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IRRADIATION EFFECTS ON URANIUM DIOXIDE MELTING

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ABSTRACT

Irradiated uranium dioxide with exposures to 11.25 at.% uranium burnup has been examined microscopically at temperatures to 3000 C. Melting temperatures were measured and mass vaporization rates compared for UO_2 with 14 different exposures.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	1
APPARATUS	2
MATERIALS	2
PROCEDURE	5
EXPERIMENTAL VARIABLES	6
Oxide Purity	6
Atmosphere Purity	6
Tungsten-UO ₂ Reactions	6
Initial Oxide Compositions	7
Heating Rate	7
RESULTS	7
UO ₂ Melting Point	7
Irradiation Effect on Melting Point	9
Vaporization and Crystal Growth of UO ₂	11
Irradiation Effect on Volatility and Crystal Growth	11
DISCUSSION	15
Chemical Stabilization by Irradiation	15
Location of the Liquidus Maximum	15
Hypothetical High Temperature Phase Relationships	17
Irradiation Effects on the Melting Process	18
APPENDIX	21
BIBLIOGRAPHY	23

IRRADIATION EFFECTS ON URANIUM DIOXIDE MELTING

INTRODUCTION

Uranium dioxide is frequently exposed to temperatures approaching the melting point in reactor fuel assemblies. The melting temperature and vaporization characteristics of UO_2 must be known to interpret the alteration in fuel structure caused by irradiation. The primary objective of this work was to measure the melting point of UO_2 after exposure to a variety of neutron doses. In addition, vaporization rates and the appearance and growth rates of vapor deposited UO_2 crystals were studied.

Hanford's study of UO_2 vaporization and crystal growth has its origin in the work of Bates and Newkirk who described the rapid growth of UO_2 crystals from the vapor.^(1, 2) Modifications of their equipment and techniques were used to measure the melting temperature of UO_2 with in-reactor exposures from 0.005 to 11.3 at. % uranium fissioned. Melting point results and observations of irradiation effects on vaporization and crystal growth are reported here.

SUMMARY

The melting point of UO_2 increases with irradiation exposure to a maximum of 2915 C at 0.09 at. % burnup. This is 125 C above the melting point of nonirradiated UO_2 . A gradual decrease to 2800 C at 1.2 at. % burnup and to 2660 C at 11.25 at. % burnup follows the maximum. Mass vaporization rates seem to vary inversely with melting point as a function of neutron dose. The change in vaporization rate is a reflection of the melting point change, and, perhaps, a dependence of vapor pressure upon irradiation.

Apparatus developed for these measurements is generally applicable to microscopic examination of any hazardous material at temperatures to 3400 C and magnifications to 100X.

APPARATUS

Specimens were heated in a water-cooled resistance furnace (Figure 1) by direct contact with the tungsten element.⁽³⁾ The power supply was a manually controlled 4 kva, 5 to 30 v, step-down transformer. A flowing, 15 psia helium atmosphere was maintained during each heating cycle. Purging the furnace for 15 min with a 3 liter/min flow of helium provided an atmosphere with less than 0.01% each of O_2 , N_2 , and $H_2O(g)$. The effluent gas passed through a charcoal filter submerged in liquid nitrogen to remove radioactive contamination.

The furnace was installed on a universal mount in a glove box made from $\frac{3}{4}$ in. Lucite and plywood (Figure 1). Lead impregnated, 0.030 in. thick neoprene gloves were used for operations within the glove box. Twenty to 100 mg specimens of irradiated UO_2 with unit gamma activities to 2500 r/hr-g were examined in this facility with no excessive personnel exposure.

Specimens were observed through a microscope located outside the glove box. This instrument, which is commercially available as a complete unit, has a working distance of 21.3 cm and a numerical aperture of 0.10. A triple-split-beam eyepiece permitted simultaneous viewing, photography, and photometry of incandescent specimens.

Temperatures were measured with an optical pyrometer calibrated against the known melting points of high purity copper, nickel, alumina, molybdenum, and tantalum. A precision of $\pm 30^\circ$ (95% confidence) for an individual measurement was achieved between 1000 C and 3000 C.

MATERIALS

Irradiated UO_2 was obtained from test capsules with fuel exposures from 0.005 at.% to 11.3 at.% uranium burnup. Brief irradiation and fabrication histories are given in Table I.

