranium appears to diffuse more rapidly across the interface than does zirconium. It can be expected that the net effect would be to increase the number of vacancies and, thus, the amount of void space on the urania side of the interface. These voids diffuse to the interface, thus increasing its total volume.

(b) The alloy zone of diffusion involves a ternary composition of higher density than the original zirconia phase. This decreased volume of the diffusion product also tends to increase the amount of void space at the interface.

(c) The diffusion process appears to provide a mechanism by which zirconia can increase density by diffusion of voids toward the original interface, which acts as a sink.

Thus, three specific contributions to the formation of the void zone can be identified. The void zone appears to grow apace with the growth of the overall diffusion zone.

(4) The composition of the alloy formed in the diffusion zone has not been determined, but on the basis of available information, it is concluded that a complete solid solution exists in that region. Metallographic evidence indicates that a face-centered cubic phase is retained because of the isotropic behavior of the phase under polarized light, and because of the cubic-etch pit pattern observed in this region. It has been reported^[6] that compositions of up to 12 mole% UO_2 and 15 to 25 mole% CaO in ZrO_2 are thermally stable. In addition, a more extensive single phase FCC region was found in this ternary system after sintering at 1700°C and higher in argon. Thus, there was no reason to expect a second phase under the conditions of these experiments.

(5) The correlation between penetration coefficient and temperature shows marked temperature dependency. It is not known whether the void zone would ultimately limit diffusion of uranium at longer times than the 8 hours used in these experiments. It could be assumed that diffusion rate would decrease as the void zone caused decreased contact area between the uranium phase and the alloy diffusion zone. Undoubtedly, the diffusion rate at this point would depend on the driving force for diffusion from the alloy phase into the pure stabilized zirconia phase. This rate may be considerably lower than the rate determined in the current experiments. Additional diffusion experiments would be required to permit the prediction of when uranium would reach the surface of the zirconia coating. It is clear that under the current conditions no problem is anticipated, because maximum diffusion measured was considerably less than the total zirconia thickness. However, extrapolation to longer times would be risky for reasons already mentioned.

(6) The behavior of the composite fuel pellet as a result of the thermal cycle accompanying the diffusion treatment was of interest. Specimens treated at temperatures where measurable diffusion occurred, ie, above 2200°C , appeared to withstand the cooling cycle by reason of the improved bond strength resulting from the diffusion process. Radial cracking in the zirconia was the salient feature of the stress relief mechanism. In general, no spalling or separation accompanied the radial cracking. Figure 15 shows a typical crack pattern exhibited by fuel pellets after diffusion. Thus, it is concluded that the diffusion bond produced by the thermal treatment was strong and could be expected to withstand many thermal cycles once the radial cracking stress relief pattern had been established. On the other hand, specimens in which negligible diffusion had occurred cracked radially and tended to separate at the original interface as a result of the thermal cycle, probably the cooling stage. On the basis of these observations, it can be concluded that zirconia-clad uranium pellets could be employed with confidence in nuclear applications after either a preliminary diffusion bonding step or by permitting the bond to take place during the early stages

of the reactor operation at temperature. A temperature of 2200°C appears to be suitable for developing the necessary bond strength.

(A)

3X

Typical specimen showing radial cracks in
ZrO₂ coating

(B)

S-484, Pellet No. 67

Etch--50 grams NH₄F in
50 cc H₂O

150X

Typical microstructure showing radial crack
at interface

Fig. 15 Typical radial cracks in diffusion-annealed specimens. Stabilized ZrO₂-UO₂ system.

V. CONCLUSIONS

The temperature dependence of the penetration coefficient for UO_2 diffusion into stabilized ZrO_2 is given by

$$K = K_0 \exp (-172,000/2RT)$$

where

$$K_0 = 1.6 \times 10^7 \text{ mil/hr}^{1/2}$$

T = Absolute temperature, °K

R = Gas constant = 1.987 cal/mole/°K

Based on this investigation, no problems would be anticipated relative to penetration of stabilized ZrO_2 cladding by urania for periods of up to 8 hours at temperatures up to the melting point of the cladding.

Plasma-spray coating of UO_2 pellets appears to provide a feasible method of fabricating insulated fuel pellets for reactor applications.

