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IONIC DIFFUSION IN HIGH TEMPERATURE URANIUM DIOXIDE

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Abstract

Uranium dioxide nuclear fuels are being subjected to increasingly higher central temperatures and larger thermal gradients which contribute significantly to changes in the physical properties, to the distribution of fission products, to the oxide composition and specifically to the mechanism of material transport. The purpose of this paper is to discuss recent high temperature property measurements of UO_2 made both in- and out-of-reactor that pertain to atomic movement and to suggest further areas for high temperature thermodynamic research.

High temperature measurements of electrical conductivity, thermoelectric emf, solid state fission fragment migration and studies of phase equilibria in the oxygen-uranium system suggest that ionic diffusion in an electrical potential gradient contributes significantly to the movement of fission products and oxygen atoms.

The electrical property measurements of uranium dioxide show evidence of a high Seebeck coefficient, a p-type to n-type conductivity change and an ionic character at high temperatures. These data are being confirmed by in-reactor electrical property measurements.

The distribution of solid fission fragments observed in irradiated UO_2 fuel elements cannot be explained solely in terms of diffusion in a thermal or concentration gradient. Solid fission fragments were shown to diffuse in an electrical potential gradient at high temperatures in the absence of any thermal gradient. The thermal emf produced by the thermal gradient in a fuel element during irradiation is thought to contribute to the migration of fission fragments by ionic diffusion. In-reactor tests of this hypothesis are under way.

The measurements and interpretation of high temperature property data are complicated by changes in stoichiometry. Phase equilibria and melting point studies in the temperature range 1600-300°C show a wide range of single phase UO_{2-x} existing above 1600°C. The melting point of UO_{2-x} reaches a maximum at approximately $\text{UO}_{1.95}$ and decreases substantially at both lower and higher O:U ratios. Out-of-reactor experiments show the formation of UO_{2-x} to be enhanced by the application of an electric potential presumably because of transport of oxygen atoms.

Introduction

Uranium dioxide nuclear fuels are being subjected to increasingly higher central temperatures and larger thermal gradients which contribute significantly to changes in physical properties. Atomic movement by thermal diffusion, vaporization-condensation, void migration and the decomposition of UO_2 can occur at these high temperatures. the purpose of this paper is to discuss recent preliminary in- and out-of-reactor high temperature experiments relative to atomic movements in UO_2 . These experiments, which on cursory examination appear unrelated, suggest that diffusion of ions in uranium dioxide in an electric potential gradient contributes to the movement of oxygen and fission products in UO_2 .

Mass Transport of Fission Products and Oxygen During Irradiation

Gross relocation of fission fragments occurs in UO_2 fuel elements irradiated with high central temperatures and large thermal gradients [1-5]. Well-defined annular bands of fission product concentrations or of fission product depletions are formed about the thermal center. The bands are directly related to the characteristic microstructures of the UO_2 which are formed during irradiation at these high temperatures. Both the microstructures and fission product bands are centered about the thermal center of the fuel system and are characteristic of specific isotherms existing during irradiation.

For example, a typical fuel system irradiated to short exposures has multiple bands, each band having a different fission product concentration [2,3] (Figure 1). A depletion is observed in the high density, porosity-free portion of the large columnar grains, and a fission product concentration is found near the thermal center. A narrow band of high fission fragment concentration is found in the small columnar grains immediately outside the depletion band. In most instances, the boundary between these bands is distinct.

Uranium metal inclusions are also observed in UO_2 irradiated at high temperatures and large thermal gradients [6]. Under certain conditions, the metal concentrates in radial bands around the thermal center (Figure 2). Laboratory studies have demonstrated that UO_2 will dissociate at high temperatures to form an oxygen deficient phase (UO_{2-x}) which on cooling reverts to $\text{UO}_{2.00}$ and metallic uranium. This decomposition also occurs during irradiation, as evidenced by metallic uranium inclusions [6] observed in fuel elements irradiated with central temperatures high enough to produce extensive grain growth. The concentration of the uranium varies across the diameter of the fuel element, with largest concentration nearest the thermal center. However, in many fuel elements the uranium inclusions are concentrated in bands, similar to the fission product bands. The fission products tend to concentrate in or near the areas of uranium inclusions [3][6] (Figure 2).

The non-uniform distribution of fission products and oxygen in the fuel system is difficult to explain in terms of the more common methods of

material transport, i.e. diffusion in a thermal and concentration gradient, mass transfer by liquid or vapor phases, or entrainment by voids that diffuse along a temperature gradient. Although conditions during irradiation are difficult to define, it is apparent that the unusual concentrations of uranium and fission fragments result from a combination of transport mechanisms, some of which may not be readily apparent.