FIGURE 1

Apparatus For High Temperature Examination of Radioactive Materials

TABLE 1
UO₂ IRRADIATION AND FABRICATION HISTORIES

<u>Irradiation</u>	<u>Fabrication</u>
0 005 at % U burnup at temperature less than 100 C	94% dense extruded, hydrostatically pressed, and sintered, 1/4 in diam rods micronized, natural, UO ₂ powder
0 014 at % U burnup at temperature less than 100 C	91% dense, extruded, hydrostatically pressed, and sintered, 1/4 in diam rods micronized, natural, UO ₂ powder
0 021 at % U burnup at temperature less than 100 C	87% dense, extruded, hydrostatically pressed, and sintered, 1/4 in diam rods, micronized, natural UO ₂ powder
0 051 at % U burnup at temperature less than 100C	92% dense, extruded, hydrostatically pressed, and sintered 1/4 in diam rods, micronized, natural, UO ₂ powder
0 09 at % U burnup with core temperatures to 1750 C	93% dense, pressed, and sintered pellets PWR type, natural, UO ₂ powder
0 11 at % U burnup with core temperatures to 2600 C	80% dense, loosely packed, fused, natural UO ₂ O U ratio uncertain
0 17 at % U burnup with core temperatures to 2800 C	80% dense, pressed, sintered, and crushed, loosely packed PWR type, 1 6% enriched UO ₂ powder
0 20 at % U burnup with core temperatures to 2100 C	97% dense, pressed, and sintered pellets, PWR type, natural, UO ₂ powder
0 38 at % U burnup with core temperatures to 1800 C	86% dense, pressed, sintered, and crushed PWR type, natural, UO ₂ powder
1 2 at % U burnup with core temperatures to 2800 C	84% dense, pressed, sintered, and crushed PWR type 2 44% enriched powder
8 4 at % U burnup with core temperatures to 1200 C	Pressed and sintered plates, 37% enriched UO ₂
11 3 at % U burnup with core temperatures to 1200 C	Pressed and sintered plates, 53% enriched UO ₂

UO₂ with 8 4 and 11 3 at % burnup were supplied by Bettis Atomic Power Laboratory

Oxides with burnups to 1.2 at. % were sintered in hydrogen for 12 hr at 1750 C and had O:U ratios between 2.00 and 2.01 before irradiation. Ten grams of each irradiated material (as -10 +30 mesh particles) were obtained for melting point determinations and high temperature photomicrography.

PROCEDURE

Mendenhall V type tungsten filaments⁽⁴⁾ were used for melting point determinations. These were $\frac{1}{4}$ in. wide, 0.005 in. thick strips with a 15° "V" in the center. The standard procedure for measuring a melting point was to:

- (1) place the specimen in the filament V and purge the furnace with helium
- (2) raise the temperature at a rate of approximately 50°/sec until the specimen, as seen through the microscope, melted
- (3) with the pyrometer, measure the temperature of the tungsten V at which the specimen began to melt at the tungsten-specimen interface.

Two operators were required—one to increase the temperature and observe the specimen and the other to simultaneously measure the temperature. A minimum of three, and usually at least five, melting point measurements were made for each material examined.

Motion or still pictures were taken through the microscope as each specimen was heated to melting. These pictures record the vaporization and crystal growth characteristics of UO_2 with various irradiation exposures. Still pictures were taken at each of three thermal arrests made in the course of heating one specimen from each sample of irradiated oxide. These pictures were at 2400 C, 2750 C, and the melting point with holding times of 1 min at each temperature.

Irradiated and nonirradiated UO_2 were compared directly by simultaneously heating a specimen of each placed side by side on a common tungsten filament. This technique provided the most precise indications of irradiation effects on both melting point and mass vaporization rates.

EXPERIMENTAL VARIABLES

Effects of variation in oxide composition and heating rate on melting and vaporization characteristics were studied to establish experimental procedures which separate irradiation effects on melting behavior from extraneous effects.

Oxide Purity

Variations in UO_2 composition can cause significant differences in melting behavior. For example, the addition of 0.4 wt% TiO_2 or Nb_2O_5 to UO_2 causes the shape of vapor deposited crystals to change from well defined tetrahedrons to irregular globules and also results in a melting range rather than a discrete melting point.⁽⁵⁾ Possible sources of impurities which could influence the observations include (1) the annealing atmosphere, (2) the tungsten filament, and (3) variable initial oxide composition.

