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THE FABRICATION AND PHYSICAL PROPERTIES
OF URANIA BODIES

by

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ABSTRACT

The fabrication methods employed in forming urania bodies are reviewed. The density of urania appeared to increase with a decrease in the particle size of urania used, and with an increase in firing time and temperature. The melting point of urania was redetermined, and found to be $2880 \pm 20^\circ \text{C}$. The thermal expansion of urania was found to be linear up to 950°C and the average thermal expansion from room temperature to 950°C was found to be $10 \times 10^{-6} \text{ cm/cm/}^\circ \text{C}$. The thermal conductivity is reported to be $0.016 \text{ cal/sec/cm/}^\circ \text{C}$ at 100°C , and the hardness was found to be approximately 6 to 7 on Moh's scale. The specific resistance was found to be 315 ohm-centimeters at room temperature, and the modulus of rupture was found to be approximately 26,200 psi.

Specimens were corroded in water, hydrogen peroxide solutions, and NaK eutectic alloy. The urania was found to be resistant to corrosion in water up to 315°C , and to dilute hydrogen peroxide solutions. Specimens of high density urania heated slowly in NaK alloy to 600°C were found to be in good condition after 72 hours. This would indicate that urania is resistant to corrosion by NaK alloy. Specimens dropped in NaK alloy at 400°C were found to fracture, which would indicate that urania is susceptible to thermal shock. Specimens irradiated to low burnups showed cracking, presumably due to the thermal gradients existing in the specimens during irradiation.

The phase systems $\text{UO}_2\text{-O}$, $\text{UO}_2\text{-Al}_2\text{O}_3$, $\text{UO}_2\text{-Nd}_2\text{O}_3$, $\text{UO}_2\text{-ZrO}_2$, $\text{UO}_2\text{-ThO}_2$, $\text{UO}_2\text{-MgO}$, and $\text{U}_3\text{O}_8\text{-MgO}$ are reviewed.

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1.0 - Introduction:

The high melting point and relative chemical stability of urania make this material suitable for special refractory shapes, and would indicate a possible use of urania as a ceramic fuel element. The use of urania, however, has been limited, due to the lack of sufficient information concerning the physical properties of various urania bodies.

Methods of fabricating urania bodies have been investigated at ANL, and the physical properties of some of these bodies have been evaluated. Much of this information is scattered through the literature, and is not readily available to the casual worker. For this reason it was felt that a contribution to the literature could be made in compiling information from both published and unpublished ANL sources into a form which would make these data available.

2.0 - Raw Materials:

The raw material used in the major part of the work was Mallinckrodt minus 325 mesh urania which presumably came from the regular production line for the manufacture of uranium metal. A typical chemical analysis of this material is shown in Table I. The absolute density of the urania was determined to be 10.25 g/cc by means of a pycnometer with water. This is somewhat lower than the X-ray density of 10.95 gm/cc. The lowered apparent density might be due to slight admixtures of U_3O_8 , adsorbed oxygen on the surface of the finely divided powder or simply to the difficulty in removing all gas bubbles from the sample.

3.0 - Fabrication Methods:

Urania may be fabricated by most methods common to the ceramic industry. Corwin and Eyerly⁽¹⁾ have published techniques and methods employed for dry pressing and slip casting of urania crucibles, and urania has been fabricated by such methods as extrusion, hydrostatic pressing, and hot pressing.

3.1 - Dry Pressing:

In dry pressing the urania is first tempered with six to eight per cent by weight of distilled water. The damp mixture is then pressed in steel dies under pressures of six to twenty tons per square inch. As no organic binder or lubricants are used, the possibility of contaminating the urania is eliminated. The green ware formed by this method is extremely fragile, and it is necessary to resort to mechanical supports and die strippers in fabricating large pieces.

3.2 - Slip Casting:

Slip casting of urania can be accomplished by the acid leaching technique. The urania is first ground in steel pebble mills with steel balls, removed, and leached with hydrochloric acid to remove the iron contamination. This acid slip can then be cast into plaster molds. A small amount of organic binder is recommended to improve the dry strength of the cast ware.

3.3 - Extrusion:

Urania mixed with organic resins may be extruded in a variety of shapes. In this process the urania acts as a filler, and the resin as a lubricant. This method may prove to be the cheapest method for fabricating urania shapes. Ware produced by plastic extrusion is generally of low density; however, improvements in the method may make it possible to produce high density ware.

3.4 - Hydrostatic Pressing:

High density urania ware is usually produced by either hydrostatic pressing or by hot pressing. In hydrostatic pressing urania powder is packed in a rubber mold. The mold and the powder are placed in a pressure vessel containing a fluid and equipped with a pressure piston where it is pressed under pressures in the neighborhood of thirty-five tons per square inch. After pressing, the compact is ground to size prior to firing. This method has been used commercially to produce ceramic insulators of other materials.

3.5 - Hot Pressing:

The technique of hot pressing requires the simultaneous application of heat and pressure. In hot pressing, graphite molds are used generally, and there is always the possibility of contaminating the urania with uranium carbide. This method has not yet been used at ANL, but equipment is now being prepared to investigate the applications of this method at this laboratory.

