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ORNL-2011
Metallurgy and Ceramics

THE TECHNOLOGY OF URANIUM DIOXIDE

A REACTOR MATERIAL

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METALLURGY DIVISION

THE TECHNOLOGY OF URANIUM DIOXIDE

A REACTOR MATERIAL

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Price \$ 0.40

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Introduction

Consideration has been given to various forms of fissionable material for use in atomic reactors, including the pure metals, their alloys and compounds. Of particular interest is the dioxide of uranium which is refractory and corrosion resistant in some environments.

The oxide is useful in both granular and bulk forms. Small grains of uranium oxide can be mixed with other materials to form matrix type elements where they serve either as a convenient or necessary form of fuel or fertile material. For other applications the oxide may be fabricated in bulk form such as pellets, rods, plates or blocks.

There is a need for knowledge of the properties of this oxide, particularly as it affects fabrication in the various forms required. This knowledge is also required by reactor designers and engineers. There is in addition a challenging field for basic studies of sintering rates, oxidation behavior and other phenomena.

Fabrication techniques have been developed to produce uranium oxide in various forms with consideration given to the economy of production. The continued application of basic knowledge of these materials has led to simpler, more practical means of fabrication and has thus widened the scope of their use in atomic reactors.

Physical Properties

Uranium dioxide is a dark brown material in powder form. Its crystal structure is the face-centered cubic CaF_2 type, the uranium ions occupying

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corners and faces. Figure 1 shows a unit cell. The cell dimension is $5.469 \text{ \AA}$, from which is calculated a theoretical density, 10.95. It may be noted that the lattice is relatively "open." The index of refraction of UO_2 is 2.355.

The melting point of UO_2 is stated by most investigators to be about 2800°C . It develops an appreciable vapor pressure much below this temperature, however. Weight losses from UO_2 during sintering have been noted as low as 1400°C . Furnace walls where UO_2 has been sintered are often colored and are radioactive indicating its volatility. The presence of foreign material, such as BeO , seems to increase its volatility. The vapor pressure of UO_2 as reported by Relin and Cefola⁽¹⁾ is shown in Table I. It is not clear, however, as to the nature of the volatility of UO_2 . Uranium has a number of oxidation states and while UO_2 is the stable phase above ca. 1200°C , U_3O_8 has been observed on the surface of UO_2 grains fired at 1800°C in relatively pure hydrogen or CO . The effect of the oxygen on volatility even in very small amounts, may be pronounced.

The thermal conductivity of UO_2 is relatively low among the oxides.⁽²⁾ Debye's⁽³⁾ theoretical treatment of thermal conductivity is given as:

$$K = 1/4 \text{ cv } \lambda \rho$$

K = thermal conductivity

ρ = density

c = specific heat

v = velocity of heat wave

λ = mean free path of wave

In comparing UO_2 with other oxides, it may be noted that while it has a higher density, it also has a lower specific heat. It may be concluded that the mean free path of the thermoelastic wave is less in UO_2 than in other

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Fig. 1. Unit Cell UO_2 .

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Table I⁽¹⁾

Vapor Pressure of UO ₂		(Effusion Method) ⁽¹⁾
Temp. ° C		P (mm Hg x 10 ³)
1600		.071
1750		1.7
1800		4.0
1900		18
2000		72

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oxides. Kingery⁽¹⁾ has summarized the factors affecting λ . In a perfect lattice with harmonic interactions between atoms, λ would be infinite. Anything which may cause inharmonic interactions will cause λ to be smaller. The basic structure of silicate glasses is believed to be a random network of $(\text{SiO}_4)^{4-}$ tetrahedra. In the sense that this may be considered a disordered lattice, it serves to show the effect of disorder on K. At low temperatures the thermal conductivity of silica glass is nearly 50 times less than that of crystalline silica (quartz). As will be shown below, UO_2 is usually not stoichiometric after fabrication and readily assumes what might be considered defective structures. ThO_2 of similar structure apparently may be readily saturated with anion vacancies. There is also an effect on harmonic interactions as a result of the large difference in the masses of U^{+4} and O^{-2} in UO_2 .