VI. REFERENCES

1. Private communication from J. T. Mommsen, Manager, Fuels Laboratory, General Electric Company.
2. Private communication from G. L. Frederic, Quality Assurance Department, Wah Chang Corporation.
3. F. M. Cain, Jr., "Technique for Preparation of UO_2 Compacts for Microscopic Examination" in Research of Uranium Oxide Data--III, Z. M. Shapiro (ed), WAPD-PMM-197 (September 19, 1955) Appendix B, pp 8-13.
4. I. Cohen and B. E. Schaner, A Metallographic and X-Ray Study of the UO_2 - ZrO_2 System, WAPD-253 (June 1962) AEC Research and Development Study.
5. D. R. Mash and B. Disselhorst, Uranium-Zirconium Diffusion Studies, AECD-3701 (June 1954).
6. G. Zuromsky and W. P. Chernock, Irradiation Testing of Ceramic Fuels, CEND-158, Combustion Engineering, Inc. (September 1962).

APPENDIX
PELLET INFORMATION AND SPECIFICATIONS

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TITLE: PELLETS, Uranium Dioxide (UO₂) -- Natural or Depleted

1. PURPOSE:

To specify the physical and chemical properties of UO₂ pellets.

2. SCOPE, APPLICABILITY, and DELEGATED RESPONSIBILITY

This specification includes minimum requirements for Uranium Dioxide pellets.

Pellets will be coated with various types of material.

The Quality Control Supervisor is responsible for receiving and disposition of purchased pellets.

3. CHEMICAL PROPERTIES:

3.1 Purity -- 99.75% minimum UO₂

3.2 Oxygen: Uranium ratio must be 2.00 - 2.02.

4. PHYSICAL PROPERTIES:

4.1 Dimensions: "D" (outside dia.) may be selected by vendor from 0.4 - 0.55 inches.

"L" (length) may be selected by vendor from 1 to 2 times "D".

Axial hole ID is 0.125 inch.

APPROVED:

Q. M. Coleman
Quality Control

Edward Buchanan
Production Engineering

4.2 Tolerances:

I. D. ± 0.005 inch

O. D. $\pm 1/2\%$ "D"

L $\pm 1/2\%$ "L"

OD T. I. R. = 0.003 inch

4.3 Density--10.31 gram/cc minimum; all values must be within $\pm 1\%$ of each other.

5. QUALITY CONTROL

5.1 Surface conditions:

5.1.1 Total area of all chips on each pellet shall not exceed five (5) percent of the cylindrical surface area of the pellet and in no case shall exceed 0.05 square inch.

5.1.2 Area of a single chip shall not exceed two (2) percent of the cylindrical surface area and in no case shall exceed 0.02 square inch.

5.1.3 No cylindrical surface chip shall exceed 0.010 inch in depth.

5.1.4 On the cylindrical surface of any pellet, any two (2) chips, in their closest proximity, shall not be closer than the maximum dimension of the small chip (the maximum dimension taken on the cylindrical surface, and not along the edge of the pellet).

5.1.5 Total area of edge chips on each pellet in the plane of the pellet transverse cross sectional area shall not exceed ten (10) percent of that area. The portion of edge chips on the cylindrical surface shall meet the requirements of Sections 5.1.1, 5.1.2, and 5.1.3.

5.1.6 No longitudinal crack shall exceed twenty-five (25) percent of the length of the pellet and no other cracks on any surface shall exceed 1/3 of the circumference of the pellet.

5.2 Each pellet shall be numbered consecutively and identified.

5.3 Dimensions of each pellet shall be provided.

5.4 Density of each pellet shall be provided, using the following method of calculation:

$$5.4.1 \text{ Density} = W / \frac{\pi L}{4} (O. D.^2 - I. D.^2)$$

O. D. , I. D. and L shall be maximum values based on three measurements.

W shall be weighed within accuracy of 0. 02 gms. O. D. , I. D. and L shall be measured to 0. 001 inch accuracy.

5.5 All material should be from one lot and identified as to lot number.

5.6 Chemical analysis is required.

5.7 Brief processing history is required.

5.8 Deviations from this Specification may be suggested, if appreciable cost saving is anticipated.

6. SKETCH: Uranium Dioxide Pellet

"D" may be selected by vendor from 0.4 - 0.55
inch.

