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Preparation of uranium metal and dense UO₂ shapes by the carbon reduction of U₃O₈

James Keith McClusky
Iowa State University

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by

James Keith McClusky

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Nuclear Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Preparation of uranium metal and dense UO_2 shapes
by the carbon reduction of $U_3O_8^*$

James Keith McClusky

Under the supervision of H. A. Wilhelm
From the Department of Nuclear Engineering
Iowa State University

PART I. THE PREPARATION OF URANIUM METAL BY
THE CARBON REDUCTION OF U_3O_8

The carbon reduction of U_3O_8 has been successfully employed to yield high purity uranium metal in massive form by a two-step laboratory-scale process.

The first step or operation consists of preparing an electrically conducting uranium intermediate product (oxycarbide) by partially reducing U_3O_8 with 7.2 moles of carbon in a graphite crucible under vacuum conditions at temperatures between 1550° and $1950^\circ C$. The refining step consists of heating this product by self-induction under vacuum to yield liquid metal in a uranium oxide crucible assembly at temperatures up to about $2200^\circ C$.

*USAEC Report IS-T-460. This work was performed under contract W-7405-eng-82 with the Atomic Energy Commission.

Uranium containing a total carbon, oxygen and nitrogen concentration of less than 400 ppm can be prepared by this process. The yield of metal in the ingot on a 200-g-of-metal scale is greater than 80%.

PART II. THE PREPARATION OF DENSE UO_2 SHAPES
BY THE CARBON REDUCTION OF U_3O_8

A laboratory-scale process for the preparation of dense UO_2 shapes and crucibles by the carbon reduction of U_3O_8 has been developed. The starting oxide, production grade UO_3 , is first wet ball-milled. Next, excess ammonium hydroxide is added to the slurry to precipitate the soluble uranium compounds. The resulting uranium trioxide-ammonium diuranate slurry is then filtered, washed, dried, powderized and calcined to U_3O_8 at $700^\circ C$. Compacts prepared from charges of this U_3O_8 with 0.7 mole of carbon (graphite powder) by cold pressing at $30,000 \text{ lb/in}^2$ sintered to greater than 95 percent of theoretical after two hours in CO_2 at $1400^\circ C$.

Results of this study were then applied to preparing dense UO_2 crucibles by jolt packing. This was accomplished by a two-step process. In the first step, the mixed charge of U_3O_8 and carbon is jolt-packed in the form of a crucible within a graphite mold and then heated to $900^\circ C$ under

nitrogen. Enough densification is produced so that the crucible can be removed and sintered under a CO₂ atmosphere at 1400°C in a graphite-free environment.

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PART I. THE PREPARATION OF URANIUM METAL
BY THE CARBON REDUCTION OF U_3O_8

INTRODUCTION

Prior to World War II, commercial uses of uranium in all chemical forms were less than 100 tons per year. The widest applications were as coloring agents in glassware and glazes used in making porcelain and chinaware. Early in 1940, uranium began to take on new stature when plans were being developed in the United States for pursuing the release of atomic energy by the fission process that had been discovered in 1939. In planning the first self-sustaining nuclear chain reaction experiment in early 1942, Fermi and his coworkers needed tons of high purity uranium, preferably in metallic form, but only gram quantities as metal were available from two industrial laboratories. This need brought about a highly expanded effort to develop processes for large-scale production of the metal. By the time the self-sustaining chain reaction was demonstrated on December 2, 1942, a satisfactory large-scale process for the metal was in operation.

The methods of interest for the preparation of uranium metal during the major development period (1941 and 1942) involved using either a halide or an oxide of the metal. Efforts were focused on the reduction of a uranium halide by electrolysis or by a reactive metal and the reduction of an

oxide by a reactive metal or by carbon. The two laboratory-scale processes that were in operation earlier were expanded during 1942 in hopes of meeting the growing demand for uranium metal (1). These processes were the fused salt electrolytic reduction of KUF_5 developed at Westinghouse and the calcium reduction of an oxide developed at Metal Hydrides, Inc. The metal prepared at Westinghouse was of good quality, but the metal made by the calcium reduction had high oxygen content. However, the probability of early tonnage production from either of these processes appeared quite dim.

Other approaches to the preparation of uranium metal were studied including the carbon reduction of oxide which was explored briefly at Iowa State. The quality of the metal obtained by the carbon reduction indicated that considerable development work would be required if satisfactory metal could be obtained. Thus, attention was directed elsewhere and when uranium tetrafluoride became available in early August 1942, investigators at Iowa State demonstrated that high quality uranium metal could be produced by the calcium reduction of UF_4 in a bomb type process. Later developments employed magnesium instead of calcium and since then that process has been used for large-scale production of uranium metal.

The exploratory work, in 1942, on the carbon reduction of uranium oxide, however, indicated some of the factors that would have to be investigated in order to develop a carbon reduction process for the metal. Since then, further work has occasionally been done on this reduction, but the metal product has been obtained either in low purity or in low yields. The work reported here was undertaken in an effort to develop a method for obtaining high yields of good quality metal directly from the oxide by carbon reduction.

It was obvious, from earlier work, that rather high temperatures would be required to essentially complete the carbon reduction of the oxide to yield good quality metal. Containment of the product metal at the high temperatures presented one major problem. Since uranium dioxide appeared to be a favorable material for use in the fabrication of containment crucibles, a study on the preparation of a more dense and stronger uranium crucible was begun. Exploratory tests indicated a number of factors that influenced the final quality of the fabricated crucible. Also derived in this study were methods for preparing high density uranium oxide compacts like those employed in nuclear reactor fuel elements. The results of this study on the preparation of dense UO_2 crucibles and shapes are considered in the second part of this report.

LITERATURE REVIEW

The carbon reduction of oxide as a means for preparing uranium metal is not a new approach. Klaproth (2), in 1789, using the highest temperature furnace available at the time, thought he had prepared the metal by carbon reduction of a yellow oxide extracted from pitchblende. In 1841, Peligot (3) demonstrated that Klaproth's method did not give metal but gave only a lower oxide of uranium. More than 100 years after the discovery of uranium, however, Moissan (4) demonstrated that uranium metal could be prepared by carbon reduction. Moissan's success was attributed to his carbon-arc furnace which was capable of heating a charge of oxide and carbon to the high temperature required to produce metal under atmospheric pressure. The presence of excess carbon in the environment, however, contaminated the metal that was formed and caused it to be quite brittle. Other workers that followed Moissan's technique also obtained metal that was highly contaminated with carbon (approximately 2 wt %).

Following the organization of the Plutonium Project in America in late 1941 (1), various possible means for the preparation of uranium metal were explored at Iowa State College. Included was a carbon reduction method similar to

that employed by Moissan. The charge was heated by induction employing a graphite crucible, but the resulting metal was still highly contaminated with carbon. Since it appeared to these investigators that considerable time and effort could be required to adequately develop this process and since the need for large amounts of good quality metal at an early date was urgent, efforts were directed then toward developing other methods for uranium metal preparation.

The carbon reduction of oxide for preparing uranium metal was not given further serious consideration in the United States during the next decade. In 1953, workers at Sylvania (5) undertook a program to develop a method for preparing uranium metal by such a process. Early exploratory investigations were promising enough to warrant an expansion of the program. Pilot plant operations were set up on a 100-lb batch bases at Sylvania-Corning and by 1957, the process there had been tested and evaluated.

The process derived was basically an extension of the approach reported by Moissan about 60 years earlier. An ingot of massive uranium metal, contaminated with carbide, was first formed by reducing a charge of UO_2 and carbon under vacuum at temperatures up to $2200^{\circ}C$. This product was then crushed and

the carbide phase hydrolyzed. The remaining metal (in the form of spongy granules) was separated from the oxide product of the hydrolysis and further processed to give compact metal in yields of 30%.

Another study on the carbon reduction process was reported by Wilhelm (6) in 1960. In this research, considerable effort was directed toward evaluating potential materials for preparing crucibles suitable for use in the carbon reduction process. Of the materials tested, good metal was prepared in crucibles shaped by jolt-packing UO_2 , but considerable vaporization of this crucible material occurred under heating in the graphite susceptor during metal preparation. Other crucibles prepared from thoria and yttria were quite refractory, but tended to react with the carbon heater and, to a slight extent, with the liquid metal.

Another investigation of the carbon reduction of uranium oxide, wherein UO_2 was employed as the crucible material was reported by Smiley (7), in 1963. In this brief investigation, four reductions, calculated to yield about 7 grams of metal each, were carried out by reducing a charge of UO_2 and carbon in a urania crucible heated by a tantalum susceptor. In these experiments, long periods of heating in vacuum at temperatures

below 2000°C were employed. Even though the quality of metal, as reported, appeared to be comparable to that obtained by the present large-scale uranium process, metal yields were less than 60%.

In 1966, Wilhelm, Strain and Neubauer (8) reported some further developments in the carbon reduction of uranium dioxide. Their approach was to employ a graphite crucible as the induction heating susceptor, a suitable ceramic crucible to contain the product metal at the high temperature required to essentially complete the reaction and a shield between the graphite heater and ceramic crucible to inhibit their reaction. Crucibles of yttria were employed to contain the molten uranium at temperatures up to 2100°C in a tantalum-lined graphite heater assembly. Yields of at least 90% were obtained, but the final metal usually contained 0.25 wt % carbon. Most of this carbon precipitated in the form of uranium carbide dendrites as the liquid metal cooled. Granulation or fragmentation of these dendrites in the liquid metal permitted segregation of the less dense carbide near the top of the melt and, after solidification, a cropping of the ingot permitted recovery of a major part of the primary metal with relatively low carbon content.

Results of the efforts reported above partially defined conditions that would have to be met in order to prepare good-quality uranium metal in high yields by this reduction of oxide. It was obvious that other materials would have to be employed or new concepts for the processing would have to be put into operation in order to more nearly approach the full potential of producing uranium metal by carbon reduction of oxide. Utilization of the electrical conductivity of an intermediate reduction product for self heating of the charge by induction to essentially complete the reaction, constitutes a major and novel part of the process for carbon reduction of uranium oxide reported here.