The thermal expansivity of UO_2 is relatively high as compared with most ceramics. It increases slightly with increasing temperature.

The strength and modulus of elasticity of UO_2 are of the same order as those of most other oxides. It is interesting to note that Burdick of the NBS reports⁽⁴⁾ that the strength of UO_2 increases with increasing temperature, at least up to 1000°C . Moduli of rupture values are given from 12,000 psi at room temperature to 18,000 psi at 1000°C . At temperatures above 1400°C , however, UO_2 , like other oxides at high temperatures, seems to become subject to plastic deformation and rapidly loses strength with increasing temperature.

The petrographic examination of UO_2 can be divided into two methods: examination of powdered samples ($\sim 100 \text{ M}$) and examination of thin sections taken from sintered compacts. The method used depends upon the form of the

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sample and the information desired. If the grain sizes of powdered samples are less than three to five microns, the petrographic microscope cannot be used effectively to examine the sample.

Determinations which can be made on powdered samples are the measurement of refractive index, measurement of grain sizes, evaluation of grain shapes, and a qualitative evaluation of surface area.

From thin sections of UO_2 compacts the crystal sizes and compact porosity can be measured. Standard thin sections of nonopaque materials are 0.03 millimeters thick. However, due to the low transmission of light by UO_2 , thinner sections are required for petrographic examination.

A summary of physical property data is given in Table II.

Oxidation Behavior

General

There have been numerous investigations of the oxides of uranium. It has been well established that UO_2 is readily oxidized at temperatures just above room temperature. There is no universal agreement, however, as to the compositions of the oxides which are formed. UO_2 , U_4O_9 , U_3O_7 , U_2O_5 and U_3O_8 have all been reported.⁽⁵⁾ In addition, it has been reported that UO_2 takes oxygen into its structure up to a composition, $\text{UO}_{2.30}$, with the cubic unit cell shrinking to a minimum value, 5.430 Å, at this composition.⁽⁵⁾

Seven different source materials (Table III) were examined in a number of DTA-Gravimetric tests. Typical results for each kind of material are shown in Figures 2, 3, 4, 5, 6, 7 and 8. There are two major exothermic reactions and two oxide weight levels shown by these curves. As a typical

TABLE II
 PROPERTIES OF UO_2 AND ThO_2
 ORNL CERAMICS

Property	UO_2	ThO_2
Crystal Structure	face centered cubic (CaF_2)	face centered cubic (CaF_2)
X-ray Density	10.95	10.00
Melting Point	2800° C	3200° C
Thermal Conductivity cal-cm/°C-cm ² -sec (corrected to 100% density)	0.02-20° C 0.008-1000° C	0.02-20° C 0.007-1000° C
Expansivity °C ⁻¹	ca. 10×10^{-6} (0-1000° C)	9×10^{-6} (0-1000° C)
Specific Heat cal/g-°C	0.056 (0-200° C)	0.058 (0-800° C)
Tensile Strength	ca. 5000 pounds per square inch	ca. 5000 pounds per square inch
Modulus of Elasticity	25×10^6 pounds per square inch	21×10^6 pounds per square inch
Metal atoms/cc in oxide	51.5 per cent	78.5 per cent
Index of Refraction	2.35	2.09

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TABLE III

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UO₂-U₃O₇ OXYGEN CONTENTS FROM D.T.A. - WT.