"L" may be selected by vendor from 1 to 2 times
"D"

Tolerances: I. D. : ± 0.005 inch.
O. D. : $\pm 1/2\%$ "D"
L: $\pm 1/2\%$ "L"
O. D. T. I. R. : 0.003

TABLE IV

DIMENSIONAL AND WEIGHT MEASUREMENTS OF PELLETS USED IN TEST PROGRAM

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7	Col. 8	Col. 9	Col. 10	Col. 11	Col. 12	
Spec. No.	O. D. Max. *	O. D. Min.	I. D. Max. *	Uranium Dioxide		Length Min.	Length Max. *	Weight (gms.)	Den- sity	Concen- tricity	Zirconia	Coating
				I. D. Min.	Length Max. *						Coat. thick. ZrO ₂	% Theo. density**
1	.5466	.5464	.1225	.1223	.6015	.6010	22.85	10.40	.0010			
2	.5465	.5463	.1223	.1221	.6022	.6020	22.87	10.39	.0035	.052	87.7	
3	.5465	.5463	.1225	.1223	.6036	.6034	22.94	10.40	.0000	.052	88.1	
4	.5465	.5463	.1225	.1223	.6043	.6038	22.97	10.40	.0015	.052	90.7	
5	.5465	.5463	.1225	.1223	.6033	.6030	22.92	10.39	.0002	.052	87.5	
6	.5463	.5460	.1225	.1223	.6042	.6038	22.93	10.42	.0010	.052	87.5	
7	.5464	.5462	.1235	.1223	.6034	.6029	22.91	10.41	.0035			
8	.5464	.5463	.1225	.1223	.6039	.6036	22.93	10.41	.0010	.052	87.9	
9	.5469	.5467	.1225	.1223	.6026	.6022	22.94	10.41	.0005	.052	88.1	
10	.5457	.5455	.1226	.1223	.6037	.6032	22.87	10.41	.0035	.052	87.7	
11	.5464	.5462	.1225	.1223	.6039	.6034	22.91	10.39	.0002	.052	86.0	
12	.5465	.5462	.1226	.1224	.6024	.6017	22.86	10.40	.0035	.052	94.7	
13	.5462	.5460	.1226	.1224	.6040	.6035	22.91	10.40	.0010	.052	93.7	
14	.5464	.5462	.1226	.1224	.6052	.6048	22.97	10.40	.0006	.052	91.6	
15	.5464	.5462	.1223	.1220	.6058	.6050	22.99	10.40	.0035	.052	89.2	
16	.5465	.5462	.1225	.1223	.6037	.6033	22.92	10.40	.0000	.056	90.0	
17	.5465	.5462	.1225	.1223	.6031	.6025	22.90	10.40	.0005	.056	90.7	
18	.5464	.5462	.1225	.1223	.6032	.6026	22.89	10.40	.0016	.056	90.1	
19	.5465	.5463	.1226	.1224	.6045	.6040	22.94	10.39	.0045			
20	.5466	.5463	.1226	.1224	.6033	.6030	22.89	10.39	.0010	.056	90.1	
22	.5465	.5463	.1225	.1223	.6046	.6040	22.95	10.39	.0005	.056	91.3	
23	.5464	.5462	.1225	.1223	.6020	.6014	22.83	10.39	.0005	.056	88.1	
24	.5466	.5464	.1226	.1224	.6024	.6020	22.84	10.38	.0035	.056	89.0	
25	.5466	.5464	.1225	.1223	.6046	.6041	22.95	10.39	.0010	.056	87.1	
26	.5462	.5461	.1226	.1224	.6043	.6041	22.95	10.42	.0010			
27	.5465	.5463	.1226	.1224	.6045	.6042	22.93	10.39	.0020			
29	.5463	.5461	.1225	.1223	.6022	.6018	22.82	10.39	.0035			