1. Atmosphere Purity

Varying the oxygen and nitrogen content of the helium atmosphere from <0.01% to 0.18% and <0.01% to 0.67% for O_2 and N_2 respectively did not affect either the melting point or the vaporization and redeposition characteristics of UO_2 . An atmosphere with 0.18% O_2 caused excessive oxidation of the tungsten filament.

2. Tungsten- UO_2 Reactions

UO_2 and tungsten react slightly at 2800 C in time periods of a week or less.⁽⁶⁾ The reactions which occurred between filaments and UO_2 specimens yielded a thin, refractory product which formed between the UO_2 and the tungsten and seemed to inhibit further attack. Neither the presence of the reaction product nor of WO_3 formed by reaction between the tungsten filament with oxygen in the furnace atmosphere had an effect upon UO_2 melting behavior.

3. Initial Oxide Composition

UO₂ compositions between UO_{1.96} and UO_{2.67} behaved similarly when heated at 50 C/sec to the UO₂ melting point. During heating, hyperstoichiometric oxides dissociated to UO₂ which remained stable to the melting point. The substoichiometric oxides were two-phase at room temperature with uranium metal inclusions in a UO_{2.00} matrix. They appeared to melt at the same temperature as UO_{2.00}. Since the same atmosphere composition was used for all heating, it is reasonable to assume that the UO₂ either dissociated or oxidized to the equilibrium composition corresponding to the partial pressure of oxygen in the atmosphere and the melting temperature. The composition of the oxide as it melts is then dictated, not by the initial composition, but by the oxygen pressure in the furnace atmosphere.

Heating Rate

A heating rate of approximately 50 C/sec was chosen for melting point measurements of both irradiated and unirradiated UO₂. The melting point of compositions between UO_{2.00} and UO_{2.24} was constant and independent of heating rate in the range 1000 C/sec to 1000 C/hr. These heating rates provide sufficient time for the UO_{2+x} to disproportionate to an oxygen-rich vapor and a UO₂ residue which subsequently melts at the UO₂ melting point.

RESULTS

UO₂ Melting Point

A melting point of 2790 ± 20 C (95% confidence) was measured for UO₂. The primary standard was 95% dense UO₂ pressed and sintered in hydrogen for 12 hr at 1750 C. Composition of the standard before and after melting is given in Table II.

TABLE II
MICROSTRUCTURE AND COMPOSITION OF UO_2
BEFORE AND AFTER MELTING

	<u>BEFORE</u>	<u>AFTER</u>
<u>Magnification:</u> 500X
<u>Etchant:</u> 10% H_2SO_4 - 90% H_2O_2		
<u>O:U Ratio*</u>	<u>2.04 + 0.01</u> ppm	<u>2.00 + 0.01</u> ppm
W	50	870
Al	100	200
As	< 2	< 2
B	< 0.1	< 0.1
Cr	< 2	< 2
Cu	2	2
Fe	10	15
Ge	< 0.5	< 0.5
Mg	< 1	< 1
Mn	< 1	< 1
Ni	< 5	< 5
P	< 100	< 100
Pb	2	5
Si	< 10	14
Sn	< 0.5	< 0.5
Tl	< 200	< 200
V	< 50	< 50
Zn	< 50	< 50

* O:U ratios were determined by controlled potential coulometry which does not permit measurements below 2.00.

Approximately 50% of the 100 mg UO_2 specimens was lost as vapor during fusion. This rapid vaporization obscures the melting point and introduces difficulties in its measurement not encountered with less volatile

compounds. Reported values for the UO_2 melting point range from 2200 to 2900 C^(7, 12) with the lower figure probably resulting from mistaken interpretation of rapid vaporization as melting. Recent results are concentrated around 2800 C which is generally accepted as the melting point of $\text{UO}_{2.00}$.

$\text{UO}_{2.24}$ melted at 2400 ± 100 C when heated at a rate of 1200 C/sec. A 4 sec heating cycle (room temperature to 2400 C to room temperature) decreased the O U ratio from 2.24 to 2.07. When $\text{UO}_{2.24}$ was rapidly brought to 2400 C, it fused and then resolidified as loss of oxygen yielded the more refractory $\text{UO}_{2.0}$.