3.6 - Fusion:

Urania has been arc melted; however, no shapes have been made by casting urania melted in this manner. At ANL the urania was melted in tungsten crucibles in an argon atmosphere. The fused samples were found to be contaminated with tungsten. The Norton Company has produced some fairly pure fused urania, and this material has been used in determining some of the physical properties of urania.

4.0 - Firing:

The firing shrinkage, fired strength, and ultimate density of urania ware depends upon the treatment of the urania before and during firing. Dry pressed ware, when fired to 1600° C in a hydrogen atmosphere, was found to be too soft and lacking sufficient strength for most applications. Dry pressed crucibles, when fired to 1700° C in a hydrogen atmosphere, were found to be satisfactory for most purposes; however, dry pressed ware when fired to 1750° C in a hydrogen atmosphere appeared to be of better quality. Temperatures above 1750° C may be desirable for producing ware of high density, but these temperatures are not practical with the present equipment at ANL.

Firing shrinkages of dry pressed urania are generally lower than the firing shrinkages of slip cast ware. Dry pressed crucibles fired at 1750° C in hydrogen for eight hours had a total shrinkage of nine per cent. Crucibles formed by slip casting followed by a hydrostatic pressing had a total shrinkage of thirty per cent when fired in a hydrogen atmosphere for twelve hours at a temperature of 1750° C. The optimum firing time and temperature for urania has never been determined, but the density of dry pressed crucibles fired at 1700° C for various time intervals was found to increase as the firing time increased up to 230 hours.

5.0 - Density:

The lattice parameter of a sample of fused urania was measured and found to be $5.4708 \pm 0.0002 \text{ \AA}$. From this the theoretical density of the urania was calculated and found to be 10.95 g/cc.

A number of factors which affect the density of urania bodies have been investigated, but these studies are not complete. The effect of particle size on the density of urania bodies was studied by Gunzel and Lambertson.⁽²⁾ In this investigation the particle size distribution was measured for "as received" Mallinckrodt urania, and two samples which had been ground in a pebble mill for 56 and 140 hours. The particle size distribution of a fourth sample of urania was also measured. This sample was calcined at 1750° C in a hydrogen atmosphere prior to being ground for 16 hours in a pebble mill. The particle size distribution of the "as received" urania is shown in Figure 1, while the effect of grinding on the urania is shown in Figure 2. An electron micrograph of the urania after 140 hours of grinding is shown in Figure 3.

Specimens were fabricated by isostatic pressing at 70,000 psi and then sintering in a hydrogen atmosphere at 1750° C for eight hours. The densities of the specimens were measured, and these densities are given in Table II. A trend was noted whereby the density of urania bodies appeared to increase as the particle size of the urania decreased. This trend was also evident as shown by the decrease in porosity of the urania body ground for 140 hours as compared with the porosity of the urania body which had been ground for 56 hours. Photographs of these two bodies are shown in Figures 4 and 5. Specimens formed from the calcined urania ground for 16 hours were found to have an average density of 10.37 g/cc, while specimens formed from the uncalcined urania ground for 56 hours were found to have an average density of 10.25 g/cc. This would indicate that a heat treatment prior to grinding would serve to shorten grinding time in producing high density urania ware.

The method employed in forming a urania body also affects the final density of the body. Table II shows the effect of various changes in fabricating procedures on the final density of urania ware. The low density from the extruded urania is due to the amount of lubricant used, and to the type of extrusion apparatus employed. An increase in pressure in dry pressing will result in higher densities. This is shown by samples A and B (Table II). In comparing the methods used in producing urania ware, it appears that the highest densities are obtained by isostatic pressing. However, particle size data are lacking, and it might be possible to produce high density ware by using a modified dry pressing procedure and an extremely fine urania grain.

The firing time and temperature are also known to affect the density of urania ware. A firing temperature of 1700° C was necessary to produce good fired strength in dry pressed urania ware. However, the density of this dry pressed urania ware fired at 1700° C was found to increase as the firing time increased up to 230 hours. Dry pressed ware fired in a vacuum at 2000° C, and dry pressed ware fired at 2700° C in an atmosphere of purified helium tended to decrease in density. This loss appeared to stem from vaporization of the urania from the pores of the ware, and would indicate that the firing temperature necessary to produce ware of maximum density would be between 1700° and 2000° C.

6.0 - Melting Point:

The melting point of uranium dioxide in an atmosphere of nitrogen was reported by Ruff and Goecke⁽³⁾ to be 2176° C. Friederich and Sittig⁽⁴⁾ found the melting point of urania to be between 2500° and 2600° C, while the melting point of urania as given in the Project Handbook⁽⁵⁾ is between 2200° and 2600° C. In order to have a more precise melting point for phase equilibrium work, the melting point was redetermined at ANL.

High purity Mallinckrodt uranium dioxide (analysis - Table III), having a particle size smaller than 74 microns, was placed in a tungsten crucible. The crucible containing the urania was heated in a tungsten resistance furnace⁽⁶⁾ using a purified helium atmosphere.