Electrical Property Measurements

Electrical property measurements of uranium dioxide show a high Seebeck coefficient, a p-n transition in the electrical conductivity and a possible ionic contribution to the electrical conductivity at high temperatures. Thermoelectric properties have been measured between 800 and 1800°C in single crystal and polycrystalline UO_2 . An initially Seebeck coefficient (Figure 3) changes from positive to negative with increasing temperature between 1100 and 1400°C. This change indicates a p-n transition in the electrical conductivity.

Similar electrical property measurements have been made during irradiation (Figure 4). Although not as precise as the laboratory data, the results confirm the out-of-reactor experimental results of an appreciable thermoelectric emf and a p-n transition. Measurements were made with the use of insulated, tungsten-clad capsule containing sintered UO_2 irradiated at temperatures up to 2650°C. Electrical potential and temperatures were measured with tungsten and tungsten-rhenium thermocouples and with tungsten probes. The temperature of the oxide was controlled by varying the capsule position in the neutron flux gradient. The maximum cladding temperature was 1800°C and the maximum UO_2 temperature was estimated at 2650°C. Total irradiation time was four hours.

The Seebeck coefficient during irradiation was substantially smaller than that measured out-of-reactor. However, this may reflect an error in estimating the thermal gradient and central temperature. The p-n transition during irradiation occurred at 1300°C, slightly higher than the transition temperature in the out-of-reactor tests.

Preliminary electrical conductivity measurements of single crystal UO_2 show evidence of ionic conductivity at high temperatures. Specimens were

heated to 2000°C by radiation from a tantalum tube heater in a purified argon atmosphere¹. Tungsten electrodes positioned the specimen in the furnace. The ionic conductivity was determined by measuring the electrical resistance as a function of the frequency of the applied potential (DC and AC to 500 kc). The electrical conductivity varied among specimens, apparently because of differences in initial stoichiometry, purity and in the oxygen partial pressure of the furnace atmosphere. In some specimens there was evidence of an ionic conductivity (Figure 5, curve MR-2) while in other crystals no such evidence was observed (Figure 5, curve MR-3).

Proposed Transport Mechanism

Based on both the in- and out-of-reactor electrical property data, it is suggested that the large thermal gradients present in high temperature UO_2 fuel elements produce a thermal emf of a magnitude substantial enough to cause fission products and oxygen to diffuse as ions during irradiation. Since the temperature overlaps the p-n transition temperature for UO_2 , the direction and magnitude of the applied electric force varies with radius, causing ions to migrate in different directions; hence, the bands of fission product depletion and the bands of fission product and uranium concentrations. Obviously this cannot be the only competing transport mechanism since the driving force of the thermal gradient and the formation of concentration gradients will tend to alter the concentration bands. The final distribution most probably represents the steady-state conditions at the time of fuel discharge.

A series of preliminary experiments was begun to determine if electrodiffusion is a significant factor in the migration of fission products and oxygen during irradiation.

Fission Product Migration in Electric Potential Gradient

Solid fission products were transferred with a potential gradient from an irradiated to a non-irradiated specimen of UO_2 [7]. An irradiated, rectangular, polycrystalline UO_2 bar was butted to an identical non-irradiated bar as illustrated in Figure 6. The specimens were supported between tungsten

¹Argon contained < 1 pp O_2 and < 10 ppm H_2)

electrodes and heated from adjacent tungsten resistance heaters. A gradient of approximately 1 v/cm was applied to the specimens during 24 hours at 1500°C. Radiochemical analyses revealed transfer of fission products from the irradiated to the non-irradiated UO_2 (Figure 6). This relocation cannot be wholly accounted for by a concentration activated diffusion. In the samples analyzed (Figure 6), the nearly uniform concentration of fission products in the non-irradiated specimen suggest an ionic diffusion mechanism rather than a thermal diffusion process. In the case of thermal diffusion, a significant concentration gradient would be expected in the non-irradiated specimen.

An interesting observation was made relative to an unusual fission product distribution in a UO_2 fuel element containing tungsten. During fabrication, a radial crack in the oxide was filled with tungsten shot, which, during irradiation, sintered into a solid tungsten probe (Figure 7). The probe extended from the high temperature regions into the cooler portion of the UO_2 . Post-irradiation examination showed that the tungsten probe had altered the symmetrical distribution of the fission products without significantly altering the temperature profile (as evidenced by the small change in the characteristic UO_2 microstructures). Because of this, it is believed that the change in fission product symmetry reflects a change in the electrical potential immediately surrounding the tungsten probe.

Diffusion of Oxygen in Electric Potential Gradient

Mass transfer of oxygen can be achieved in UO_2 with an applied electric potential gradient. High temperature experiments suggest that ionic diffusion in an electric potential gradient contributes significantly to the movement of oxygen and the formation of a UO_{2-x} phase.