CHANGE DATA, ORNL CERAMICS

Source Material	Fused Oxide	Ammonium Diuranate Ppt. Oxide	Mallinckrodt Oxide	Hydrogenated Steam Oxidized Oxide	Oxidized U Chips	Peroxide Ppt. Oxide	UO ₃ Hydrate Crystal Oxide
Initial Oxide calculated by wt. change UO ₂ + x	UO _{2.005}	UO _{2.129}	UO _{2.153}	UO _{2.02}	UO _{2.023}	UO _{2.056}	UO _{2.013}
Intermediate Oxide U ₃ O ₇ + x	----	UO _{2.383}	UO _{2.375}	UO _{2.336}	UO _{2.351}	UO _{2.369}	UO _{2.339}
H ₂ O/g.	.003	.0015 ¹	.0020	.0003	.0003	.0004	.0003
Initial Oxide Chemical Analysis	-----	UO _{2.091}	-----	UO _{2.021}	UO _{2.044}	UO _{2.083}	UO _{2.005}

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Fig. 2. Ammonium Diuranate PPT. UO_2 - D.T.A. and Weight Change from UO_2 to U_3O_8 .

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Fig. 3. Y-12 Steam Oxidized U Chips - Combined D.T.A. and Weight Change from UO_2 to U_3O_8 .

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Fig. 4. Hydrogenated Steam Oxidized UO_2 - D.T.A. and Weight Change from UO_2 to U_3O_8 .

Fig. 5. Peroxide PPT. UO_2 - D.T.A. and Weight Change from UO_2 to U_3O_8 .

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Fig. 6. Mallinckrodt UO_2 - D.T.A. and Weight Change from UO_2 to U_3O_8 .

Fig. 7. Fused UO_2 - D.T.A. and Weight Change from UO_2 to U_3O_8 .

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Fig. 8. UO_2 from Hydrogen Reduced UO_3 - D.T.A. and Weight Change from UO_2 to U_3O_8 .

UO_2 is heated, a slight weight decrease occurs about 100°C , accounted for as water loss. It then gains weight continuously until a temperature of about 200°C is reached. From 200°C - 400°C its weight is relatively stable after which it once more gains weight, becoming relatively stable again above 450 - 500°C . Two peaks occur on the DTA curve at about 200°C and 400°C , the latter being larger. The oxide above 500°C is U_3O_8 . The intermediate oxide is U_3O_7 . Figure 9 summarizes the oxidation behavior of UO_2 . A description of the DTA-Gravimetric apparatus and its use are given in the Appendix.

Uranium Oxides

Of the uranium "dioxides" used in the DTA investigations, four were nearly stoichiometric UO_2 . X-ray diffraction patterns of all the oxides were similar, showing the same cubic lattice; however, an increase in $2-\theta$ for the cubic lines was noted with increasing oxygen content. Precision measurements⁽⁶⁾ showed the unit cell dimension, a_0 , to be 5.4694 for $\text{UO}_{2.02}$ and 5.4635 for $\text{UO}_{2.13}$, for example. The X-ray diffraction lines are broad and indistinct in the back reflection region for this latter composition indicating a partial loss of symmetry. This shrinkage of the unit cell and a corresponding increase in powder density has been reported by other workers.⁽⁵⁾ It is postulated, therefore, that oxygen atoms enter into the lattice as interstitial defects and take part to some extent in the structure as bonded ions.

U_3O_7 , stable only in a narrow temperature range, about 200°C - 400°C , was found to have a face-centered tetragonal structure with $a = 5.37$ and $c = 5.55$. It also was found to exist with varying oxygen contents. For example, $\text{UO}_{2.02}$ oxidized to $\text{UO}_{2.336}$, very nearly the stoichiometric U_3O_7 , while $\text{UO}_{2.13}$ oxidized to $\text{UO}_{2.38}$. Thus apparently U_3O_7 as well as UO_2 can accommodate excess oxygen in

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Fig. 9. UO_2 Oxidation States.

its structure. No effect on the tetragonal cell size was noted, however.