Temperature measurements were made with a Leeds and Northrup optical pyrometer previously calibrated by the Bureau of Standards. The sight glass absorption was calculated by means of a G. E. tungsten filament calibration bulb, and extrapolating to the high temperatures involved. Using this technique the melting point of platinum was found to be between 1771° and 1773° C.

The first sample of urania was observed to melt at a temperature of 2889° C. This sample when cool was analyzed spectrochemically and found to be better than 99.95 w/o uranium dioxide. An oxygen analysis (Table III) of the melted sample indicated that the melting point determined was for UO_2 , and not for a lower oxide. The lattice parameter of the melted sample was determined by means of X ray, and found to be $5.4725 \pm 0.0001 \text{ \AA}$.

As a slight overshooting of the melting point may have occurred in melting the first sample, a second sample of urania was heated to 2866° C without melting. This would indicate that the melting point of urania would be $2880 \pm 20^\circ \text{ C}$.

7.0 - Thermal Expansion:

The thermal expansion of slip cast urania fired in a hydrogen atmosphere to a temperature of 1750° C was measured from 18° C to 950° C by means of a fizeau-type interferometer. This interferometer was equipped with a vacuum furnace, and an automatic recording camera which measured the absolute expansion in terms of a known monochromatic light source.

Specimens in the form of small cones were cut from the cast and fired urania slugs. These cones were then heated at the rate of 205° C/hour under a vacuum which varied from 10^{-4} to 10^{-7} mm of Hg during the run. The contraction of the urania specimens was also recorded. However, during the cooling cycle considerable difference in temperature existed between the thermocouple and the specimen.

The thermal expansion of urania (Figure 6) was found to be essentially linear from 100° to 850° C as shown by the straight line drawn next to the expansion curve in Figure 6. The slight deviation below 100° C was thought to be due to the seating of the interferometer specimens, and the temperature difference which may have initially existed between the specimens and the thermocouple. At 850° C a slight increase in the rate of expansion was observed. As no phase changes were indicated, no explanation for this increase in rate of expansion could be formulated. The calculated

linear expansion of urania for 100° C intervals are given in Table IV. The average linear expansion of urania was found to be $10 \times 10^{-6} \text{ }^{\circ}\text{C/cm}$ for the temperature interval 100° to 800° C.

The deviation of the cooling curve from the heating curve was due to the difference in temperature between the specimens and the thermocouple. This difference in temperature reached a maximum of 45° C at a temperature of 125° C.

8.0 - Thermal Conductivity:

The thermal conductivity of a urania body having a density of 10.23 g/cc was determined by Weeks by means of a steady state apparatus⁽⁷⁾ which accommodated a cylinder of urania 1-15/16 inch in length and 0.227 inch in diameter. By passing known amounts of heat axially through the specimen, temperature gradients of 20° C and 11° C per centimeter of length were established. From this the thermal conductivity of urania was calculated to be $0.0226 \pm 0.003 \text{ cal sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at 87.3° C, and $0.0225 \pm 0.003 \text{ cal sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at 61.3° C.⁽⁸⁾ From these data the thermal conductivity of urania of theoretical density was calculated by simple proportion, and found to be $0.0241 \text{ cal sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at 87.3° C and $0.0240 \text{ cal sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at 61.3° C.

Kingery and Vasilos^(9, 10) determined the thermal conductivity of a urania body having a density of 8.08 g/cc over a range of temperature from 100° to 1000° C, and then calculated the thermal conductivity of urania of theoretical density. These conductivities are shown in Table V, and a plot of Weeks' and Kingery's data is shown in Figure 7.

9.0 - Specific Resistance:

The electrical properties of urania for the most part have not been investigated. The resistance of a urania rod, measuring 0.94 cm in diameter and 8.74 cm in length and having a density of 10.4 g/cc, was calculated from Ohm's law by placing a known voltage across the specimen and measuring the current which flowed through the sample. The specimen was found to have a resistance of 400 ohms. This would indicate that urania would have a specific resistance of 315 ohms-cms at room temperature.

10.0 - Hardness:

Hardness measurements were made on a sample of electrically fused urania having a lattice parameter of 5.471 Å. These measurements were taken in areas which were free from inclusions, and the urania was found to have an average Knoop hardness of 666 ± 14 . This hardness would compare to a hardness of 6 to 7 on Moh's scale, and would be approximately the same as quartz parallel to the c axis.

11.0 - Mechanical Properties:

Three samples of urania measuring 0.25 inch in diameter and 2 inches in length, having a density of 10.6 g/cc, were broken by bend testing in a Tinius-Olsen 2000 pound capacity electromechanical Lo-Cap Universal testing machine. One rod was loaded at a fast rate and failed at a modulus of rupture of 10,000 psi. The remaining two rods were loaded at a rate of 0.05 inch per minute. One of these rods failed at a modulus of rupture of 27,500 psi while the second rod failed at a modulus of rupture of 24,800 psi.

The deflection was measured on the rod which had a modulus of rupture of 24,800 psi, and Young's modulus of elasticity was calculated. This was found to be 21×10^6 psi and is similar to that found for thoria.