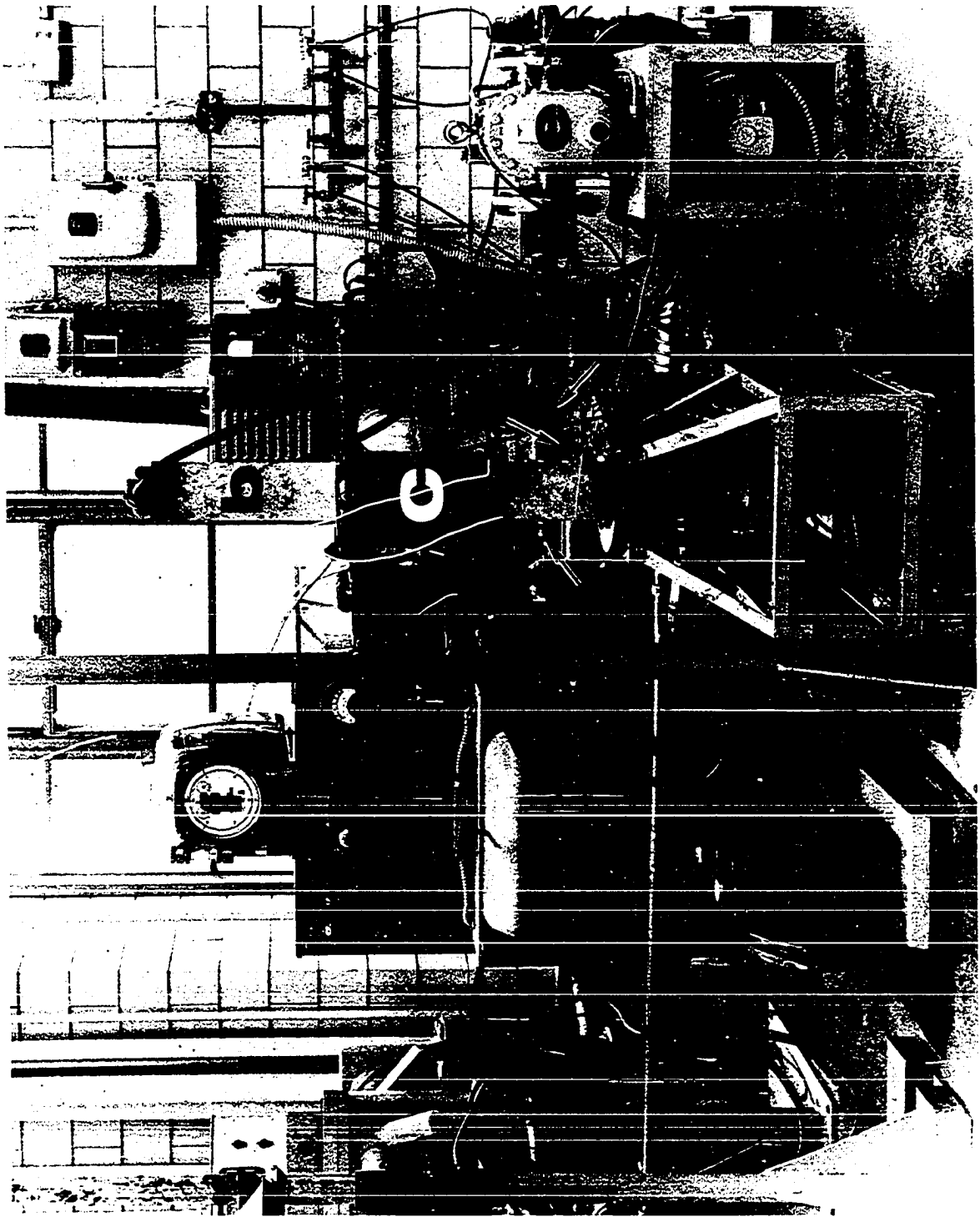
APPARATUS

Two types of induction heating power units, or converters were used in this investigation. One was a 6 KW Ajax mercury arc-gap type unit, while the other was a 25 KW Westinghouse radio-frequency (450 kilocycles) generator. The preparation of an oxycarbide intermediate product and the sintering of most of the crucibles were carried out using the 6 KW unit, while the self-induction heating step to yield metal was carried out using the RF generator.

A photograph of the 6 KW Ajax converter and its associated equipment is shown in Figure 1. Power from this converter was supplied to a hoist-type, water-cooled induction coil. Two coil sizes were available, one four inches inside diameter and the other seven inches inside diameter, however, a description of only the unit employing the smaller coil size will be discussed. The smaller coil was ten inches in height and consisted of 40 turns. The vacuum furnace chamber used in this setup was composed of a water-cooled base which supported a silica sleeve three and three-eighths inches inside diameter with a one-fourth inch wall thickness and about 32 inches in length. The vacuum seals used at the ends of the silica sleeve were neoprene gaskets. A water-cooled head equipped

Figure 1. ... Photograph of 6 KW Ajax vacuum induction furnace

- A. 6KW Ajax converter
- B. Silica sleeve
- C. Induction coil (hoist-type)
- D. Oil diffusion pump
- E. Roots-type booster pump
- F. Wet test meter
- G. Thermocouple gauge
- H. Ionization gauge
- I. Thermocouple and ionization gauge control



with an observation port served as a lid for the chamber. The port was used to make visual observations during the course of a reduction and to make temperature measurements with an optical pyrometer. Figure 2 is a diagrammatic representation of this chamber.

The vacuum system employed consisted of a three-stage six-inch diameter oil diffusion pump with a Roots-type booster pump backed by a Welch Duo-Seal mechanical fore pump. This vacuum pumping system could readily decrease the furnace chamber to less than 5×10^{-5} mm Hg. Two thermocouple gauges and an ionization gauge were used to indicate the pressure that developed and a wet test meter connected to the exhaust of the fore pump gave a measure of the quantity of gas evolved during the course of a reduction.

A typical furnace assembly which was supported inside the silica sleeve vacuum chamber and heated by the Ajax power unit is shown diagrammatically in Figure 3. It is composed of a graphite crucible with carbon powder insulation packed in a silica beaker. The graphite crucible which served as a susceptor was one and seven-eighths inches inside diameter and six inches in height with a three-sixteenths inch wall. This crucible was fitted with a threaded cap that had a