U_3O_8 is formed from U_3O_7 by oxidation about $400^\circ C$. It may be noted that U_3O_8 begins to lose oxygen at temperature above $550^\circ C$ - $600^\circ C$, reverting to UO_2 between $1150^\circ C$ and $1400^\circ C$. Thus U_3O_8 is also non-stoichiometric over most of its "stability" range, this, however, involving oxygen deficiency rather than excess as in the case of the two lower-oxides described. U_3O_8 is a black powder having an orthorhombic structure. Its lattice dimensions are $a = 6.70$, $b = 3.97$, and $c = 4.14$. A theoretical density of 8.39 may be calculated for this structure.

UO_2 Reactions

The thermodynamic properties of uranium oxides are given by Brewer⁽⁷⁾ as shown in Table IV.

Water

UO_2 is not reactive with water up to $300^\circ C$. Sintered or hot pressed UO_2 specimens have been heated to this temperature in autoclaves with no apparent change in physical properties and no weight change.

Acids

UO_2 is insoluble in HCl (except fuming) but is soluble in HNO_3 , aqua regia and $HNO_3 + HF$. It reacts with HF (gas) to form UF_4 .

Bases

UO_2 does not react with sodium hydroxide solutions but is soluble in sodium peroxide forming $Na_2UO_4^{(5)}$.

Carbon

Experiments have shown UO_2 to react with carbon at temperatures as low as $1800^\circ C$ when the UO_2 is a very fine powder. On the other hand UO_2 has been

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TABLE IV

Oxide	ΔF_{298} (k cal.)	ΔH_{298} (k cal.)	ΔS_{987} (k cal.)
UO	-123	-129	-21
1/2 UO ₂	-123.3	-129.6	-21.2
1/8 U ₃ O ₈	-100.5	-106.7	-20.8
1/3 UO ₃	- 91	- 97.3	-20.7

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observed in graphite- UO_2 specimens which have been heated as high as 2300°C . In general, UC_2 or U_2C_3 are the reaction products.

Hydrogen

UO_2 does not react with hydrogen at temperature up to its melting point.

Fluorine

UO_2 reacts with HF to form UF_4 ⁽⁵⁾.

Oxides

According to Lang ⁽⁸⁾, UO_2 does not react with Al_2O_3 , MgO and BeO up to 1800°C or with SiO_2 to 1600°C . It forms solid solutions with ThO_2 and ZrO_2 . There is a compound with ZrO_2 , $\text{ZrO}_2 \cdot \text{UO}_2$. UO_2 forms compounds with CaO , but takes CaO into solid solution up to about 40% (mol) CaO . ⁽⁹⁾

Silicon

UO_2 reacts with boiling silicon to form silicides, generally USi_3 at temperatures in the range, 1900°C - 2100°C .

Aluminum

UO_2 reacts with Al at about 500°C to form UAl_4 and UAl_3 . The reaction is relatively slow at this temperature with UO_2 grains larger than 40 microns.

Columbium

UO_2 reacts with Cb at about 1000°C to form solid solution, (Cb-U) and an unknown phase. ⁽¹⁰⁾

Preparation of UO_2 Powders and Grains

UO_2 may be prepared by a number of methods, some of which are given below. For subsequent use in making dense oxide bulk shapes, a fine grain powder is generally desirable. Where the ultimate use is in matrix type fuel elements, a coarser grain is often desired.

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Peroxide Precipitate Method ⁽¹¹⁾

UO₄ dihydrate is made by precipitation in a uranyl nitrate solution with hydrogen peroxide. The UO₄.2H₂O is washed and dried after which it is reduced to UO₂ at 900° C with hydrogen. The UO₂ is sub-micron in size, the particles often being about .05 to .1 microns in at least one dimension.

Ammonium Precipitate Method ⁽¹¹⁾

Ammonium diuranate is precipitated from a uranyl nitrate solution with aqueous ammonia. The precipitate is washed, dried and heated in hydrogen at 900° C.

An extremely fine grained UO₂ results which may be pyrophoric, burning to U₃O₈. It rapidly takes up oxygen from the air in any case, generally stabilizing at about UO₂.15.