12.0 - Aqueous Corrosion Resistance:

Small cylinders of urania having a density of 10.6 g/cc were corroded by Draley, Ruther, and McWhirter of ANL. These urania samples were exposed for four weeks to distilled water at 100° C, distilled water at 315° C, and to a 9×10^{-4} N hydrogen peroxide solution at 100° C. The tests at 100° C were conducted in a closed Pyrex specimen chamber which was supplied continuously with fresh solution. The temperature was maintained by applying heat to the bottom of the specimen chamber in quantities sufficient to maintain boiling. The hydrogen peroxide solution was saturated with helium gas and the samples exposed to this solution were degreased with ethyl alcohol before testing. The urania samples exposed to water were tested without degreasing. The test at 315° C was conducted in a small stainless steel autoclave which was heated by placing the autoclave in an electric oven.

Weight change data were recorded. As previous experience had shown that the weight of urania samples was sensitive to the method used in drying and weighing, a fixed routine was established. The samples, as removed from the test solutions, were vacuum dried for twenty minutes, then transferred to a room maintained at 75° F and 40% relative humidity. After thirty minutes in this room, the samples were weighed.

At 100° C in distilled water there were essentially no changes in appearance or weight (Table VI) during the four-week test. There was, however, a slight increase in the weight loss in the samples which were removed and dried at the end of one, two, and three weeks when compared to the weight losses of the samples which were exposed continuously for four weeks. Samples exposed to the hydrogen peroxide solution were found to have small weight losses (Table VII). These samples were quickly covered with a thin film of a light gray color. As the exposure time increased, this film developed a mottled appearance with areas of a yellowish gray color. The film did not appear to be of a uniform thickness and did not

appear to increase in depth during the exposure. The formation of this film would tend to make the weight change data misleading when these data are taken as an indication of deterioration of the specimen.

The samples of urania exposed to distilled water at 315° C also were found to have small weight losses (Table VIII). These samples lost their original shiny glaze after three weeks' exposure and turned to a dull, brown-black color. The weight-change data for sample F is somewhat misleading due to a slight chipping of the specimens, which took place during the opening and closing of the autoclave.

These tests indicate that urania is quite stable when exposed to distilled water at temperatures up to 315° C and to dilute hydrogen peroxide solutions at 100° C. The film formed on the samples exposed to the hydrogen peroxide solution and the loss of glaze on the samples exposed to 315° C water may be an indication of deterioration, such as loss of strength, which would not be apparent from weight change data. A photograph of the exposed urania samples is shown in Figure 8.

13.0 - NaK Alloy Corrosion Resistance

Four samples of urania fabricated by cold pressing and by slip casting were subjected to corrosion tests in static "pure" and "impure" NaK alloy. The densities and firing temperatures of the urania specimens are shown in Table IX. The main contaminant in the "impure" NaK alloy was thought to be oxygen. In this test four samples of urania were placed in NaK alloy and heated rapidly to 600° C. Exposure time at this temperature was 72 hours. A photograph of the stainless steel bomb used in testing these specimens is shown in Figure 11.

Photographs of the urania specimens before and after exposure to the NaK are shown in Figures 9 and 10. From the appearance of the specimens after exposure, it appeared that the urania was severely attacked by NaK alloy at 600° C. However, this test was not conclusive as there was an indication that the urania specimens fractured because of thermal stress and not by reacting with the NaK alloy.

Pellets of sintered urania having a density of 10.6 g/cc and measuring 3/16 inch in diameter and 1/2 inch in length were dropped into molten NaK alloy at 400° and 550° C. At 400° C the pellet fractured into pieces approximately 1/8 inch in diameter. At 550° C the pellet fractured into a fine powder. These tests indicated that high density urania would not withstand thermal shocks of from 400° C to room temperature.

Five additional pellets having a density of 10.4 g/cc were placed in NaK alloy, and heated to 600° C in 2.5 hours. Uranium chips were placed in the alloy to insure its being free of oxygen. A leak developed in the system after 72 hours at 600° C, and the test was discontinued. The weight

loss of the samples varied between 0 and 3 mg/cm², and averaged 0.1 mg/cm². A photograph of one of the pellets after testing is shown in Figure 12. This test would indicate that high density sintered urania has good corrosion resistance to NaK alloy.

14.0 - Thermal Shock Resistance:

Very little data are available concerning the resistance of urania ware to thermal shock, and no standard tests have been devised to evaluate the resistance of urania to heat shock. During the NaK alloy corrosion tests, four samples of urania (Table IX) were placed in NaK alloy, and rapidly heated to 600° C. These specimens were found to be fractured after 72 hours' exposure (Figures 9 and 10). Pellets of sintered urania, having a density of 10.6 g/cc, were dropped into molten NaK alloy at 400° and 550° C. At 400° C the pellets were found to fracture into small pieces approximately 1/8 inch in diameter, while at 550° C the pellets were found to fracture into a fine powder. These tests would indicate that high density urania has little or no resistance to thermal shock.