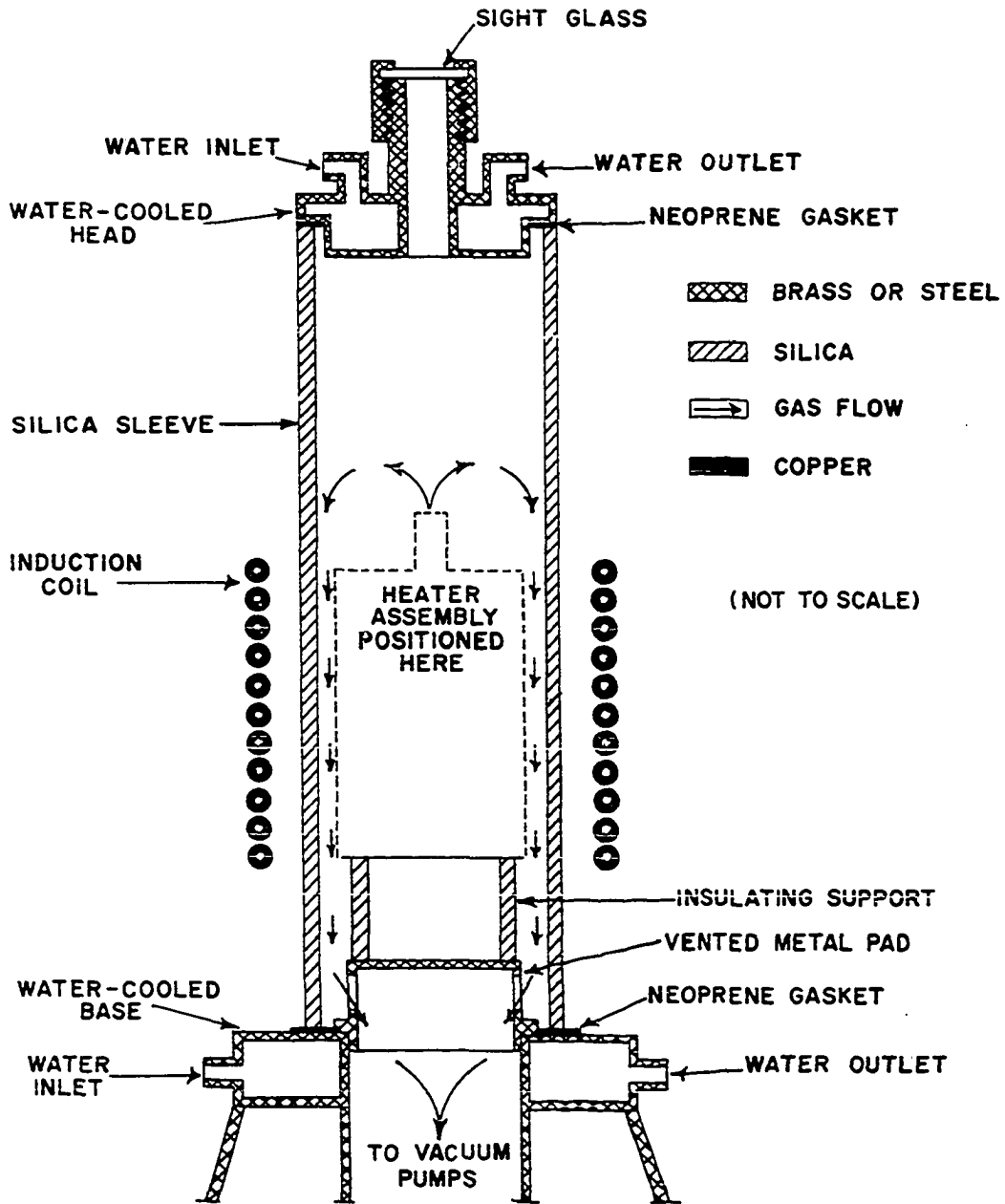


Figure 2. Diagram of induction furnace vacuum chamber

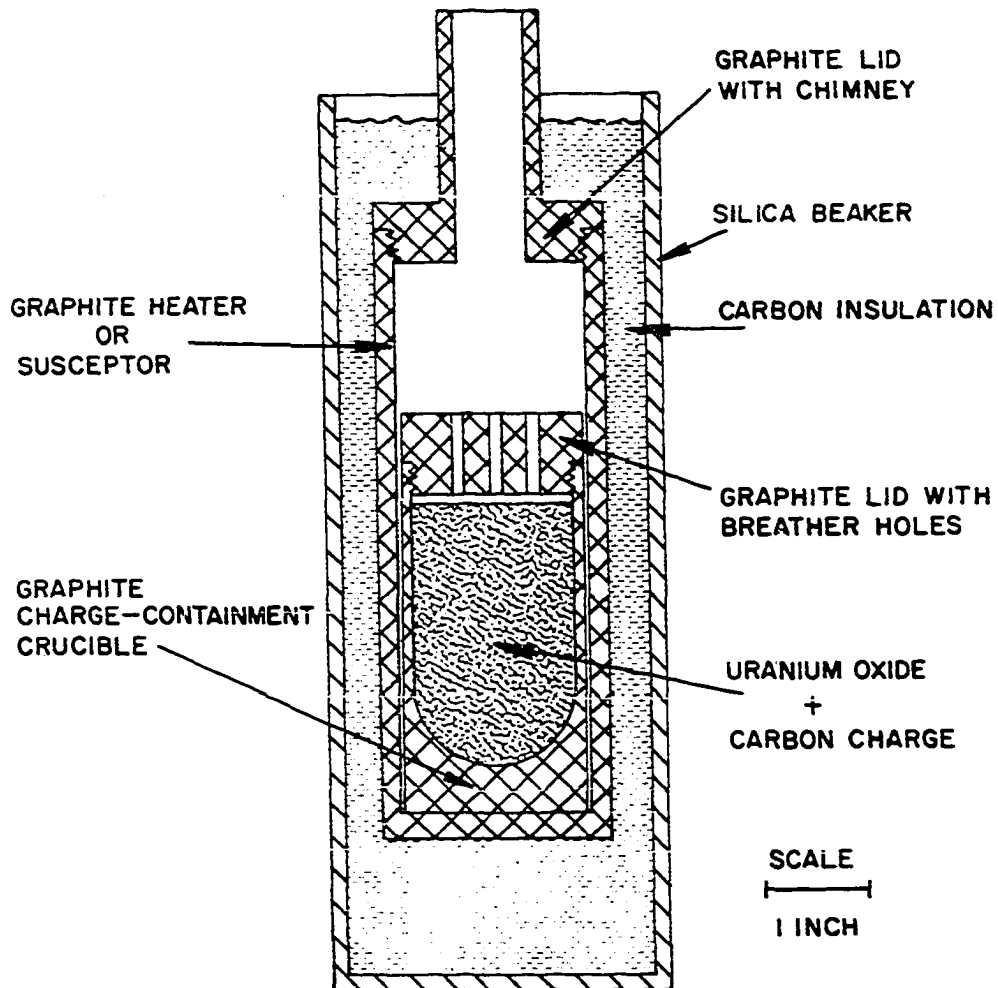


Figure 3. Furnace assembly used in uranium intermediate product (oxycarbide) preparation

chimney which served as an observation port and an exit for product gases during a reduction. Whenever a substance was heated that could conceivably react with the graphite heater, a liner of 30 mil sheet tantalum or molybdenum was employed. The fused silica beaker was three inches inside diameter and nine inches in height with a one-eighth inch wall. The carbon black insulation was a mixture of Shawinigan Black and Thermax carbon black mixed in a one to one volume ratio. In later experiments, the silica beaker-carbon black insulation combination was replaced by wrapping the susceptor with graphite felt and holding it in position with graphite thread.

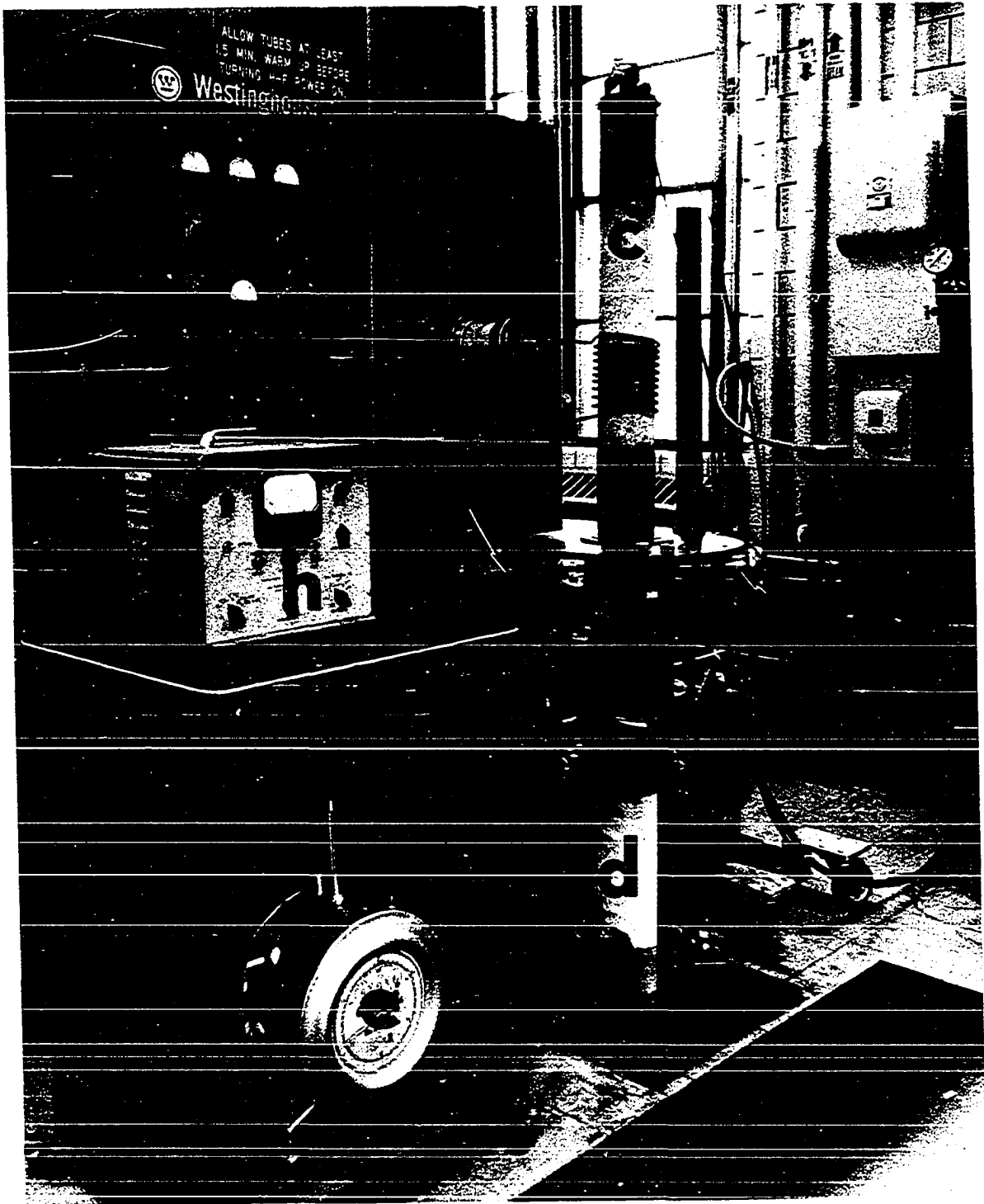
When the uranium oxycarbide was heated to the liquid state, the Westinghouse RF generator was employed to increase the efficiency or coupling between the induction coil and the conducting charge. This generator supplied power to a stationary water-cooled induction coil four inches inside diameter and six inches in height consisting of ten turns. The vacuum furnace chamber used with this unit is essentially the same as described for the 6 KW Ajax unit. The vacuum pumping system consisted of a three-stage four inch diameter oil diffusion pump with a Welch Duo Seal mechanical pump as the fore pump. This pumping system could evacuate the furnace

chamber to pressures of less than 5×10^{-6} mm Hg. System pressure was determined using either a thermocouple gauge or an ionization gauge while a wet test meter was used to monitor gas evolution. Figure 4 is a photograph of this entire setup.

The furnace assembly used in the self-heating experiments is shown schematically in Figure 5. The uranium intermediate product prepared by a preliminary heating of a mixture of uranium oxide and carbon in graphite composes the charge. This partially reduced charge is positioned within a UO_2 crucible and covered with a UO_2 lid that is fitted with a chimney. The uranium crucible is about one and seven-eighths inches outside diameter and three inches in height with a one-eighth inch wall. These dimensions varied slightly from crucible to crucible depending upon the heating schedule used when they were fabricated. The containment silica beaker measured two and three-eighths inches outside diameter and four inches in height with a one-sixteenth inch wall. The UO_2 powdered insulation between the uranium crucible and containment silica beaker has a thickness of about three-sixteenths of an inch.