Preheated to 1200°C, UO_2 cylinders were centrally melted by direct induction coupling (10 megacycles/sec) in a slightly oxidizing argon atmosphere²

²The argon contained ~ 50 ppm O_2 and > 500 ppm H_2O

and were thus maintained with a solid surface and a molten core [8]. Subsequent ceramographic and x-ray examination revealed an extensive U_4O_9 second phase which increased in concentration toward the center of the UO_2 specimen. The two-phase microstructure is similar to that of specimens having an O:U ratio between 2.15 and 2.18 [9]. It is suggested that the oxygen moved to the center of the specimens under the influence of a potential field induced by the induction field and/or in the thermal emf resulting from the temperature gradient.

During electrical property measurements at high temperatures, UO_2 was electrolyzed because of the applied electric potential [10]. Tungsten encapsulated UO_2 was self-resistance heated to 2800°C by direct current for five minutes. The UO_2 , acting as a parallel conductor in the capsule at high temperatures was heated to 2800°C where the UO_2 melted and apparently was electrolyzed. Examination of the capsule showed extensive evidence of oxygen diffusion to the positive end of the capsule. Free uranium was found near the negative end, reflecting the decomposition of the UO_2 to UO_{2-x} . When an alternating current was used to heat the capsule, otherwise identical experiments showed no evidence of electrodecomposition or of diffusion of oxygen.

More refined experiments conducted at lower temperatures also demonstrate electrodiffusion and decomposition of UO_2 . Small crystals of UO_2 (0.50 cm diameter and 0.64 cm long) were supported between two tungsten electrodes and heated to 1600°C in a tungsten tube furnace in purified argon¹. An electric potential gradient of approximately 3 v/cm (3 amperes) was applied for 11 hours. Ceramographic analysis after quenching revealed (a) formation of metallic uranium near the negative end of the UO_2 cylinder and (b) porosity near the UO_2 surface and evidence of a W-O reaction near the positive end of the cylinder (Figure 8). (The UO_2 had adhered slightly to the positive electrode at the termination of the experiment.)

The concentration of uranium particles decreased uniformly from the negative toward the positive end of the specimen (Figure 8). The uranium inclusions were confined to approximately 0.25 cm nearest the negative end. It has not been determined whether this represents equilibrium or steady state conditions or whether the tungsten acted as a receptor for the diffused oxygen.

High Temperature Phase Equilibria

The measurements and interpretation of high temperature property data for UO_2 are complicated by changes in stoichiometry [12-15]. The formation of $\text{UO}_{2\pm x}$ phases at high temperatures is undoubtedly significant in the study of mass transport in UO_2 , especially the diffusion of oxygen. Phase equilibria and melting point studies in the temperature range 1600-3000°C show a wide range of single phase UO_{2-x} existing above 1600°C. UO_2 cylinders, (~ 1.5 cm diameter and 1.9 cm long) with axial holes (0.5 cm diameter) drilled part way through the pellets were filled with uranium metal. The cylinders were heated for times between 10 and 120 minutes in 10^{-5} torr at temperatures between 1600 and 2600°C. These were rapidly cooled to room temperature. Each specimen was examined ceramographically and the O:U ratio of the originally stoichiometric UO_2 was determined by oxidation to U_3O_8 .

After being heated, each specimen contained: polycrystalline UO_2 (originally the stoichiometric, sintered UO_2) with uranium metal at the UO_2 grain boundaries; large crystals of UO_2 with large uranium inclusions (these crystals were formed during the oxidation of the original metal core); and unreacted uranium. The amount of unreacted uranium decreased, and the amount of UO_2 crystal growth increased with increasing temperature.

The unreacted uranium contained a uniformly dispersed second phase. The relative amount of this phase increased with increasing heating temperature. In those specimens cooled from the higher temperatures, 2200 and 2400°C, this phase precipitated along grain boundaries and in a preferred crystallographic pattern. This second phase is assumed to be UO_2 precipitated from a higher temperature oxygen-rich uranium solution.

The uranium metal was uniformly dispersed throughout the UO_2 . The specimens cooled from the higher temperatures contained greater amounts. This phase appeared as round or tubular inclusions at the grain boundaries and pores in the small grained UO_2 . In the large crystals of UO_2 , formed from the uranium core during heating, the uranium inclusions were crystalline and were observed throughout the UO_2 crystals as well as at the grain boundaries.

The O:U ratio of the small grained UO_2 decreased as the heating temperature was increased (Table I). The O:U ratios are consistent with the ceramic observations.

The melting points of the substoichiometric UO_2 are shown in Table I. Melting points were determined in purified argon¹ in a tungsten "V" filament furnace. The furnace system was calibrated with the use of ceramics and metals of known melting points, e.g. Al_2O_3 , Nb, Mo, and Pt. Approximately 15 measurements were made of each uranium dioxide specimen.