15.0 - Irradiation Effects on Urania:

Four specimens of urania measuring 3/16 inch in diameter and 1/2 inch in length, having densities estimated to be from 8.2 to 10.5 g/cc, were irradiated in MTR. Two specimens were irradiated submerged in NaK alloy in aluminum capsules, while the remaining two specimens were packed in steel wool in their aluminum irradiation capsules. The two specimens submerged in NaK alloy were exposed for 8 days and had a total uranium burnup of 0.048 (Table X). Figures 13 and 14 show the appearance of the specimens before and after irradiation. The fractures which occurred could be due in part to mechanical shocks imposed by normal handling and irradiation of rabbit capsules at the MTR. It is unlikely, however, that all the smaller pieces could have been produced in this manner.

The two specimens packed in steel wool were irradiated to a total uranium burnup of 0.16 and 0.38 (Table X). Figures 13, 15, and 16 show the appearance of these specimens before and after irradiation. Both specimens were fragmented, and as these specimens were cushioned by steel wool from mechanical shock, this fragmentation must have resulted from stress induced by irradiation or thermal shock.

16.0 - Uranium Oxide Binary Phase Equilibrium Systems:

Several binary phase equilibrium systems involving uranium dioxide and one other oxide have been studied. Mixtures of these oxides were pressed into pellets and fired. These fired pellets were then reheated to various temperatures and quenched. Chemical and X-ray analyses were made and the phase relationships were thus established.

16.1 - Uranium-Oxygen System:

The uranium-oxygen system was investigated and uranium dioxide was found to be quite stable when heated either in a hydrogen atmosphere, a purified helium atmosphere, or a vacuum. Small changes in the lattice parameters were detected. These changes were attributed to small changes in the oxygen content of the samples, but these changes were so small that it was indicated that the uranium oxide remained very close to the composition UO_2 . The lattice parameter of a sample of UO_2 which had been melted in a helium atmosphere was measured by means of X rays, and found to be $5.4725 \pm 0.0001 \text{ \AA}$. This sample when analyzed chemically was found to have a composition corresponding to $\text{UO}_2 \pm 0.005$. The lattice parameters of two additional samples were measured and found to be $5.467 \text{ \AA}$, and $5.4708 \pm 0.0002 \text{ \AA}$. These values compare favorably with the lattice parameter of urania of $5.4691 \pm 0.0005 \text{ \AA}$ as reported by Rundle, Baenziger, Wilson, and McDonald, (11) and with a lattice parameter of $5.467 \text{ \AA}$ for UO_2 as reported by Alberman and Anderson. (12) Other values reported are: $5.457 \text{ \AA}$ by Slowinski and Elliott; (13) $5.4568 \pm 0.005 \text{ \AA}$ by Zachariason; (14) and $5.455 \text{ \AA}$ by Trzebiatowski and Selwood. (15) Rundle et al. (11) point out that the lattice parameter of UO_2 decreases with additional oxygen; however, Alberman and Anderson (12) found no such change. From the studies at ANL it is indicated that a decrease in lattice parameter occurs with an increase in the oxygen content.

A mixture of 50 mol per cent of U_3O_8 and 50 mol per cent of UO_2 was heated in a tungsten crucible to 2000°C in a helium atmosphere. During the heating a considerable amount of gas was given off by the sample. The sample was then quenched and the residue was identified as UO_2 . Several pellets of U_3O_8 were pressed and heated in air to 1700°C . These pellets disintegrated and no evidence of sintering was observed. A sample of U_3O_8 was heated in a stream of oxygen and a record of the weight change of the sample was made. There was a slight loss in weight in heating the sample to 370°C , which was thought to be due to the absorbed moisture in the sample. The sample then gained weight up to 800°C . Above 800°C a loss in weight was observed. The rate at which the sample lost weight appeared to increase as the temperature increased up to 1400°C . From these observations it would appear that U_3O_8 , when heated in the presence of oxygen, would decompose to the lower oxide UO_2 . A study of the literature (16,17,18) was made and sufficient information was obtained to plot a curve (Figure 17) showing the change in oxygen content in the oxides of uranium with an increase in temperature. Sheft and Fried (19) report that U_3O_8 can be stabilized through the use of inhibitors. This should make it possible to fabricate bodies of U_3O_8 .

16.2 - UO₂-Al₂O₃ System:

The equilibrium points of the UO₂-Al₂O₃(20) system were established by heating mixtures of urania and alumina for periods of time as long as one month. X-ray examinations of these mixtures indicated that no solid solution or new phases were formed.

The liquidus of the system was determined by heating mixtures until the sample lost its original shape and flowed. The data obtained are shown in Table XI and a plot of these data is shown in Figure 18. The theoretical eutectic composition and temperature were calculated according to the method developed by Epstein and Howland(21) and found to be at 1900° C at 74% Al₂O₃. After the eutectic temperature had been calculated from the ideal solution theory, the same theory was used to explain the entire liquidus curve. These data are shown in Table XII and in Figure 18. The experimental liquidus was found to be somewhat lower than the theoretical liquidus, and from 50% to 75% Al₂O₃ there was little change in the liquidus temperature. This would indicate the possible existence of two immiscible liquids, so several samples of 38% UO₂-62% Al₂O₃ were heated into the liquid region, held 5 minutes, and quenched. Macroexamination of the quenched samples showed relatively large areas of two different colored phases. Micropolished sections of these samples showed regions of high and low UO₂ concentrations. This would indicate the existence of two immiscible liquids. Based on these data the UO₂-Al₂O₃ binary system was proposed as shown in Figure 19.