Figure 4. Photograph of 25 kilowatt Westinghouse RF Generator

- A. RF Generator
- B. Induction coil (stationary)
- C. Silica sleeve
- D. Oil diffusion pump
- E. Wet test meter
- F. Thermocouple gauge
- G. Ionization gauge
- H. Thermocouple and ionization gauge control



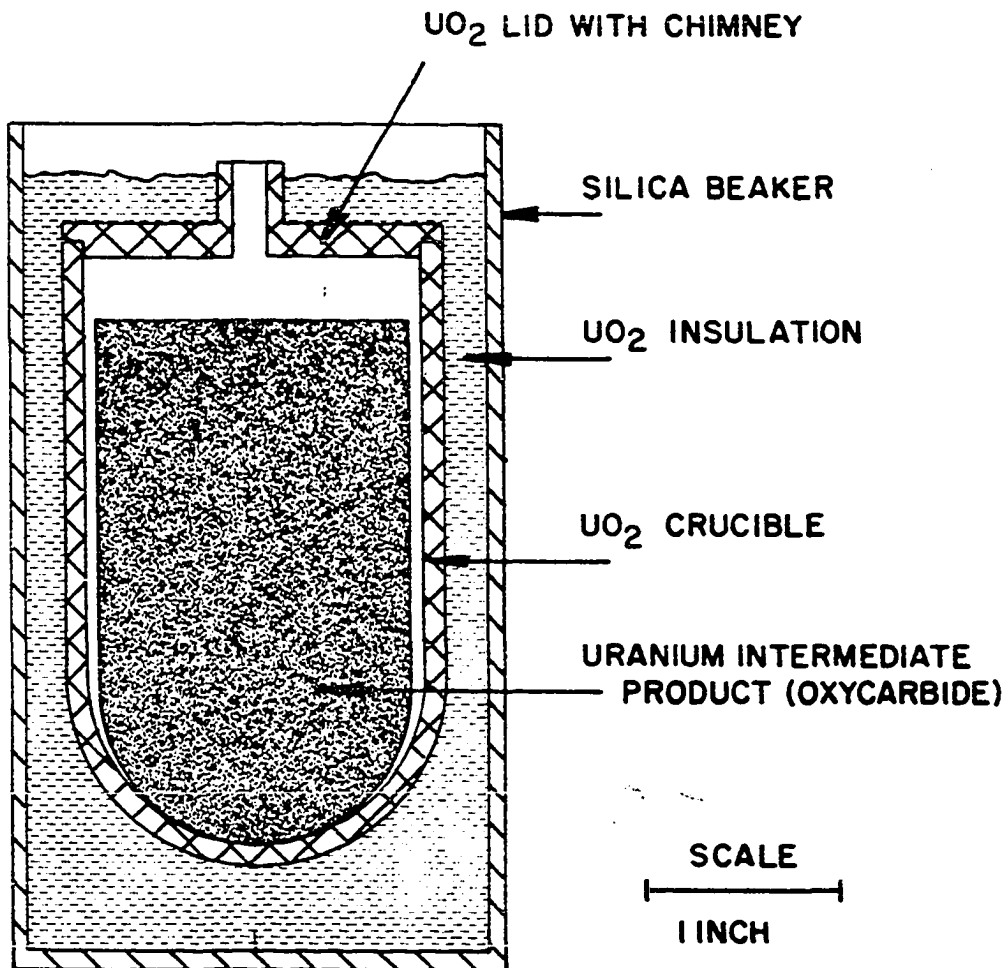


Figure 5. Furnace assembly used in self-induction heating of uranium intermediate product

MATERIALS

Since the greater portion of the overall reaction is carried out with the reactants in the solid state, an initial uniformly mixed charge composed of finely divided particles is desirable.

Charge Materials

Carbon

Carbon (graphite or amorphous) is obtainable in various particle sizes, packing densities and purities. An acetylene black, for example, has an average particle size of about 420 Å. However, its packing density is only about one-third to one-fourth that of some other carbons. Similarly, carbons with varying degrees of purity are available although low-ash content carbon is desired.

Two grades of graphite powder were used in this investigation. Initially, Grade 48 graphite powder purchased from the Union Carbide Corporation was used. Greater than 99% of this carbon would pass a 200 mesh screen and chemical analysis revealed it to have an ash content of 0.02 wt %. Later in the investigation, when this grade of carbon was discontinued in production by Union Carbide, Grade 195 graphite powder was employed. Although it had essentially the same particle size

as the Grade 48 graphite, it was analyzed to contain 0.2 wt % ash. Since most of the ash impurities are volatile under the conditions of the reaction and the equivalent weight of carbon is very small compared to that of uranium, the contribution of the carbon-contained impurities can be expected to be considerably less than 0.01 wt % in the uranium metal.

Uranium oxides

In the production of UF_4 for use in metal preparation or for further processing in gaseous diffusion plants, two oxides are formed as intermediates along the process path after preparation of a purified uranyl nitrate hexahydrate [$UO_2(NO_3)_2 \cdot 6H_2O$]. They are uranium trioxide (UO_3) and uranium dioxide (UO_2).

The orange oxide (UO_3) as normally prepared on a large scale is unsatisfactory as a charge material since it contains variable quantities of residual "nitrate" and moisture, the amount being dependent on the conditions of preparation. Furthermore, some batches of UO_3 also contain residual sulfur which is added as sulfate to increase the dioxide's activity during the hydrofluorination step (9).

Two different batches of UO_3 were used in this investigation. They were sulfated production grade UO_3 and unsul-

fated production grade trioxide, both obtained from the National Lead Company of Ohio. Results of analyses on these starting materials are summarized in Table 1. Impurity levels reported in this table were obtained spectrographically except for the sulfur and carbon values that were determined chemically. The moisture content and the nitrate content in both materials were about 1.20 wt % and 0.45 wt % respectively.

Table 1. Analyses in ppm of production grade UO₃ batches used in investigation

Element	Sulfated UO ₃	Unsulfated UO ₃
C	200	180
Na	5	0.9
Al	2	3
Si	30	4
S	400	11
Cr	10	6
Fe	50	20
Ni	20	1
Cd	ND ^a	0.1

^aElement not detected.

As these results indicate, the impurity levels of the elements listed are similar in the two oxides with the exception of the sulfur content which is about 40 times as high in the sulfated oxide as it is in the unsulfated oxide.

Table 2 lists sieve analyses obtained on the two tri-

oxides. As can be seen from Table 2, the unsulfated production-grade trioxide used in this investigation has a much higher percentage of the minus 325 size than the production grade sulfated trioxide.

Table 2. Sieve analyses of production grade UO_3 samples used in investigation

Screen No.	% of oxide retained	
	Sulfated	Unsulfated
65	3.98	2.26
100	8.27	2.47
150	5.05	2.20
200	16.46	7.09
325	19.40	10.28
>325	46.84	75.70

The refractory brown oxide (UO_2) is a very stable uranium oxide if kept in an inert or reducing atmosphere. These properties have made it attractive as a crucible material for use in studies of metal preparation by carbon reduction and as high temperature thermal insulation. The composition of this oxide is not always UO_2 , however. It can, on standing in an oxygen atmosphere, adsorb oxygen; the rate and extent of oxidation are functions of the temperature, the partial pressure of oxygen and the physical properties of the dioxide specimen (10). Compositions of $UO_{2.10}$ are common and even a composition of $UO_{2.25}$ (U_4O_9) is known to exist. The uranium

dioxide used in this investigation was production grade UO_2 obtained from the National Lead Company of Ohio. Determination of the oxygen to uranium (O/U) ratio showed the composition to be $UO_{2.06}$. A sieve analysis for this material is shown in Table 3.

Table 3. Sieve analysis of production grade UO_2 used in this investigation

Sieve No.	65	100	150	200	325	>325
% of oxide retained	3.01	7.76	4.38	14.49	45.05	25.34

Since the production grade UO_2 shown in Table 3 was probably derived from the sulfated trioxide, its particle size distribution pattern could resemble somewhat that obtained on the sulfated UO_3 sample providing no significant particle size change occurs during the conversion of UO_3 to UO_2 . A comparison of the sieve analyses for the sulfated trioxide in Table 2 with the dioxide in Table 3 shows that the percentages of oxides retained on the 65, 100, 150 and 200 mesh screens are similar. Thus, the total percentage of oxide passing a 200 mesh screen is about the same in both cases. However, there is a possibility indicated here that the very fine (through 325) UO_3 particles underwent some sintering in the conversion to UO_2 . The higher percentage of UO_2 retained on the 325 mesh

screen could be due to its tendency to ball up and stick in the fine screen during sieving.

The green-black oxide (U_3O_8), which is also known as the octaoxide was employed by Moissan in his studies of the preparation of metallic uranium by carbon reduction. This oxide is probably the most easily reproduced oxide. All of the oxides of uranium and even the metal can be converted to U_3O_8 by heating them in air at $800^{\circ}C$. The U_3O_8 used in this investigation was obtained by heating either UO_3 or UO_2 in the above manner. This treatment also served as a purification step since the residual uranium compounds (nitrate, etc.) present in the trioxides were also converted to U_3O_8 .

Crucible Materials

Uranium oxides

The uranium oxides used for crucible fabrication originated from the production grade oxides that were previously described.

Stabilized zirconia (ZrO_2)

Zirconium dioxide stabilized with lime and designated Zircoa-B was obtained from the Zirconium Corporation of America. Analysis supplied by the vendor of this material revealed it to contain 93.5 wt % ZrO_2 and 4.8 wt % CaO with the

remainder being HfO_2 . Greater than 99% would pass a 325 mesh screen.

Thoria (ThO_2)

The ThO_2 was prepared by calcining thorium oxalate precipitated from thorium nitrate with oxalic acid. The purity of this material prepared at the Ames Laboratory was greater than 99.9% ThO_2 (11).

Graphite

Grades AGSR and AGSX graphite obtained from the National Carbon Company were used. The purity of the material depended on the initial diameter of the rod stock and varied from 0.12 wt % to 0.96 wt % ash.

Insulating Materials

Shawinigan Black

The Shawinigan Black used was prepared by the continuous thermal decomposition of acetylene at temperatures above 1500°C . It was supplied by Shawinigan Chemicals Limited and reportedly had an ash content of less than 0.04 wt %.

Thermal insulating carbon

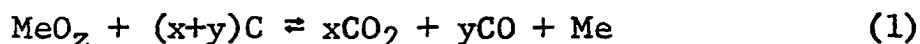
Thermal Thermatomic carbon was obtained from the R. T. Vanderbilt Company. Chemical analysis showed it to have an ash content of 0.09 wt %.

Graphite felt

Graphite felt of about one-fourth inch in thickness was obtained from the Union Carbide Corporation. Analysis of this material revealed it to be essentially ash free.

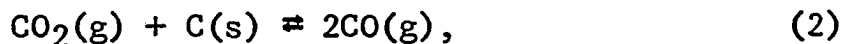
GENERAL THEORETICAL CONSIDERATIONS

The reduction of a metal oxide with carbon can be represented in general terms by the following equation:



where $z = (2x+y)$.