The melting points of the substoichiometric UO_2 change after melting or after annealing for 1 to 2 minutes at temperatures slightly below the melting point. Samples with O:U less than 1.95 increased after melting; whereas samples with O:U greater than 1.95 decreased after melting. A second melting point obtained after melting and after heating approximately 2 minutes at $\sim 2500^\circ\text{C}$ was 2790°C , i.e., near the melting point of stoichiometric UO_2 . Conversely, the initial melting point of an oxide sample with an O:U ratio of 1.927 decreased from 2840°C to 2800°C after initial melting and subsequent heating.

The melting point change in the substoichiometric UO_2 is considered to result from an O:U increase during heating. Although a purified argon atmosphere was used during melting point determinations, the oxygen partial pressure is sufficiently large to increase the O:U ratio of the specimens during heating. This resulted in changes in equilibrium oxygen-uranium conditions and subsequent increases in the melting point of the $\text{UO}_{1.780}$ and a decrease in the melting point of the $\text{UO}_{1.927}$.

The melting point of the UO_{2-x} appears to reach a maximum at an O:U ratio near 1.95 and to decrease at lower O:U ratios to substantially less than that of $\text{UO}_{2.00}$.

A tentative phase diagram (Figure 9) for UO_{2-x} was constructed from the reported melting points, assuming that an equilibrium O:U ratio was reached at each annealing temperature. Also included is the reported melting point for $\text{UO}_{2.16}$.

The partial molar enthalpy of UO_{2-x} between 1800-2400°C was estimated from a plot of log partial mole fraction and $1/T$ to be 20 kcal/mole (solidus line only of Figure 9).

The maximum in the melting curve need not occur at the stoichiometric composition in compounds which dissociate below the melting point. The melting points reported for UO_{2-x} appear consistent with the dissociation of UO_2 to form an oxygen deficient UO_{2-x} at high temperatures. They are also consistent with the increase in melting point (2930°C) of UO_2 observed after low exposure, neutron irradiations [16].

Conclusion

High temperature measurements of the electrical conductivity, thermoelectric properties, solid state migration and uranium-oxygen phase studies suggest that ionic diffusion in an electric potential gradient is significant in the movement of fission products and oxygen in uranium dioxide. Although no attempt has yet been made to examine the electrodiffusion in UO_2 in detail, the preliminary and qualitative data is of significant importance to merit further high temperature thermodynamic research.

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TABLE I
O:U RATIO AND MELTING CHARACTERISTICS² OF SUBSTOICHIOMETRIC UO₂

<u>Annealing Temperature, °C</u>	<u>O:U Ratio</u>	<u>Melting Point, °C</u>
1600	1.917	2750 +36 -48
	1.889	2752 +36 -51
	1.871	2729 +39 -67
1800	1.927	2845 +90 -50
	1.823	2687 +30 -20
2000	1.878	2735 +58 -62
2200	1.841	2703 +42 -73
2270	1.778	2672 +21 -65
2400	1.780	2675 +60 -105
Ref. UO ₂	2.001	2803 +22 -43

² Melting Points measured in argon atmosphere with oxygen content
<1 ppm and H₂O <10 ppm.

FIGURE CAPTIONS

Figure 1

Macrophotograph and Autoradiograph of Vibrationally Compacted UO_2 Fuel Capsule Showing Fission Fragment Relocation Relative to Structural Changes in UO_2 [2, 3]. The dark areas of autoradiograph represent high concentrations of fission products. (halves are mirror images).

Figure 2

Concentration of Uranium Inclusions in Columnar Grains of Irradiated UO_2 Fuel Capsule [2,3,6] Showing Concentration of Fission Products in Same Position. (Halves are mirror images.)

Figure 3

Seebeck Coefficient of UO_2 Showing p-n transition.

Figure 4

Seebeck Coefficient of UO_2 During Irradiation.

Figure 5

Electrical Conductivity of Single Crystal UO_2 .

Figure 6

Fission Product Migration in UO_2 Along a Potential Gradient of 1 volt/cm at 1500°C for 24 Hours.

Figure 7

Autoradiograph of Irradiated UO_2 Showing the Distortion of the Symmetrical Fission Fragment distribution Resulting from a Tungsten Probe. Dark area of autoradiograph represents concentration of fission products.

Figure 8

Microstructure of UO_2 Single Crystal Heated to 1600°C for Twelve Hours with 2 volt/cm Potential Gradient Showing Formation of Uranium Metal at Negative End and Formation of Porosity at Positive End.

Figure 9

Tentative Oxygen-Uranium Phase Diagram.

AUTORADIOGRAPH

MACROPHOTOGRAPH

0.10 inch

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

Negative End

0.13 cm from Negative End

0.25 cm from Negative End

Positive End

0.005 cm

FIGURE 8

FIGURE 9