16.3 - UO₂-Nd₂O₃ System:

The investigation of the system UO₂-Nd₂O₃(22) (Figure 20) indicated that a rather unusual and extensive series of solid solutions was formed. Neodymia appeared to form an extensive solid solution with UO₂ while the UO₂ appeared to be only slightly soluble in the Nd₂O₃. The proposed phase diagram is not exact as the Nd₂O₃ (Table XIII) used was impure. This, however, should not affect the formation of compounds which might exist in the system.

In order to check the stabilizing effect of Nd₂O₃ on UO₂, small samples of several compositions of Nd₂O₃-UO₂ were sintered at 1600° C in hydrogen, and then reheated to 1000° C in air. X-ray diffraction patterns of the 0 - 45% Nd₂O₃ showed the presence of the orthorhombic U₃O₈ phase plus a face centered cubic phase. Between 45 - 80% Nd₂O₃ only a face centered cubic phase was evident, and above 80% Nd₂O₃ the hexagonal Nd₂O₃ was present before and after heating in air. In view of the large amount of Nd₂O₃ necessary to maintain a face centered cubic phase, Nd₂O₃ would not be considered a good stabilizer.

16.4 - UO₂-ZrO₂ System:

The UO₂-ZrO₂ phase equilibrium system, (22) as shown in Figure 21, contained an extensive solid solution but no new compounds were found in this system. The UO₂ solid solution was cubic and extended up to 52 mol per cent of ZrO₂. The ZrO₂ solid solution was tetragonal and extended from 53 to 100 mol per cent of ZrO₂. In this system there were some indications that the zirconia transformed to a polymorphic form other than the monoclinic or tetragonal forms at approximately 1900° C. The eutectic composition was found to contain approximately 52.5 mol per cent of zirconia and the eutectic temperature was found to be approximately 2550° C.

16.5 - UO₂-ThO₂ System:

Urania and thoria (23) form a continuous series of solid solutions as shown in Figure 22. The solidus-liquidus extended from 2875° C for urania to above 3200° C for thoria. The portion of the liquidus curve above 3232° C was extrapolated as shown by the broken line. Methods employed in an attempt to determine the melting point of thoria were not satisfactory.

16.6 - UO₂-MgO System:

In the system UO₂-MgO (24) (Figure 23) no new compounds or solid solutions were found. The eutectic composition was found to be between 70 and 80 mol per cent of magnesia, and the eutectic temperature was found to be approximately 2100° C. The uranium dioxide was oxidized to some extent by the magnesia, and at temperatures above 2000° C the magnesia vaporized rapidly. The oxidization of the urania by the magnesia distorted the binary system so that a very small portion of the ternary system UO-MgO-O was in effect studied. This distortion is shown in Figure 24 between the dotted lines drawn from the points representing the compositions UO₂ and MgO.

The experimental liquidus was found to deviate from the theoretical liquidus in much the same manner as the UO₂-Al₂O₃ liquidus. Polished sections were made of samples heated into the two immiscible liquid regions, and while regions of high and low MgO could be detected, the evidence of two immiscible liquids was not conclusive. The existence of the two immiscible liquids as shown is therefore based on the melting points of compositions in this region.

16.7 - U₃O₈-MgO System.

A larger portion of the UO-MgO-O system (21) was also investigated. This portion is shown by the cross hatched area in Figure 24, and is in the system U₃O₈-UO₂-MgO. Two compounds approximating the compositions of MgUO₄ and MgU₃O₁₀ were formed at temperatures below 1000° C. At higher temperatures an extensive solid solution phase was formed. A suggested phase equilibrium diagram of the binary system UO_{2.67}-MgO is shown in Figure 25.

17.0 - Summary:

The properties of urania which have been investigated at ANL are condensed and tabulated as follows:

Melting Point	$2880 \pm 20^{\circ} \text{C}$
Thermal Expansion	$10 \times 10^{-6}/^{\circ} \text{C}/\text{cm}$ (room temperature to 850°C)
Thermal Conductivity	$0.021 \text{ cal/sec } ^{\circ} \text{C}$ (87.3°C)
Specific Resistance	315 ohm-cm 21°C
Hardness	6 to 7 Moh's scale
Young's Modulus	$21 \times 10^6 \text{ psi}$
Aqueous Corrosion Resistance	Good
NaK Corrosion Resistance	Good at 600°C
Thermal Shock Resistance	Poor (400°C to room temperature)

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Table I

SPECTROCHEMICAL ANALYSIS OF MALLINCKRODT URANIA

Oxide	Weight Per cent	Mol Per cent
Alumina	0.002	0.005
Copper Oxide	0.001	0.003
Ferric Oxide	0.001	0.002
Magnesia	0.083	0.554
Silica	0.001	0.005

Table II

FACTORS INFLUENCING THE DENSITY OF UO_2 A. Pressing Pressure Versus Density

Dry pressed "as received" urania fired at 1750°C for 8 hours in hydrogen.