It is to be observed that, by this reaction, both CO_2 and CO are generated by the presence of free carbon. Since CO_2 may react with carbon to form CO by the equation:



consideration should be given to the influence of this reaction on conditions for the oxide reduction. The mole fractions of CO and CO_2 in equilibrium with free graphite as a function of temperature and pressure are represented by Figure 6 which is based on free energy data (12) for the components of this reaction.

At a total system pressure of 1 atmosphere, the equilibrium gas phase is composed of essentially all CO_2 at temperatures below 300°C . As the temperature is increased, the proportion of CO in the gas phase tends to increase; at 1100°C , the equilibrium gas phase is nearly all CO . A decrease in the total system pressure to 0.10 atmosphere tends to increase markedly the fraction of CO in the gas phase at all tempera-

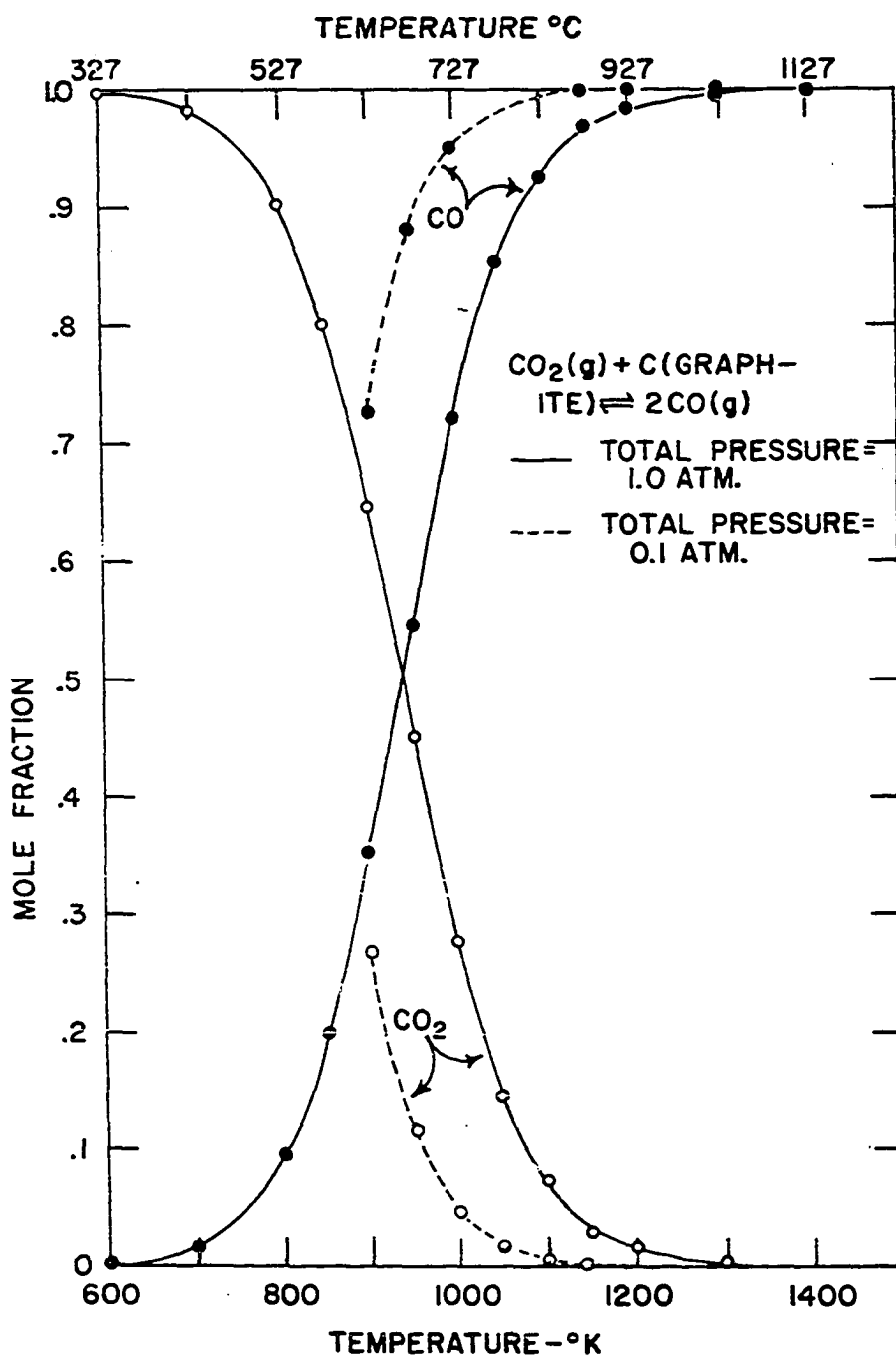
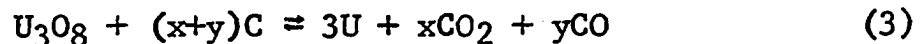


Figure 6. The mole fractions of CO and CO₂ in equilibrium with free graphite as a function of temperature and pressure

tures. Although equilibrium will not be obtained, some consideration must be given this system in choosing the charge materials used in metal preparation by carbon reduction of oxide.

Two oxides of uranium can be conveniently used, the dioxide, UO_2 or the octaoxide, U_3O_8 . If the oxide-carbon reaction occurs at well below $900^\circ C$, some of the gas should be evolved as CO_2 . Unless the stoichiometry and conditions are sufficiently reproducible, the final metal could contain either an excess of carbon or oxygen due to the potential variability of the CO to CO_2 ratio in this low temperature range. Considering U_3O_8 as the most likely oxide to react at low temperatures, a general equation for the reaction can be written as follows:



where $(2x+y) = 8$.

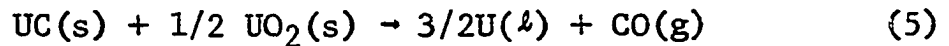
If, on the other hand, UO_2 is used as the starting oxide, the initial reaction temperature could be high enough so that essentially all the gas is evolved as CO . In this case the overall reaction could be represented as:



These two reactions, as written, appear to be quite

simple. However, an analysis of the conditions, if the reaction initiates as written, would show that the first uranium metal would be formed in the presence of free carbon with temperature conditions suitable for forming uranium carbide. Therefore, when all residual carbon has been reacted to form uranium carbide, the remainder of the oxide has to be reduced by carbide instead of free carbon.

Free energy data can be used to estimate the minimum temperature necessary to obtain metal under a particular pressure by an assumed reduction represented as:



Using thermodynamic data given by Rand and Kubaschewski for uranium compounds (13) and carbon monoxide (12), the standard free energy change for this reaction can be expressed as:

$$\Delta F_{(s)}^{\circ} = 128,990 - 70.88T + 7.7T \log T = -RT \ln K \quad (6)$$

The equilibrium constant K for the reaction represented by Equation 6 could be considered as being equal to the partial pressure of the CO gas in atmospheres, if it is assumed that the activities of the other product and reactants are unity. Table 4 summarizes the calculated temperature at four different assumed pressures. It should be noted that this simpli-

fied analysis did not take into account any reaction rates which must be considered in the development of a feasible process.

Table 4. Calculated minimum temperature required to obtain uranium metal by carbon reduction at various pressures

Pressure		Temperature	
atmospheres	mm Hg	$^{\circ}\text{K}$	$^{\circ}\text{C}$
10^{-2}	7.6	2385	2112
10^{-4}	7.6×10^{-2}	2025	1752
10^{-6}	7.6×10^{-4}	1760	1487
10^{-8}	7.6×10^{-6}	1555	1282

Even though calculations based on Equation 5 indicate that metal might be obtained using a variety of conditions, for all practical purposes, an elevated temperature with reduced pressure would be required in order to accelerate the reaction. Furthermore, consideration of conditions that probably prevail for the assumed reaction would lead to complications not indicated by this simplified equation.

Several studies including those by Chiotti and coworkers (14) and Stoops and Hamme (15) have indicated that uranium oxycarbide $\text{UO}_x\text{C}_{1-x}$ is an equilibrium phase in the uranium-oxygen-carbon system. If it is assumed that the oxycarbide

has the composition $UO_{.5}C_{.5}$, which can also be represented as $[\frac{1}{2}(UO+UC)]$, higher temperatures than those calculated in Table 4 would result since UO should have a more negative standard free energy of formation per oxygen than UO_2 .

Furthermore, as the reaction proceeds, the liquid metal that is formed undoubtedly becomes saturated with the oxycarbide and the unit activities assumed in making these calculations are not valid. As the reaction nears completion, then, it is quite likely that the temperatures required at the specified pressures would be much higher than those listed in Table 4.

The containment of uranium in the liquid state at elevated temperatures presents a problem. Two possibilities that exist for holding the metal liquid, yet unreactive, are to melt it on a water-cooled hearth, like that used in arc melting or electron-beam melting, or to contain it in an inert-type of crucible.

Because of the apparent high finishing temperatures required to yield good metal, one criterion that such a crucible material should exhibit would be satisfactory strength at temperatures in excess of $2100^{\circ}C$. Consequently, the melting temperature of this material will probably be well above this temperature and preferably greater than $2500^{\circ}C$. Although a

number of materials which include borides, carbides, nitrides, oxides, sulfides and some metals meet this temperature requirement, this investigation was limited to considering certain refractory oxides.

Other considerations may also limit the choice of an oxide as a container material for liquid uranium. For example, some refractory oxides exhibit phase transitions that require certain chemical additions to insure stability, while others, though quite stable are toxic and require special handling. Furthermore, while other materials are both stable and nontoxic, they could introduce contaminants into the metal.

EXPERIMENTAL

Procedures

A process may be derived on the basis of the results of a number of related experiments in which certain parameters are varied and their effects evaluated with regard to such factors as feasibility, quality of product, yield and economics. During the research and development stages for a process, however, certain established procedures, methods and techniques are frequently employed. In the first part of this study on metal preparation, charge preparation, crucible preparation and control and evaluation techniques fall into this category.

Charge preparation

Each reactant in a charge, which contained from 200 to 250 grams of uranium as oxide, was weighed to the nearest hundredth of a gram and placed in a suitable container for mixing in a ball mill. A number of one-half inch diameter alundum grinding stones were placed with the charge to aid in mixing. The length of time a sample was mixed depended on the charge size; however, instead of mixing a charge for a specified period of time, it was observed periodically and mixing was stopped when it appeared homogeneous.