Irradiation Effect on Melting Point

Low irradiation exposures caused a UO_2 melting point increase of up to 130 C (Figure 2). A rapid increase from 2790 C at zero burnup to 2920 C at 0.05 at. % burnup occurred followed by an estimated maximum of 2930 C at 0.09 at. % burnup. Following the maximum, a gradual decrease in melting temperature with increasing exposure occurred. At 1.75 at. % burnup, the curve is nearly horizontal and has decreased to 2800 C.

FIGURE 2

Melting Point vs In-Reactor Exposure for Irradiated UO_2

The melting point of UO_2 decreased to 2760 and 2660 C during irradiation to 8.4 and 11.3 at. % burnup, respectively. Plotting these values in Figure 2 resulted in the point of inflection at approximately 7.5 at. % burnup followed by a rapidly increasing rate of melting point decrease with additional irradiation.

Melting point data for the oxides with 0.005, 0.014, 0.021, and 0.051 at. % burnup are most significant. The samples were all prepared from the same lot of powder, fabricated by identical methods, and irradiated at temperatures less than 100 C in the same reactor for varying lengths of time. Calculated and measured exposures for these materials agreed to within less than 10%. The melting points of these samples establish the orderly, increasing pattern leading to the maximum at 0.09 at. % burnup.

UO_2 with 0.09 and 0.11 at. % burnup had melting points well below the trend established by the lower burnup oxides. The oxide with 0.11 at. % burnup was the only sample of fused UO_2 examined. The O:U ratio of this material before irradiation varied from 1.95 to 2.05 with most results below 2.00. If the irradiated specimens were substoichiometric, they might be expected to melt at the same temperatures as nonirradiated UO_2 as explained in the appendix. The oxide with 0.09 at. % burnup should have melted at 2930 C if the extrapolation of low burnup results is correct. Instead, it melted at 2840 C, 50 C above the melting point of nonirradiated UO_2 . No explanation for this departure is available, except a possible error in burnup measurement.

An analysis of variance of all data showed that, at the 99% level of significance, a definite change in melting point resulted from irradiation. A similar analysis considering only data for nonirradiated UO_2 and for UO_2 with 0.051 at. % burnup showed a significant melting point increase at the 99% level. This enhanced thermal stability was not influenced by the rate at which the melting point was approached. Also, several high melting samples were heated repeatedly to the temperature at which the UO_2 in contact with the hot filament fused with no noticeable change in melting point.

Vaporization and Crystal Growth of UO_2

Because of its high vapor pressure, UO_2 sublimates rapidly at temperatures near the melting point. The vapor pressure at 2750 C is estimated to be 50 mm of mercury.⁽¹³⁾ The vapor from a UO_2 specimen heated in a tungsten wedge is rapidly chilled by the cool furnace atmosphere, thus a supersaturated UO_2 vapor is formed above the specimen. Part of this vapor redeposits on cooler portions of the specimen and filament and the balance plates out on the furnace walls. The thermal gradient in the specimen is toward the portions farthest from the hot filament, thus most of the redeposited vapor solidifies on the relatively cool, outermost surfaces of the UO_2 specimen. A cyclical process occurs in which UO_2 vaporizes rapidly from the specimen surface in contact with the hot filament and partially redeposits on cooler specimen surfaces. During this process, convex portions of the cooler UO_2 tend to become more convex because of a greater heat transfer efficiency. As the convex portions expand, they assume regular, pointed shapes, the points growing at the expense of flat sides because UO_2 molecules can arrive at a point from any direction.⁽¹⁴⁾ The resulting vapor deposited crystals have regular dendritic shapes and are true single crystals with a pronounced preferred orientation. Crystals grown from UO_2 vapor have their (111) direction parallel to the growth direction.⁽¹⁵⁾ Crystal growth rates of $\frac{1}{4}$ in. /min are common from UO_2 at 2750 C. Typical vapor deposited UO_2 crystals are shown in Figure 3.

Irradiation Effect on Volatility and Crystal Growth

Mass vaporization rates of irradiated UO_2 appeared to vary inversely as the melting point as a function of neutron dose. Neither the mass nor the surface area of each specimen was measured, thus quantitative vapor pressure data cannot be formulated. The specimens were, however, approximately the same size and shape so that any gross differences in volatility were discernable. Specimens with exposures less

FIGURE 3

Uranium Dioxide Crystals
Deposited From the Vapor at 2750 C

than 1.75 at. % burnup exhibited increased melting points and vaporized more slowly than nonirradiated UO_2 during anneals at 2400 C, 2750 C, and the melting point. UO_2 with higher exposures had melting points below 2800 C and vaporized more rapidly than either unirradiated UO_2 or low burnup UO_2 when held at the same temperatures.