30	.5464	.5462	.1226	.1224	.6021	.6014	22.83	10.39	.0005			
31	.5464	.5462	.1225	.1224	.6037	.6034	22.90	10.39	.0035	.056	88.1	
32	.5464	.5462	.1225	.1223	.6020	.6013	22.81	10.39	.0035	.056	90.5	
35	.5462	.5460	.1225	.1223	.6030	.6025	22.87	10.40	.0035	.052	87.6	
36	.5465	.5462	.1226	.1224	.6020	.6015	22.83	10.39	.0020	.057	88.8	
37	.5464	.5462	.1226	.1224	.6046	.6040	22.94	10.39	.0005	.056	94.3	
38	.5465	.5463	.1225	.1223	.6044	.6035	22.94	10.39	.0000	.056	89.8	
39	.5465	.5463	.1226	.1224	.6034	.6029	22.91	10.41	.0006	.057	88.2	
42	.5465	.5463	.1225	.1223	.6020	.6012	22.79	10.37	.0010	.057	87.7	
43	.5465	.5463	.1225	.1223	.6013	.6001	22.77	10.37	.0050			
44	.5465	.5463	.1225	.1223	.6020	.6013	22.82	10.38	.0035			
45	.5465	.5463	.1225	.1223	.6022	.6019	22.83	10.38	.0035			
46	.5465	.5462	.1225	.1223	.6035	.6030	22.86	10.37	.0035			
48	.5465	.5462	.1225	.1223	.6027	.6020	22.82	10.37	.0015			
49	.5464	.5461	.1225	.1223	.6046	.6040	22.91	10.38	.0002			
50	.5465	.5462	.1226	.1224	.6026	.6021	22.87	10.40	.0015			
51	.5463	.5461	.1225	.1223	.6021	.6013	22.81	10.39	.0020			
52	.5465	.5462	.1225	.1223	.6022	.6018	22.82	10.38	.0020	.057	93.2	
53	.5465	.5462	.1225	.1223	.6025	.6018	22.87	10.40	.0016			
54	.5465	.5462	.1224	.1223	.6019	.6014	22.78	10.36	.0045			
55	.5465	.5462	.1225	.1223	.6024	.6016	22.79	10.36	.0000	.057	88.6	
56	.5465	.5463	.1225	.1223	.6026	.6020	22.85	10.39	.0008	.057	87.9	
57	.5465	.5462	.1225	.1223	.6022	.6015	22.82	10.37	.0010	.057	87.0	
58	.5465	.5462	.1225	.1223	.6020	.6012	22.79	10.37	.0040			
59	.5465	.5463	.1225	.1223	.6033	.6028	22.90	10.39	.0040			
60	.5465	.5463	.1225	.1224	.6015	.6009	22.77	10.37	.0012	.057	93.2	
61	.5465	.5463	.1225	.1223	.6029	.6022	22.86	10.40	.0020	.057	86.9	
62	.5465	.5463	.1226	.1224	.6026	.6022	22.84	10.38	.0010	.056	88.7	
63	.5467	.5465	.1225	.1223	.6027	.6021	22.86	10.38	.0004	.056	92.3	
64	.5467	.5465	.1226	.1224	.6016	.6012	22.81	10.38	.0010	.056	86.6	
65	.5467	.5465	.1225	.1223	.6028	.6023	22.86	10.38	.0040			
66	.5467	.5465	.1225	.1223	.6013	.6010	22.79	10.37	.0005	.056	92.0	
67	.5467	.5464	.1225	.1223	.6042	.6036	22.93	10.38	.0022	.058	83.2	
68	.5467	.5465	.1225	.1223	.6027	.6022	22.88	10.39	.0016	.057	85.6	
69	.5467	.5465	.1225	.1223	.6034	.6029	22.91	10.39	.0006	.056	87.2	