Sample	Pressure (psi)	Density (g/cc)
A	800	5.0
B	70,000	8.9

B. Particle Size Versus Density

Dry pressed 70,000 psi fired at 1750°C for 8 hours in hydrogen.

Sample	Density (g/cc)	Treatment
B	8.90	"As Received" Urania.
C	10.37	Calcined 1750°C. Pebble Milled 16 Hours.
D	10.25	"As Received" Urania Pebble Milled 56 Hours.
E	10.60	"As Received" Urania Pebble Milled 140 Hours.

C. Production Method Versus Density

Sample	Density (g/cc)	Fabrication
F	3.8	Extruded, Fired 1700°C.
A	5.0	Dry Pressed, Fired 1750°C.
G	9.2	Slip Cast, Fired 1750°C.
H	9.6	British Hot Press, 1800°C.
E	10.6	Isostatically Pressed, Fired 1750°C.
K	10.9	Electrically Fused - Norton.

Table III

SPECTRO AND CHEMICAL ANALYSES OF URANIA
MELTING POINT SPECIMEN

A. Before Melting:UO₂ Spectrochemical Analysis

<u>Oxide</u>	<u>Weight Per cent</u>	<u>Mol Per cent</u>
Alumina	0.002	0.005
Copper Oxide	0.001	0.003
Ferric Oxide	0.001	0.002
Magnesia	0.083	0.554
Silica	0.001	0.005

UO₂ Chemical Analysis

UO ₂	99.8%
Wt. Ratio U/O	7.30/1.0
Mol Ratio U/O	1.00/2.039

B. After Melting:

Magnesia 5 parts per million

Oxygen Analysis

Mol Ratio U/O 1.0/2.0 $\pm$ 0.005

X-Ray Analysis

Fluorite Structure,
Lattice Constant 5.4725 $\pm$ 0.0001 Å

Table IV

THERMAL EXPANSION FOR URANIA

Temp. Range °C	Average Linear Coefficient of Thermal Expansion, cm/cm/°C
18-100	7.07 $\times 10^{-6}$
100-200	9.90 $\times 10^{-6}$
200-300	10.00 $\times 10^{-6}$
300-400	9.80 $\times 10^{-6}$
400-500	10.00 $\times 10^{-6}$
500-600	10.20 $\times 10^{-6}$
600-700	10.00 $\times 10^{-6}$
700-800	9.60 $\times 10^{-6}$
800-900	11.20 $\times 10^{-6}$
900-950	11.60 $\times 10^{-6}$

Table V

THERMAL CONDUCTIVITY OF UO_2 (KINGERY AND VASILAS)
THERMAL CONDUCTIVITY (cal/cm-sec-°C)

Temp. °C	Measured Density 8.08 g/cc	Calculated Density 10.95 g/cc
100	0.0164	0.022
200	0.0140	0.019
400	0.010	0.014
600	0.009	0.012
800	0.007	0.009
1000	0.006	0.008

Table VI

WEIGHT CHANGE OF URANIUM DIOXIDE CYLINDERS EXPOSED
TO BOILING DISTILLED WATER (100°C)

Sample	Weight Change in Milligrams per cm^2			
	1 week	2 weeks	3 weeks	4 weeks
A-1	-0.07	-1.0	-1.3	-1.3
B-1	-0.5	-0.9*	-	-
C-1	-0.6	-1.1	-1.3	-1.2
D-1	-0.3	-0.8	-1.0	-0.9
E-1	-	-	-	-1.0
F-1	-	-	-	-1.0
G-1	-	-	-	-1.0
H-1	-	-	-	-1.0

*Sample shattered by fall.

Table VII

WEIGHT CHANGE OF URANIUM DIOXIDE CYLINDERS EXPOSED
TO 9×10^{-4} N HYDROGEN PEROXIDE SOLUTION AT 100°C

Sample	Weight Change in Milligrams per cm ²			
	1 week	2 weeks	3 weeks	4 weeks
I	+0.2	+0.3	+0.3	+0.2
J	+0.2	+0.2	+0.3	+0.2
K	+0.2	+0.2	+0.2	-0.1
L	+0.2	+0.2	+0.2	+0.1
M	-	-	-	+0.1
N	-	-	-	+0.2
O	-	-	-	+0.2
P	-	-	-	+0.2

Table VIII

WEIGHT CHANGE OF URANIUM DIOXIDE CYLINDERS EXPOSED
TO DEGASSED DISTILLED WATER AT 315°C

Sample	Weight Change in Milligrams per cm ²			
	1 week	2 weeks	3 weeks	4 weeks
A	-	-	-	-0.1
B	-	-	-	-0.2
C	-	-	-	-0.1
D	-	-	-	-0.7
E	-0.1	-0.2	-0.6	-0.6
F	-0.0	-4.8*	-4.8*	-4.7
G	0.0	0.0	+0.1	+0.1
H	-0.1	-0.1	-0.1	+0.2

*Sample visibly chipped.