Crucible preparation

The refractory oxide crucibles used in this study were prepared by jolt packing. In the jolt-packing technique, the refractory oxide was shaped in a graphite mold which consisted of a graphite crucible, mandrel and collar of such sizes and shapes as to yield a finished sintered ceramic crucible of the desired specifications. The graphite mold pieces and other parts made of graphite were prepared by machining from either AGSR or AGSX Graphite stock. In the packing operation, enough of the finely divided oxide is placed in the bottom of the graphite mold crucible to yield a base for the mandrel to rest on. This quantity of refractory depends on the thickness of the base, but most of the crucibles used in this phase of the study had about a one-eighth inch thick base. Next, the mandrel is positioned and the oxide added to fill the approximately one-eighth inch wide annular space between mandrel and crucible. The collar is then placed around the mandrel at the top of the crucible and the entire assembly placed on a pneumatic jolting table. As the refractory oxide compacts, more is added. This step is repeated until the entire mold is lined with the jolt-packed oxide. With the collar in position, the mandrel is removed leaving a graphite crucible lined with

compacted oxide. The crucible with the liner is then heated causing the liner to sinter and shrink away from the graphite mold yielding the desired crucible. A more detailed explanation of the crucible preparation phase is discussed in Part II of this study.

Control and evaluation techniques

For each experiment, control data were collected during the reduction and the product was subsequently analyzed. Process evaluation and the course of further experimentation was based on these results. The progress of the reaction was followed by monitoring temperature, cumulative gas evolution and gas evolution rate.

Temperature measurements were obtained using a Leeds and Northrup Optical Pyrometer Model 8622-C. Final temperature values were corrected for the effect of the sight glass of the vacuum assembly (Figure 2) by using a pyrometer calibrator. In making this correction, the temperature of a heated tungsten filament was measured with the pyrometer with and without the sight glass interposed. From these two readings, and a transmittancy table, the transmittance of the sight glass was determined and the corrected temperature obtained.

Gases evolved during the reduction sequence were meas-

ured with a wet test meter manufactured by American Meter Controls, Inc. Although this meter had an accuracy of $\pm 1.0\%$ at a gas flow rate greater than that realized on the small-scale reductions, this degree of accuracy was probably not realized. However, the gas evolution rates were at least relative and correlated with the pressures which the vacuum pumping system could maintain. System pressures above one micron were measured with an NRC Type 501 Thermocouple Gauge while pressures below one micron were obtained with an NRC Type 507 Ionization Gauge. Both of these gauges were used in conjunction with an NRC Model 710 Thermocouple-Ionization Gauge Control.

Analyses of the solid products formed in the course of a reduction experiment were based, for the most part, on the results obtained by standard chemical and spectrographic techniques.

Samples for metallographic examination were prepared from metal samples by cutting with an abrasive wheel. The sections to be polished were mounted in bakelite and wet ground using 200, 400 and 600 grit paper. Final surface preparation was accomplished by wet grinding with Linde A and Linde B powders. The samples were then ultrasonically cleaned in methanol,

dried in air and examined. Any photomicrographs taken were usually at 100 diameters with normal nonpolarized light. To bring out further details, some samples were etched with a 1:1 HNO₃-water solution.

Reduction Procedure Derived

Oxycarbide preparation

A uniformly mixed charge is packed in a graphite crucible that is fitted with a graphite screw-type lid (see Figure 3). This lid which has a number of small holes permits the product gases to escape yet retains any of the charge that could otherwise be blown from the crucible during the initial phase of the rather vigorous exothermic reaction that takes place under vacuum conditions. This charged crucible is then placed in an insulated graphite heater assembly as shown in the figure. After the heater lid with its chimney is positioned, insulation is packed on top of the lid and around the chimney to complete the heater assembly. If the initial reaction were to be carried out under pressure, the retaining lid to the charge crucible could be eliminated. The vacuum would then be developed after most of the initial reaction had taken place.

To prepare the vacuum furnace assembly shown in Figure 2, for carrying out the oxycarbide preparation step, the heater

assembly is first placed on the silica base and within the induction coil. The vacuum chamber is formed around the heater assembly by positioning the silica sleeve around the heater and within the induction coil; this sleeve rests on the neoprene gasket on the water-cooled base. A water-cooled head, fitted with a sight glass, is then placed on the upper end of the silica sleeve and the chamber, thus formed, is evacuated.

When the system pressure is reduced to less than 5×10^{-4} mm Hg, heating is started. The hoist-type induction heating coil is first positioned so that the hottest zone of the susceptor is near the top of the charge. Heating proceeds until the top of the charge has initially reacted. At this point, the coil is progressively lowered in a stepwise fashion until the initial reaction is promoted throughout the charge. After this initial phase of the overall reaction has been essentially completed, the reaction temperature is increased to the range between 1550 and 1950^oC where it is maintained until the reaction subsides and appears to be completed for the temperature as indicated by the low pressure in the system and the very small gas evolution rate. The heating program up to this stage of reduction, which yields an electrically conducting

intermediate uranium product (oxycarbide) containing both carbon and oxygen will depend on the oxide that is employed in making up the charge. The composition of the intermediate product will depend on the temperature-and-time-of heating program.

Metal preparation

After this intermediate product is allowed to cool under vacuum, it is next placed in a ceramic crucible in the self-induction furnace assembly as shown in Figure 5. A ceramic lid with a chimney is then placed on the crucible and further insulation added around the top in the form of refractory oxide powder. The same type of vacuum chamber is employed here as is used in the preliminary step of the process. After the system pressure is decreased to less than 1×10^{-4} mm Hg, heating is started.

Due to the low self-induction coupling of the small charge sizes employed in this experimental work, it is necessary to use the 25 KW RF generator as the power supply. Essentially no reaction occurs until the sample temperature exceeds the maximum obtained during the preparation of the intermediate product. At this point, the heating rate is adjusted to permit the gas pumping system to maintain a low

system pressure and to reduce the temperature differential throughout the charge. The temperature of the sample is increased slowly to about 2200°C where it is maintained until the system pressure decreases to less than one-tenth micron. At this point, the reaction is assumed completed and the liquid product is allowed to solidify in the crucible.

RESULTS AND DISCUSSION

Selection of Crucible Material for Metal Preparation

In an effort to find a refractory oxide that would be suitable for containing liquid uranium up to 2300°C, a number of criteria were considered. Two conditions which a potential material had to meet in order that it be given further consideration were a melting temperature of at least 2500°C and reportedly high temperature stability under reducing conditions at very low pressures. Although MgO, CaO and related oxides meet the melting temperature requirements, experience has shown that these oxides readily release their metals in the presence of uranium under the conditions specified. Y₂O₃, which has a melting temperature just below 2500°C, has been used to contain uranium metal at temperatures just below 2100°C with yttrium contamination of a few hundred ppm in the uranium metal. The high cost of gadolinium-free Y₂O₃ was another factor that gave this oxide a secondary rating in the selection of refractory oxides for use in uranium metal preparation. Beryllia was bypassed, at least temporarily, because of the toxic nature ascribed to that element. Hafnia (HfO₂) was disregarded because of its high cost and the possibility of contaminating the uranium with hafnium which has a fairly

high thermal neutron capture cross-section. The list of oxides receiving primary consideration for testing in the preparation of uranium metal was reduced to those shown in Table 5.

Table 5. Refractory oxides considered sufficiently promising for testing under conditions required for metal preparation

Oxide	Melting point (16) °C
ZrO ₂ (lime stabilized)	2677
UO ₂	2860
ThO ₂	3220

The suitability of each of these three oxides as crucible materials for containing liquid uranium was tested experimentally. A self-induction heating assembly was prepared from each of these three materials (see Figure 5). About 100 grams of oxycarbide was then reduced to the liquid state in each assembly. The reactions were completed by self-induction heating and the metal products allowed to cool in their crucibles. Each crucible was then examined.

Zirconia as a crucible material for containing the liquid uranium metal under the required conditions was unsatisfactory.

There was some evidence that the zirconia was not sufficiently stabilized. However, the liquid metal seemed to act as a solvent for the ZrO_2 causing thinning of the walls. Both ThO_2 and UO_2 , on the other hand, appeared to work quite well in containing the liquid uranium. Since thorium-232 can be converted to fissile uranium-233 by neutron capture, it was decided that even though ThO_2 might serve as a crucible material for the experimental studies, the possibility of thorium contamination of the uranium for large scale use in nuclear reactors might require special consideration. Thus, UO_2 was selected for further work.

The Reactions

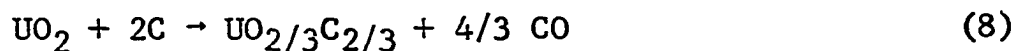
During the early stages of this investigation, uranium dioxide that corresponded to $UO_{2.06}$ was used for metal preparation. Analysis of gas evolution data, supported by analytical results, revealed that with this oxide the overall reaction as given in Equation 4 requires a slight modification. In heating a mixture of $UO_{2.06}$ and carbon, gas evolution begins around $900^{\circ}C$ instead of about $1300^{\circ}C$ as appears to be the case with stoichiometric UO_2 . When the charge temperature reaches $1000^{\circ}C$, this initial reaction step is essentially completed. It is assumed that this gas is generated by the

reaction of the extra 0.06 mole of oxygen with carbon. The temperature and pressure at which this reaction takes place would suggest by earlier reaction considerations that the gas evolved is primarily CO resulting in stoichiometric UO_2 . No noticeable reaction occurs on further heating of the mixture at temperatures up to 1300°C .