Steam Oxidation of U Chips ⁽¹¹⁾

Uranium chips are oxidized to UO₂ by passing 350° C steam over them. The product is heated in hydrogen at 900° C to stabilize it (increase grain size to prevent spontaneous oxidation). This UO₂ is about one micron in size.

Steam Oxidation of Hydrided U Chips ⁽¹¹⁾

Uranium chips are converted to the hydride by heating in hydrogen at 250° C. Further heating in an inert atmosphere at 450° C decomposes the hydride to uranium powder which is then steam oxidized as above. A stable UO₂ having particles about one to five microns in size results.

Reduced U₃O₈ ⁽¹¹⁾

U₃O₈ is made by burning uranium chips. It is reduced to UO₂ in hydrogen at 900°C-1000° C.

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Reduced UO_3 Hydrates

Uranyl nitrate is decomposed by heat to UO_3 hydrate. This powder is then reduced in hydrogen at 800°C to UO_2 . A fine grain oxide results which generally has particles less than one micron in size.

Spray Dried (Decomposed Nitrate) UO_3 Spheres

Uranyl nitrate is spray dried and decomposed in a heating chamber. Spherical UO_3 particles result. These are reduced in hydrogen to UO_2 at temperatures, 1000° to 1800°C . Particles before and after reduction are shown in Figure 10. It may be noted that an undesirable laminar "shell effect" results making a very weak product. Spheres up to several hundred microns in diameter have been made. Townsend⁽¹¹⁾ reports a very fine grain oxide may be made by this method also.

Fused Oxide

UO_2 may be fused in a carbon arc process⁽¹²⁾ to very dense lumps. Pieces more than $1/2$ " in size may be made and subsequently ground and screened to size.

Agglomerated Oxide

UO_2 powders may be sintered at 1800°C - 2000°C to a relatively loosely bonded mass. There is a tendency for finer particles to join to one another into agglomerates. The sintered mass is crushed and screened, removing the agglomerates of desired particle size. These are then resintered at 2000°C to improve the bonding and strengthen the particles. A more efficient method was developed by Sowman⁽¹³⁾ in which UO_2 powders are bonded with an organic binder and crushed and screened to the desired size. These particles are then sintered into strong agglomerates. Small (1%) additions of TiO_2 increased sintering rates such that the UO_2 particles were made dense at 1500°C - 1600°C .

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UO_2 UO_3

Fig. 10. Polished Cross Section of UO_3 and UO_2 "Spheres."

Oxide from Large UO_3 Hydrate Crystals

UO_3 hydrate crystals may be grown hydrothermally in an autoclave at 250°C . Fine grain UO_3 hydrates or UO_4 hydrates are mixed with about 10% uranyl nitrate. Sufficient water is added to maintain a concentrated liquor in the reaction vessel during crystal growth. The crystals have been grown as large as $1/16''$ in their largest dimension. Several crystal forms have been grown including bipyramids, rhombahedra and needles. The UO_3 hydrate crystals are reduced in hydrogen at 1800°C to UO_2 which maintains the same external form as its parent, but is about $2/3$ its size. Single crystals of UO_2 result from needles (gamma phase) of UO_3 which are no larger than 5 to 10 microns. The larger particles of UO_2 produced in this manner are probably composites of UO_2 single crystals about 5 to 10 microns in size. Figure 11 shows the parent UO_3 hydrate crystals and the resulting UO_2 crystals.

Fabrication of UO_2

UO_2 may be fabricated in bulk shapes such as bars, crucibles, tubes, pellets and rods by the usual ceramic methods: cold pressing, slip casting, extrusion and hot pressing. Except for the hot pressed shapes, the products must subsequently be sintered to obtain strong dense bodies. (See Fig. 12).

Three general means of obtaining high density sintered oxides include:

- a. The use of fused or dense grains sized and packed by vibration or tamping prior to sintering.
- b. The use of very fine grains having a large surface area and,
- c. The use of additives or atmosphere control to increase sintering rates by defect structures or surface modifications.