Direct comparisons between irradiated and unirradiated UO_2 made by simultaneously heating specimens of each on a common filament clearly illustrate the changes in both melting point and volatility which occur during irradiation as shown by Figure 4. The two specimens in Figure 4 were sintered UO_2 prepared from the same type of powder. They were identical in all respects (aside from slight differences in size and shape) except irradiation exposure. The specimen on the left was irradiated to 0.20 at. % burnup while the one on the right was not irradiated. The specimens were placed side by side in the center of a box-shaped tungsten filament. Picture 4A shows the two at a temperature of 2400 C before any melting or appreciable vaporization occurred. Picture 4B was taken 5 sec after raising the temperature to 2790 C. The unirradiated UO_2 fused and was about 50% vaporized while the irradiated UO_2 did not melt and vaporized only slightly. Picture 4C shows the two specimens after 20 sec at 2790 C. The unirradiated oxide continued to vaporize at a faster rate. Picture 4D was taken at 2880 C where the irradiated UO_2 melted and began to vaporize more rapidly. Pictures 4E, F, and G were taken at time intervals of 2, 3, and 5 min after raising the temperature to 2880 C. At this temperature, both materials were molten at the filament-specimen interface, and both vaporized rapidly. Picture 4H shows the refractory residue which remained solid to 3400 C where the tungsten filament melted.

At both 2790 and 2880 C, the irradiated UO_2 vaporized more slowly with the greater difference at 2790 C. This was because at 2790 C, the irradiated specimen was solid while the nonirradiated specimen melted. The melting material had an increased surface-to-volume ratio and a

FIGURE 4
Melting and Volatility Comparison, 25X
(Left Unirradiated Right 0.20% Burnup)

higher average temperature because, as it melted, it decreased in height causing a decrease in ΔT across the specimen. The difference in vaporization rate at 2790 C thus reflects, primarily, the higher melting point of the irradiated UO_2 . At 2800 C, both specimens melted; and the slightly lower volatility of the irradiated material indicates a possible suppression of the vapor pressure by irradiation.

All irradiated specimens vaporized and formed typical dendritic crystals at temperatures near the melting point. When the temperature of these vapor deposited crystals was decreased to 2750 C, vaporization seemed to occur at lower rates than from specimens of unirradiated oxide at the same temperature.

DISCUSSION

Implications of the results can be discussed either in terms of chemical stabilization, considering probable effects of irradiation upon phase relationships in the uranium-oxygen system, or from a physical point of view which estimates changes in the melting process which might be affected by irradiation. The first approach is amenable to a semi-quantitative analysis and will be discussed in more detail than the latter. The discussions are speculative because of insufficient data to formulate a rigorous quantitative theory.

Chemical Stabilization by Irradiation

Location of the Liquidus Maximum

The maximum in the liquidus of UO_2 need not occur at the stoichiometric composition. The greater solubility of oxygen than of uranium in $\text{UO}_{2.00}$ plus the oxygen-liberating dissociation which occurs indicates the existence of a liquidus maximum at some composition UO_{2+x} where x can be either positive or negative. The increase in melting point of irradiated UO_2 may reflect stabilization of an anion deficient defect lattice by metal fission fragment ions with valences $< +4$. The oxygen vacancies in the electrically neutral, stabilized structure may hold dissolved oxygen atoms, thus a UO_{2+x} solid solution, which would

normally dissociate yielding free oxygen, may be stabilized at temperatures to the melting point. Some other mechanism would have to be responsible for stabilizing lower O:U ratios if x is negative.