TABLE IV (Cont'd)

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7	Col. 8	Col. 9	Col. 10	Col. 11	Col. 12
				Uranium Dioxide						Zirconia	Coating
Spec. No.	O. D. Max. *	O. D. Min.	I. D. Max. *	I. D. Min.	Length Max. *	Length Min.	Weight (gms)	Density	Concentration	Coat. thick. ZrO ₂	% Theo. density**
70	.5467	.5465	.1225	.1223	.6026	.6021	22.86	10.38	.0010	.056	89.8
71	.5467	.5466	.1236	.1232	.5985	.5980	22.69	10.42	.0010		
72	.5467	.5465	.1225	.1223	.6020	.6014	22.83	10.38	.0024	.057	88.2
73	.5467	.5465	.1225	.1223	.6006	.6002	22.77	10.38	.0005	.058	91.0
74	.5467	.5465	.1225	.1223	.6035	.6031	22.93	10.40	.0000	.058	87.5
75	.5468	.5464	.1225	.1223	.6020	.6014	22.83	10.38	.0010	.058	88.1
76	.5468	.5464	.1225	.1223	.6016	.6011	22.82	10.38	.0022		
77	.5468	.5464	.1225	.1223	.6011	.6008	22.81	10.38	.0016		
78	.5468	.5464	.1225	.1223	.6020	.6014	22.81	10.37	.0035		
80	.5467	.5468	.1232	.1225	.5982	.5978	22.70	10.42	.0020	.057	88.2
81	.5467	.5464	.1237	.1232	.5998	.5900	22.76	10.44	.0010	.057	84.7
82	.5468	.5466	.1234	.1232	.5993	.5987	22.74	10.41	.0000	.057	90.0
83	.5469	.5466	.1233	.1228	.5463	.5962	22.61	10.40	.0010	.056	86.1
84	.5468	.5466	.1231	.1238	.5968	.5962	22.59	10.40	.0000	.057	84.2
85	.5468	.5467	.1233	.1230	.5965	.5960	22.69	10.45	.0010	.057	90.4
86	.5467	.5465	.1225	.1223	.6032	.6028	22.90	10.39	.0020		
87	.5467	.5465	.1225	.1223	.6038	.6032	22.95	10.40	.0016		
88	.5467	.5465	.1225	.1223	.6032	.6025	22.93	10.40	.0006		
89	.5467	.5465	.1225	.1223	.6059	.6055	23.04	10.41	.0018		
90	.5467	.5465	.1225	.1223	.6040	.6037	22.96	10.40	.0020		
91	.5465	.5464	.1237	.1235	.6039	.6036	22.97	10.46	.0000		
92	.5466	.5464	.1238	.1235	.6048	.6031	22.99	10.45	.0022		
93	.5468	.5464	.1238	.1235	.6065	.6062	23.09	10.01	.0010	.056	89.6
94	.5465	.5463	.1239	.1236	.6005	.6001	22.83	10.45	.0012	.057	91.1
95	.5467	.5465	.1238	.1232	.6031	.6026	22.94	10.45	.0015	.056	87.3
96	.5464	.5463	.1238	.1235	.6072	.6065	23.10	10.47	.0010		
97	.5466	.5464	.1236	.1232	.6007	.6005	22.82	10.44	.0010	.056	90.2
98	.5465	.5463	.1238	.1235	.6009	.6003	22.81	10.44	.0012	.057	89.3
101	.5465	.5464	.1238	.1236	.6006	.6003	22.83	10.46	.0016		
102	.5466	.5464	.1239	.1236	.6020	.6010	22.87	10.44	.0000		
103	.5465	.5463	.1238	.1235	.6009	.6002	22.93	10.48	.0000		
104	.5465	.5463	.1239	.1237	.6035	.6030	22.91	10.43	.0012		
105	.5465	.5463	.1239	.1236	.6012	.6010	22.85	10.45	.0005	.057	87.7
106	.5465	.5463	.1235	.1233	.6020	.6015	22.86	10.43	.0000	.056	89.9

* Maximum and minimum values obtained from minimum of three (3) readings; inches

** Value of 5.3 used as theoretical density of CaO-Stabilized zirconia

TABLE V

PELLET NUMBER USED IN TEST PROGRAM

Temperature	Pellet Numbers		
	8-Hour Tests	R. T. Control	Temp. Cy- cling Control
2650°C		31	38
2550°C		35	11
2450°C	16, 17, 18, 20, 22, 24, 25, 32, 36, 37	23	39
2350°C	42, 55, 56, 57, 60, 61, 62, 63, 64, 66	52	67
2200°C	2, 3, 4, 5, 6, 8, 9, 10, 13, 14	12	15
2000°C	73, 81, 82, 83, 84, 93, 94, 95, 98, 105	97	106

TABLE VI

DIFFUSION MEASUREMENTS -- 8-HOUR TEST

Temperature, °C:		2450		2350		2200		2000	
Position No. *		Pellet No.	Penetration Mils	Pellet No.	Penetration Mils	Pellet No.	Penetration Mils	Pellet No.	Penetration Mils
Top	1	16	7.2	42	3.8	2	0.6	73	nil
	2	17	6.8	55	4.0	3	1.8	81	nil
	3	18	7.6	56	3.4	4	1.6	82	nil
	4	20	8.0	57	4.0	5	.8	83	nil
	5	22	6.2	60	3.6	6	1.6	84	nil
	6	24	7.0	61	4.2	8	1.4	93	nil
	7	25	6.6	62	3.8	9	.8	94	nil
	8	32	7.6	63	3.4	10	1.2	95	nil
	9	36	6.8	64	4.0	13	1.0	98	nil
Bottom	10	37	7.2	66	3.6	14	1.0	105	nil
Average Values		7.1		3.8		1.2		nil	

* Position numbers are from top of furnace load. Furnace center is between positions 5 and 6.

Note: Penetration or diffusion zone growth value is the average of at least 12 readings per pellet.

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