In the case of UO_2 , the use of fused oxide for the dense grain packing method is limited by the poor economy and hazards of the fusion process. Another means of obtaining large dense grains, the hydrothermal UO_3 process described

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UO₃ HYDRATE CRYSTALS

UO₂ PRODUCT

Fig. 11.

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Fig. 12. UO_2 Rods.

above, is also limited by economy for this purpose.

A general disadvantage of using very fine oxide grains to obtain high density products is the associated high shrinkage and accompanying cracking or warping on firing. The best UO_2 products, however, have been made in this way. It is postulated that defect structures also play a part in the sintering of these products inasmuch as the fine grain oxides normally pick up oxygen during storage and handling in the air. ⁽¹⁴⁾

UO_2 must be sintered normally in an inert or hydrogen atmosphere. While atmosphere variations may be used including introduction of air or water vapor at high temperatures (above ca. 1200°C), the products must be protected as they cool through the temperature range where U_3O_8 is stable. (See Fig. 2). Thus whereas atmosphere control may be used to advantage in sintering UO_2 , there are limitations.

The use of additives to provide UO_2 also has limitations arising apparently from the multivalent nature of uranium. For example, an addition of Ca^{+2} to UO_2 might be expected to influence the sintering rate by creating anion vacancies as it does so well with ThO_2 . ⁽¹⁵⁾ That this is not the case may possibly be explained by the ability of U^{+4} to give up two more electrons, going to U^{+6} so that the oxygen ion may remain in the structure when one of the U^{+4} ion sites is occupied by Ca^{+2} . The only addition which has shown any significant effect is TiO_2 , reported by Sowman. ⁽¹³⁾ Densities of 95% of theoretical have been attained in bulk UO_2 with small additions of TiO_2 at temperatures 200°C lower than are normally used to sinter UO_2 .

UO_2 rods made by isostatic pressing, sintering and grinding are shown in Figure 4. The bulk densities of these rods are about 95% of theoretical. They were pressed without binder in a rubber envelope to 40,000 psi. After sintering

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in a clean hydrogen atmosphere at 1750° C for 4 hours, they were ground to final size using a diamond wheel rod grinder.

UO₂ bars and pellets may be made by pressing UO₂ powder plus a few percent dextrose or wax binder in a steel die at 10,000 psi. If one dimension is small (less than 1/4") high density products (> 95%) may be obtained by sintering as outlined above.

Crucibles, cylinders and other hollow thin wall shapes may be made by slip casting a water-UO₂ mix plus HCl⁽¹⁶⁾ deflocculant in a plaster mold. Control of the pH of the slip is important. Normally a pH = 2 yields the best products. Non-porous crucibles of UO₂ may be made by sintering the castings at 1700° C in hydrogen.

Rods and tubes may be extruded from steel dies using organic plasticizers. Small rods about 1/2" in diameter have been extruded at BMI using a 2% addition of Carbopol 934, 1%. The final densities of these products have in general been less than those obtained by the other methods given above.

Radiation Damage

There have been comparatively few radiation damage tests on bulk UO₂. Most of the tests have been conducted by WAPD.

One of the most significant results is that UO₂, like ThO₂, is dimensionally stable to quite high exposures (> 10²⁰ nvt) and relatively high U²³⁵ burn-up (> 50% in normal UO₂). The most serious effect is its tendency to crack as a result of thermal stresses under operating conditions. It is possible that this effect is enhanced by lattice weakening brought about by fission fragment damage.

UO₂ powders lose nearly all of the volatile fission products at temperatures in excess of 900° C. In addition to Xe, I and Te, Mo and some of the rare earths

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have been observed as vaporized fission products from UO_2 powders.⁽¹⁸⁾ The diffusion of these products in bulk UO_2 may be expected to be of the same order of magnitude as in other oxides of 95% or higher theoretical density. At 1000°C , approximately 1 to 10% of the volatile products will be lost in 24 hours from specimens having a minimum dimension of the order of $1/4$ ".