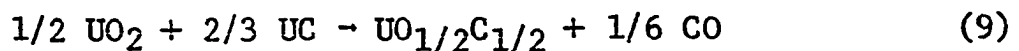
Further heating from 1300° to about 1550°C brings about another stage in the overall reduction. Here it is assumed that the free carbon combines with both oxygen and uranium leaving only some form of uranium carbide and uranium oxide for subsequent reaction. On the basis of the data obtained up to 1550°C , the net reaction might be represented as:



or

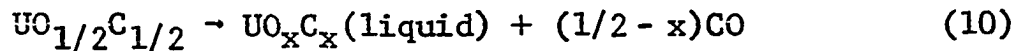


Further heating up to 1950°C produces more reaction but at a considerably reduced rate. The overall reaction in heating from 1550°C to 1950°C might be represented as:

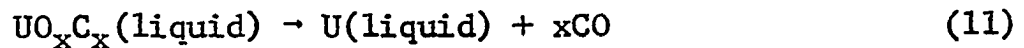


X-ray data obtained on the product formed by this heating step agree with data reported by other investigators for what they consider to be a form of uranium oxycarbide.

This oxycarbide and the product obtained by heating at 1550°C are electrically conducting, a property which serves for further heating to higher temperatures by self-induction to complete the reduction without a special susceptor. In heating the oxycarbide from 1950° to 2050°C, the reaction rate again increases. This noted increase is due to the reaction between the carbon and oxygen that are possibly in solid solution. Subsequently, as the metal phase forms at the high temperature, the carbon and oxygen are in liquid solution and the reaction progresses more slowly in forming uranium metal having very low oxygen and carbon contents. As these concentrations of oxygen and carbon decrease, their activities likewise decrease and temperatures around 2200°C are required to essentially complete the reaction in a practicable time period. The final stages in the reduction possibly can be represented by:



and



The general overall reaction given in Equation 4, then is possibly the sum of a series of reactions that follow a path represented by the preceding four equations. A graphical

representation of the cumulative gas evolution as the reaction progresses through its various stages is shown in Curve A, Figure 7. The data for this graph were obtained by heating a charge to 1300°C and then measuring the gas evolved at that temperature and at successive 50 degree increments up to 2200°C. The temperature was maintained constant after each incremental increase until the gas evolution rate became insignificant for that temperature before making the next increase.

When U_3O_8 is reduced with carbon under vacuum, the initial reaction occurs at about 750°C. Consequently, some of the gas is evolved as CO_2 and the moles of carbon required for the complete reduction to metal should be between 7 and 8 per mole of U_3O_8 .

In an effort to determine how many moles of carbon would be required to reduce U_3O_8 to metal, five charges were prepared which contained 7.0, 7.1, 7.2, 7.3 and 7.5 moles of carbon respectively. After these samples were packed into graphite crucibles, they were reacted under vacuum conditions at temperatures between 1550° and 1950°C. When most of the reaction was completed, as noted by gas evolution data, the samples were cooled and analyzed for carbon and oxygen. Table

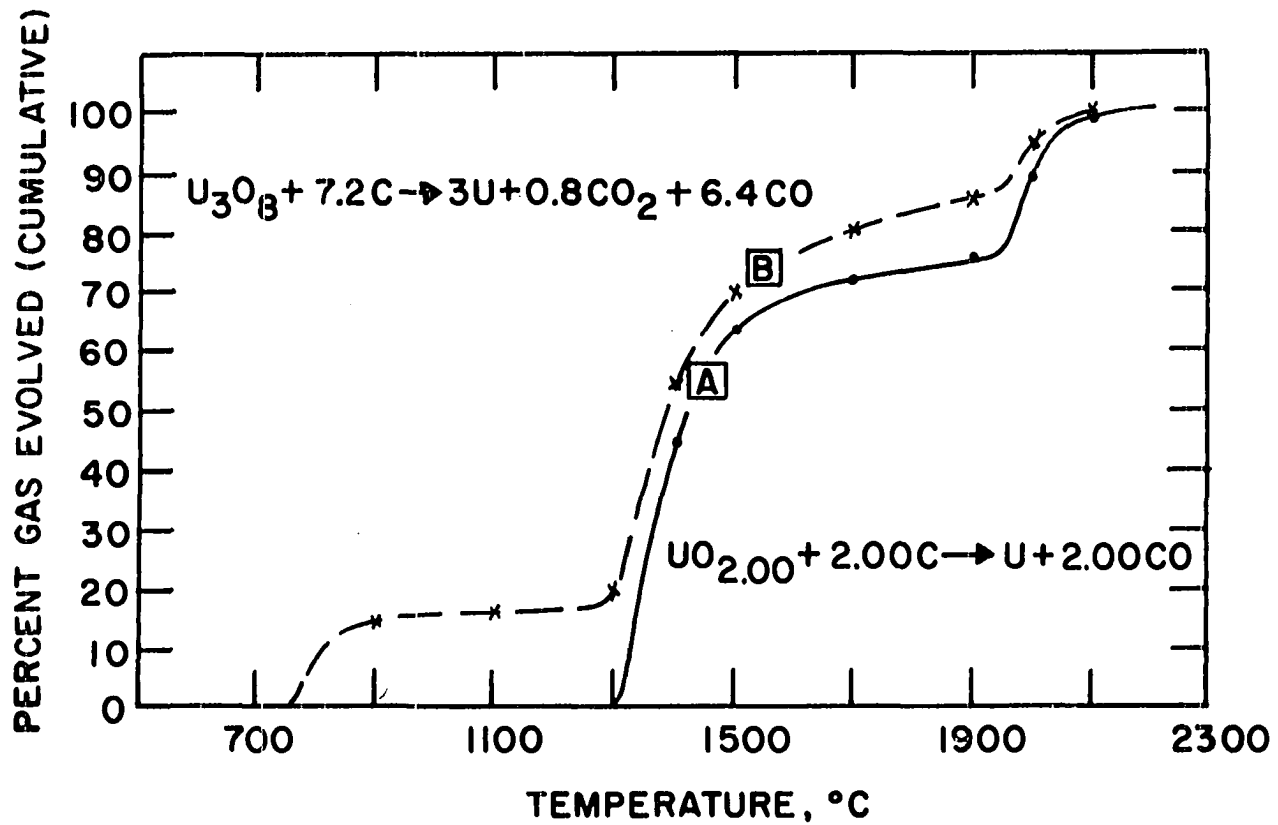


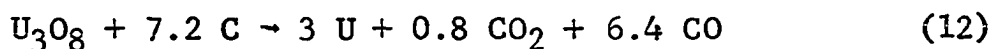
Figure 7. Cumulative percentage of gas evolved at various temperatures

6 summarizes the results obtained.

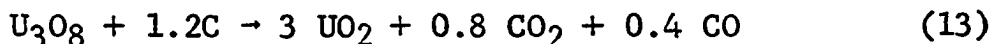
Table 6. Stoichiometric mole ratio of carbon to U_3O_8 for metal preparation calculated from charge composition and intermediate product analysis

Carbon to U_3O_8 mole ratio in charge	Intermediate product analysis		Calculated stoichiometric mole ratio
	Carbon, wt %	Oxygen, wt %	
7.0	2.85	4.26	7.22
7.1	2.98	4.18	7.20
7.2	2.90	3.82	7.18
7.3	2.82	3.40	7.13
7.5	3.08	3.45	7.19

On the basis of these charge compositions, analyses of the products and the assumption that the residual carbon and oxygen are to be removed as CO , it appears that about 7.20 moles of carbon would completely reduce U_3O_8 to metal. Thus, the overall reactions as given in Equation 3, when carried out under the conditions set up for the reaction would be



The reaction occurring below $1000^\circ C$ should then be represented by



This reaction is quite exothermic, with vigorous evolution of gas, especially when the charge contains the carbon to U_3O_8

mole ratio shown in Equation 12. As mentioned earlier, two precautionary measures were employed during this phase of the heating step to reduce sample blowout. They were: (1) fitting the graphite crucible, containing the charge, with a porous graphite lid and (2) heating the charge in a stepwise fashion from top to bottom through this initial reaction.

Curve B in Figure 7 is a plot of the cumulative percentage of gas evolved up to various temperatures from 750°C to 2200°C for a charge containing U_3O_8 and carbon. The data were obtained in the same manner as described above for Curve A.

Charge Packing Volumes

After the general overall reactions for both UO_2 and U_3O_8 with carbon were sufficiently well defined to yield good metal, it appeared that the use of U_3O_8 presented an advantage over the use of UO_2 which required a special hydrogen reduction step in its preparation. However, UO_2 has a much higher theoretical density than U_3O_8 and it requires less of the low density carbon for reduction to metal. It appeared possible, then, that more uranium per charge could be packed into a fixed volume of reduction crucible if UO_2 were employed instead of U_3O_8 . Preparing more metal per reduction would be a definite advantage favoring the use of UO_2 .

Table 7 summarizes the results obtained in these tests. Charges prepared from production grade UO_2 exhibited a uranium packing density in the charge of 2.27 grams uranium per cm^3 , while charges prepared with U_3O_8 from oxidized UO_2 yielded about a 5% decrease in the uranium packing density. However, charges of U_3O_8 prepared from the production grade trioxides showed substantial increases in the uranium packing densities. When unsulfated UO_3 was used, a 13.5% increase in the packing density over that of production grade UO_2 was realized, while a 17.5% increase in the packing density was achieved when sulfated UO_3 was used. The higher uranium packing densities shown for charges with U_3O_8 prepared from UO_3 would permit increases of between 350 and 400 g of uranium per liter of mixed charge compared to that using the UO_2 . The lower volume of U_3O_8 per gram atom of uranium as prepared directly from production grade trioxide is a major factor in yielding the favorable uranium packing density of charges with U_3O_8 . In a large scale process employing charge packing by jolting or an equivalent means, it would be advantageous to use U_3O_8 derived from production grade UO_3 in the charges rather than production grade UO_2 .