Table IX

PROPERTIES OF URANIUM DIOXIDE SPECIMENS FOR NaK
ALLOY CORROSION

Sample	Source of Specimen	Forming Method	Sintering Temperature (°C)	Specific Gravity
WR-2	Crucible Base	Cold Press	2000	10.45
WR-3	Crucible Base	Cold Press	1750	9.32
WR-4	Bomb Liner Cover	Slip Cast	1700	9.55
WR-5	Cast Solid Rod	Slip Cast	1750	9.55

Table X

BURNUP OF URANIA ATOMS

	Sample			
	AB-16-1	AB-16-2	AB-102	AB-103
Indicated U Atom Burnup	0.048	0.048	0.16	0.38
Calculated Central Temp., °C.			190	315
Calculated Surface Temp., °C.			95	140
Diameter Change, %.			0.0	0.08

Table XI

HEATING RESULTS FROM UO_2 - Al_2O_3 MIXTURES

Composition (mole %)		Temp. (°C)	Time (Min)	Resulting Phases
UO_2	Al_2O_3			
100.0	-	2866	2	UO_2
100.0	-	2889	2	Liquid*
76.9	23.1	2235	5	UO_2 and Liquid
77.2	22.8	2303	5	Liquid
49.1	50.9	1933	5	Liquid*
38.1	61.9	1948	5	Liquid
35.7	64.3	1922	5	UO_2 & Al_2O_3
35.7	64.3	1938	5	Liquid
25.7	74.3	1929	5	Liquid*
13.5	86.5	1967	5	Liquid*
12.0	88.0	1978	5	Liquid*
-	100.0	2028	2	Al_2O_3
-	100.0	2040	2	Liquid*

*Observed sample melt and then measured the temperature under black body conditions.

Table XII

CALCULATED LIQUIDUS DATA $\text{UO}_2\text{-Al}_2\text{O}_3$

Composition (mole %)		Liquidus Temp. (°C)
UO_2	Al_2O_3	
100		2878
80	20	2660
60	40	2420
40	60	2141
30	70	1976
25	75	1882
	100	2034
10	90	1986
20	80	1935
25	75	1908
30	70	1880

Table XIII

NEODYMIUM OXIDE COMPOSITION

Oxide	Weight %	Mole %
Nd_2O_3	85.22	77.80
Gd_2O_3	0.92	0.80
MgO	0.08	0.61
Pr_2O_3	2.34	2.18
SiO_2	2.14	11.00
Sm_2O_3	9.29	8.18
V_2O	0.01	
	100.00	100.57

Figure 3. Electron Micrograph of Mallinckrodt UO_2 Powder.
The As Received Powder was Ground in the Ball Mill
for 140 Hours. Black Particles are the Oxide Grains.

Figure 4. Porosity of Fired Body

Micro 14447

500X

UO₂ ground 56 hours in ball mill, hydrostatically pressed at 35 tons/square inch and fired at 1750°C for 8 hours in hydrogen. (Density = 10.25 gm/cc)

Figure 5. Porosity of Fired Body

Micro 14448 500X
UO₂ ground 140 hours in ball mill, hydrostatically
pressed at 35 tons/square inch and fired at 1750°C
for 8 hours in hydrogen. (Density = 10.6 gm/cc)

FIGURE 8. UO_2 CORROSION PELLETS

FOUR WEEKS EXPOSURE IN EACH CASE

315°C
DISTILLED WATER

100°C
DISTILLED WATER

100°C - 10^{-3} N
 H_2O_2 SOLUTION

3X

Figure 9. Sintered Uranium Dioxide Specimens Before Exposure to NaK Alloy.

Figure 10. Sintered Uranium Dioxide Specimens After Exposure to NaK Eutectic Alloy

SINTERED URANIUM DIOXIDE
SPECIMENS IMMERSSED IN
Na-K EUTECTIC ALLOY AT
600 C

AFTER EXPOSURE

Pure Alloy

Impure Alloy

Macro 13068

Figure 11. Stainless Steel Bomb Used in NaK
Corrosion Testing of Sintered Urania.

Macro 12845

Figure 12. High Density Urania Pellet After
NaK Corrosion Test.

Macro 14060 2X
UO₂ pellet having a density of 10.4 g/cc after
exposure to 600°C NaK for 72 hours.

Figure 13. Appearance of UO_2 Bodies Before Irradiation.

Macro 16126

2X

Figure 14. Appearance of UO_2 Bodies AB-16-1 and AB-16-2 After Irradiation.

Macro 15963

2X

Figure 15. Specimen AB-102 After Irradiation.

Macro 18635

2X

Figure 16. Specimen AB-103 After Irradiation.

Macro 18636

2X

Figure 20. Probable UO_2 - $\text{NdO}_{1.5}$ Phase Equilibrium Diagram

Figure 21. UO_2 - ZrO_2 Phase Equilibrium Diagram

Figure 22. UO_2 - ThO_2 Phase Equilibrium Diagram

Fig. 23. $\text{UO}_{2-2.1}$ - MgO Phase Equilibrium Diagram FIG. $\text{UO}_{2-2.1}$ - MgO PHASE EQUILIBRIUM DIAGRAM

Figure 24. UO - O - MgO Phase Relationships

Figure 25. Suggested (U_3O_8 + Oxygen) - MgO Phase Equilibrium Diagram