If the liquidus maximum is shifted to UO_{2+x} as expected, the irradiated UO_{2+x} as a stabilized solid solution, melts at a higher temperature than the nonstabilized unirradiated oxide. As higher (or lower) O:U ratios become stable with increasing fission fragment concentration (i.e., with increasing irradiation exposure), the liquidus maximum is reached and passed and the melting point decreases with further irradiation time. The bulk concentration of fission fragments required to stabilize the lattice is relatively low (about 0.1 at. %); however, it has been shown that these fragments are not uniformly distributed in a polycrystalline specimen. Instead, they are highly concentrated in the grain boundaries; and the concentration decreases exponentially as the mass gradient is traversed toward the center of each individual grain. ⁽¹⁶⁾

The concentration of fission fragments in the grain boundaries is several times the bulk concentration and may be near that normally required for significant lattice stabilization. The grain boundaries may thus be more refractory than the interior of the grains and may serve as a solid, supporting lattice-work at temperatures where the grain interiors are molten. This is the inverse of the situation normally encountered in melting pure polycrystalline bodies, in which melting is initiated at the grain boundaries or other internal surfaces.

Stabilization of an anion deficient defect lattice occurs in many oxide-additive systems. In at least one system, the addition of a second component to UO_2 results in an increased liquidus temperature, this being the $\text{UO}_2\text{-Y}_2\text{O}_3$ system in which an addition of 4 mole % Y_2O_3 yields a melting point increase of 36 C. ⁽¹⁷⁾

Hypothetical High Temperature Phase Relationships

Two features of the uranium-oxygen phase diagram tentatively established by this work are:

- (1) liquidus maximum of 2930 C at an O:U ratio of 2.006
- (2) melting temperature of 2400 C for oxide with an O:U ratio somewhere between 2.07 and 2.24.

A third consideration is the solubility of uranium in UO_2 at temperatures near the melting point. Anderson and others⁽¹⁸⁾ retained $\text{UO}_{1.97}$ by cooling molten UO_2 in argon, but some doubt is cast on this figure by recent lattice parameter measurements.⁽¹⁹⁾ The approach was to extrapolate the then accepted plot of lattice parameter versus O:U ratio to the composition corresponding to the increased parameter observed in the fused oxide. MacEwan has identified uranium metal inclusions formed in UO_2 pellets by heating to > 2000 C in an O_2 partial pressure of 10^{-7} atmospheres.⁽¹⁹⁾ His calculations show that the most feasible path by which the oxide could be reduced under these conditions is by an oxygen liberating dissociation reaction. Since the oxide was substoichiometric after heating, the net dissociation products probably were oxygen and homogeneous UO_{2-x} from which metallic uranium precipitated on cooling. Rothwell drew parallel conclusions from his study of fission gas release rates for irradiated UO_2 .⁽²⁰⁾ Similar observations have been made at Hanford and other sites.

The microstructure of commercially fused UO_2 , which is often substoichiometric, provides further evidence for the existence of UO_{2-x} . The excess uranium is present as metal, probably because of the low cooling rate after fusion, but it has the appearance of a precipitate. The metal inclusions form a fine dispersion and often appear to be preferentially oriented much as the second phase in an overaged precipitation hardening alloy.

Recent experiments at Hanford retained homogeneous $\text{UO}_{1.997 \pm 0.002}$ by quenching initially $\text{UO}_{2.001}$ from 2700 C in less than 20 sec. Specimens were $\frac{5}{8}$ in. in diameter by $\frac{1}{16}$ in. thick disks cut from adjacent positions in a 95% dense sintered pellet. These were heated from room temperature to 2700 ± 50 C in approximately 20 sec and immediately cooled at the same rate. The furnace atmosphere was helium with 0.002% O_2 . Lattice parameters were measured before and after annealing, and the O:U ratio was determined for the unheated specimen. Results are tabulated below:

<u>Specimen</u>	<u>Lattice Parameter, Angstroms</u>	<u>O:U</u>
unannealed	5.47063 ± 0.00005	2.0011 ± 0.0004
annealed	5.4710 ± 0.0001	
annealed	5.47090 ± 0.00005	

The decrease in lattice parameter during annealing is small but significant. Extrapolating Schaner's⁽²¹⁾ plot of lattice parameter versus O:U ratio yields an O:U ratio of 1.997 ± 0.002 for the annealed oxide. No metal inclusions were found in the annealed oxide at a magnification of 500X. Longer time at temperature and/or a more rapid quench should yield lower O:U ratios. The heating rate was greater than that used for measuring melting points, thus unirradiated UO_2 specimens were probably substoichiometric when the melting point was reached. The measured melting point, 2790 C, is most likely that of homogeneous UO_{2-x} rather than $\text{UO}_{2.000}$.

A tentative phase diagram for uranium-oxygen showing the features discussed above is presented in Figure 5.