UO_2 As a Reactor Material

Primary consideration has been given to the use of UO_2 as a dispersed reactor fuel in a metal or ceramic matrix. It has been recently proposed as a fuel in bulk form where $1/4$ " diameter UO_2 rods will be canned in Zr.

UO_2 is a relatively stable compound of uranium, generally unreactive with many suitable matrix materials. Its stability against high temperature water makes it a safe form of uranium to use in high pressure water reactor power systems. UO_2 is quite refractory, making possible its use in very high temperature reactors.

It is available in various particle sizes ranging from sub-micron to several hundred microns. It can be fabricated in bulk shapes from tiny pellets to rods more than one inch in diameter and 12" long.

There is a considerable technology on the fluorination of UO_2 powders and it dissolves in nitric-hydrofluoric acid solutions. Thus subsequent chemical processing of spent fuel elements can be handled by methods now developed.

The fabrication of UO_2 is more expensive than fabrication of most oxides because it must be sintered in a controlled atmosphere and because it is a potential radioactive health hazard.

UO_2 is brittle, and having only moderate strength as well as a very low thermal conductivity, it is only fairly resistant to thermal shock.

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It reacts at higher temperatures with two potentially useful matrix materials: aluminum and molybdenum.

In matrix fuel elements (stainless steel, aluminum, SiC-Si, graphite) it has been shown that less radiation damage results in the matrix if separation of the UO_2 particles is greater than ca. 40 microns. The travel of fission products from the UO_2 grains is then generally less than the distance between grains so that an undamaged matrix skeleton remains.

It is not sufficient to add agglomerated grains to matrix materials because subsequent pressing and rolling of metal fuel elements often crushes the grains to undesirable smaller sizes of "stringers." A well sintered grain, of fused UO_2 or a large grain UO_2 from the hydrothermal UO_3 process usually withstands this treatment.

In the case of aluminum- UO_2 matrix elements it was found that a reaction occurred at fabrication temperatures, $\text{UO}_2 \rightarrow \text{UAl}_4$, causing growth and warpage of fuel elements. This reaction was controlled by using large grain UO_2 (> 100 microns) from the hydrothermal UO_3 process which had a relatively low surface area. A similar reaction occurs with silicon ($\text{UO}_2 \rightarrow \text{USi}_3$) at 2000°C which may also be controlled in the same manner.

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APPENDIX

D.T.A. AND WEIGHT CHANGE

METHOD AND ANALYSIS (19)

Differential thermal analysis of a compound may be defined as a method of analysis making use of the thermodynamic changes in a compound as the sample is heated slowly over a wide temperature range. These changes are brought about by a change in chemical composition (oxidation or reduction) or by a phase change in the compound. In every case there is always an evolution or involution of heat accompanying these changes that can be picked up by means of a differential thermocouple, read and recorded either manually or by an automatic strip chart recorder. In the case of a change of chemical composition there is always a change in weight of the sample, whereas in the case of a phase change there is no accompanying weight change. Differential thermal analysis does therefore afford a very useful analytical tool in the examination of many unknown compounds, and especially so if it is accompanied with a continuous recording of weight over the wide temperature range.

The continuous weight recording device can be briefly described as follows:

"An analytical balance has been modified by adding a solenoid and magnet so that changes in weight can be balanced electrically. The operation has been made automatic by reflecting a beam of light from the balance beam into a dual phototube in a bridge circuit and amplifying the output of the bridge to provide current in the solenoid. Recording the voltage drop across a resistor in series with the solenoid gives a linear weight scale which can be made to read directly in milligrams."

By combining the D.T.A. and weight change automatic plots of both machines a very comprehensive graphic picture is obtained.

Fig. (13) shows this apparatus.

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Fig. 13. D.T.A. Weight Change Apparatus.

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