Irradiation Effects on the Melting Process

The observed increase in melting temperature with irradiation dose can also be theoretically examined by considering possible irradiation effects on the melting mechanism. Hoffman has related subcrystallite size and vacancy concentration to the entropy-energy diagram for a solid

FIGURE 5

Tentative Uranium-Oxygen Phase Diagram

by considering only the entropy of mixing of atoms and vacancies.⁽²²⁾ This simplified treatment yields energy-entropy curves similar to those in Figure 6. For small subcrystallites, these curves have positive curvature throughout; but for larger subcrystallites (the usual case), two points of inflection occur. Since the slope of the entropy-energy curves equals the absolute temperature ($\frac{\partial E}{\partial S} = T$), the double tangent denotes a temperature at which two phases exist in equilibrium. The higher entropy phase is the liquid, the lower entropy phase is the solid, and the temperature at which they coexist is the melting point. Hoffman concludes that, if a high, metastable concentration of vacancies can be produced in the solid at a temperature less than the melting point, the position, A, on the diagram can be reached. A subsequent rise in temperature at a sufficiently high rate to prevent extensive recombination of

FIGURE 6

Energy-Entropy Curves for Various Subcrystallite Sizes
($N_3 > N_2 > N_1$)

metastable vacancies should permit raising the energy and entropy to equilibrium values corresponding to the normally "forbidden" portion of the curve between the points of common tangency (Point B in Figure 6). Since the slope of the energy-entropy curve in this region is greater than at the melting point, position B represents a superheated solid which should be stable indefinitely at this temperature.

The argument above may apply to the UO_2 examined in these experiments since it was subjected to high neutron, beta, and gamma fluxes which undoubtedly produced a concentration of metastable vacancies. Heating rates during melting point measurements, however, seem too low to prevent recombination of most of the vacancies formed.

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APPENDIX A

Calculation of the Liquidus Maximum

An expression for the composition at the liquidus maximum is⁽²³⁾

$$m = \frac{pqa}{(p+q)^2} \cdot \frac{n-1}{nq/(p+q)} ,$$

where p and q are the subscripts in the general dissociation reaction: $A_p B_q = pA + qB$

m is moles of B which must be added to one mole of $A_p B_q$ to achieve the composition with the maximum melting temperature

a is degree of dissociation

n is ratio of the slopes of the two liquidus curves at their point of intersection, i.e. at the melting maximum.

The reaction for the dissociation of UO_2 may be written as

where Anderson and others⁽¹⁸⁾ have determined the limiting value for x to be 0.14 for initially $UO_{2.00}$ held in the molten state. Thus, $a = 0.07$, and the general dissociation reaction for $UO_{2.00}$ may be written as

thus,

$$p = 1, q = 1.$$

The slope of the liquidus on either side of the maximum can be estimated from the data in Figure 2 which gives the variation in UO_2 melting point with increasing irradiation exposure. It is first necessary to assume that the rate at which high oxygen concentrations are stabilized with respect to irradiation dose is constant for exposures extending slightly to either side of the maximum. If this is true, a linear correspondence exists between irradiation dose and oxygen concentration; and

the ratio of the liquidus slopes when oxygen concentration is plotted as abscissa is the same as the ratio of the slopes on either side of the maximum when irradiation dose is plotted as abscissa.

The ratio of the slopes, n , was estimated by fitting an empirical equation to the data on either side of the maximum and taking the ratio of the first derivatives of the two equations at their point of intersection. The ratio obtained was 1.28. The slope of the curve fitting the data to the left of the maximum had the greater absolute value, thus

$$n = 1.28.$$

Using the values of p , q , a , and n derived above, m was calculated.

$$m = \frac{(1)(1)(0.07)}{(1+1)^2} \cdot \frac{(1.28-1)}{1.28^{(1/1+1)}} = 0.004$$

Thus, the addition of 0.004 moles of oxygen to one mole of $\text{UO}_{2.00}$ yielding an O:U ratio of 2.004 should give the composition with the maximum melting point, 2930 C. O:U ratios of the irradiated UO_2 examined were typically between 2.005 and 2.010 before irradiation. Oxide which was initially substoichiometric would not be expected to have a higher postirradiation melting point since the excess oxygen required to achieve higher melting compositions would not be available. Presumably, this is why the fused UO_2 with 0.11 at. % burnup melted at the same temperature as nonirradiated UO_2 .

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