Table 7. Relative packing volumes and uranium packing densities of jolt-packed charges of the oxides with carbon

Charge composition normalized to 1 mole of uranium	Source of oxide in charge	Jolt-packed volumes of charge constituents and mixed charge per mole of uranium in charge			Uranium packing density of mixed charge Grams of uranium per cm ³ in charge
		Carbon cm ³	Oxide cm ³	Mixed charge cm ³	
UO _{2.06} +2.06C	Production grade UO ₂	35	81	105	2.27
1/3(U ₃ O ₈ +7.2C)	Oxidation of production grade UO _{2.06}	41	88	110	2.16
1/3(U ₃ O ₈ +7.2C)	Thermal decomposition of production grade sulfated UO ₃	41	66	89	2.67
1/3(U ₃ O ₈ +7.2C)	Thermal decomposition of production grade unsul- fated UO ₃	41	66	92	2.58

Processing Steps

The overall process for metal preparation which starts with U_3O_8 can be roughly divided into three major reduction temperature ranges. The initial reduction of U_3O_8 takes place at temperatures less than $1000^{\circ}C$ and results in the conversion of U_3O_8 to UO_2 . Reduction of the UO_2 appears to begin at about $1300^{\circ}C$; however, on continued heating the intermediate product desired for self-induction heating is formed at temperatures in the range of 1550 to $1950^{\circ}C$. The final metal product is formed in the third reduction range from $1950^{\circ}C$ to near $2200^{\circ}C$. The first two temperature ranges are covered in one continuous heating in a graphite crucible while the third takes place in a urania crucible, i.e., a two-step process.

Initial reduction of U_3O_8

Although the above experimental data were obtained with the vacuum pumping system operating at all temperatures, it is practical in some cases, to carry out the initial reductions up to $1000^{\circ}C$ under the pressure of an inert atmosphere. For example, reduction experiments carried out under vacuum conditions on charges calculated to yield 10 pounds of metal revealed that the initial reaction was so vigorous that it ruptured the graphite crucible containing the charge even

though the crucible was fitted with a vented lid. It was found that the first reaction which takes place on heating the charge up to 1000°C (U_3O_8 to UO_2) could be satisfactorily controlled by heating the charge under the pressure of an inert type atmosphere. Although several gases were considered for use in this heating step, nitrogen was employed after it was found that it did not contaminate the metal.

After the entire charge was reacted through this low temperature range, the remainder of the reaction at higher temperatures was carried out under vacuum conditions. Since a slightly larger fraction of the gas evolved below 1000°C is CO_2 , using this approach, slightly less than 7.2 moles of carbon per mole of U_3O_8 are required to essentially complete the overall reaction to form metal.

The oxycarbide intermediate product

Analytical results on charges of either $\text{UO}_{2.06}$ or U_3O_8 heated with stoichiometric carbon in a graphite crucible at temperatures up to 1550°C reveal that the resulting intermediate product (oxycarbide) contains about 3.0 wt % carbon and 4.0 wt % oxygen. Increasing the final reaction to about 1950°C decreases the carbon and oxygen contents to about 2.4 wt % and 3.2 wt % respectively. At temperatures between 1550

and 1950°C, the carbon and oxygen contents vary between these general limits. Some increase in density due to increased sintering of this product is achieved by going to the higher temperatures in this range as shown in Figure 8. However, both of these intermediate products exhibit sufficient electrical conductivity for self-heating in the proper induction field to yield uranium metal.

The metal product

During the early phases of this study, microscopic examinations of the product metal revealed a phase that was highly resistant to a 1:1 HNO₃ etch and believed to be a uranium nitride or a uranium carbonitride (17). Chemical analyses of the metal products revealed that the nitrogen contents in these samples ranged from 300 to 500 ppm. The microstructure of a sample of metal containing high nitrogen is shown in Figure 9. Since the nitrogen content of the oxide used in the initial charge was only 4 ppm (U₃O₈ derived from UO₃) and since the oxycarbide preparation and metal preparation steps were carried out under vacuum conditions, it was believed that the nitrogen pickup was occurring through exposure to air during the transfer of the oxycarbide to the self-induction furnace assembly. It was found that unless the oxycarbide

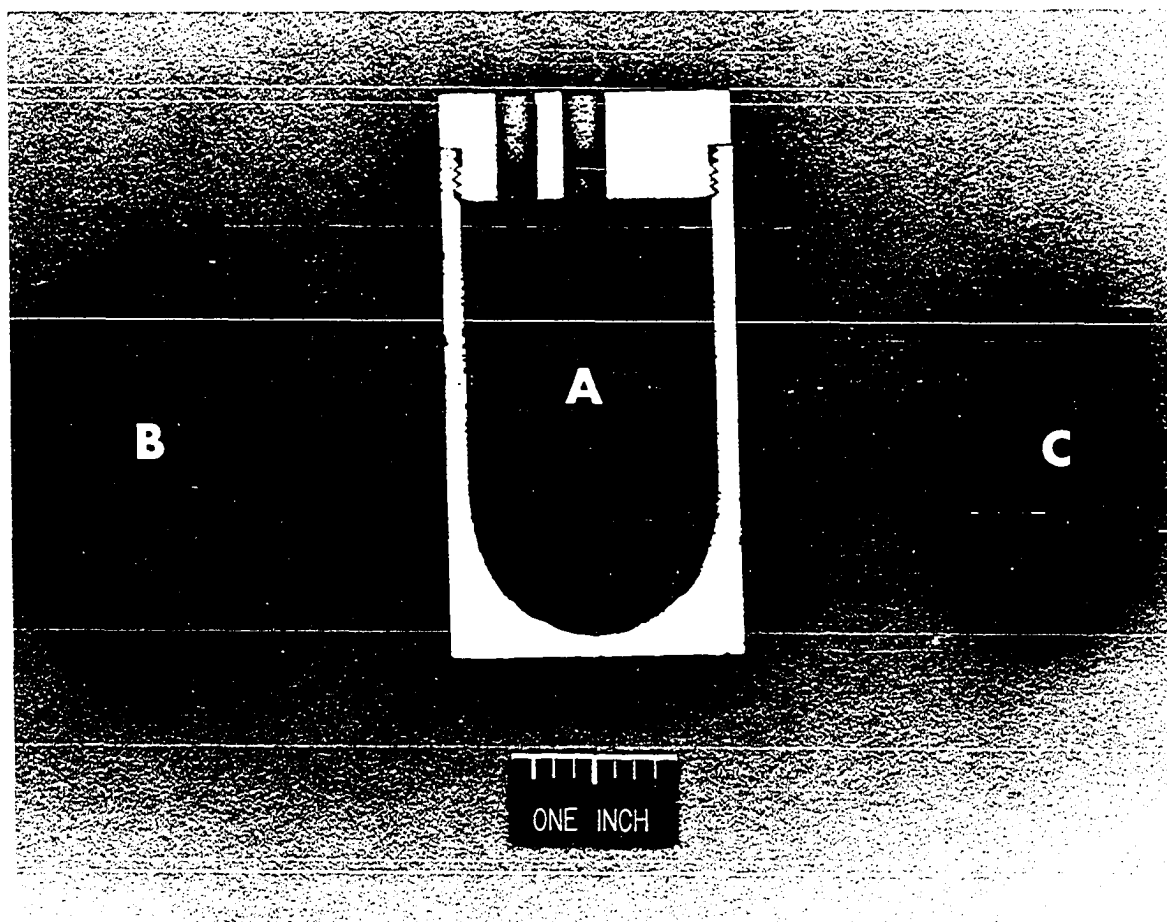


Figure 8. Cross section of a graphite crucible and lid with breather holes (A) used to contain the charge when preparing the two intermediate products shown. The larger of the two intermediate products (B) was prepared at 1550°C , while the more compact one (C) was prepared at 1950°C

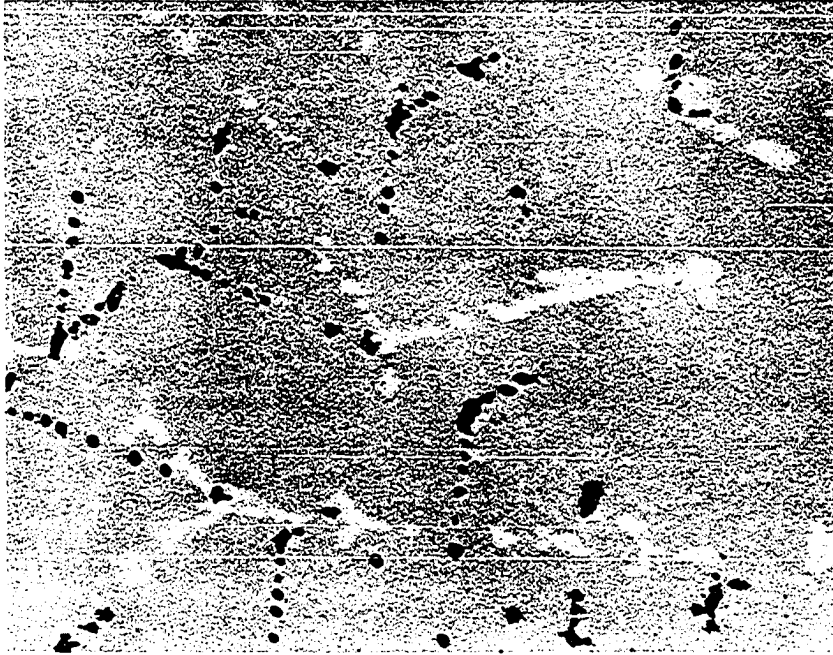


Figure 9. Microstructure of uranium metal which analyzed at 80 ppm carbon, 400 ppm nitrogen and greater than 500 ppm oxygen. Darker inclusions contain oxide and lighter inclusions contain nitride. Mechanical polish, 1:1 HNO₃ etch for 30 seconds. 100X

intermediate product was sufficiently cooled before opening the induction furnace vacuum chamber, excessive nitrogen pickup resulted. With adequate cooling, metal containing 60 ppm nitrogen or less was consistently prepared.

The metal shown in Figure 9 is also high in oxygen content but low in carbon. Although the excess oxygen pickup probably resulted in the same operation that introduced the nitrogen, the same condition of high oxygen could be obtained by a deficiency of carbon in the charge or by excessive heating of the metal product in the UO_2 crucible.

Results of a mass-spectrographic analysis of the normal metal product is shown in Table 8. The carbon, oxygen and nitrogen concentrations reported here are in good agreement with analyses of these constituents obtained by chemical means. Concentrations of all other elements detected are well below the limits accepted for reactor grade metal, with the possible exception of sulfur for which there appears to be no specification. An electron microprobe analysis has shown that the sulfur is associated with the inclusions, while the matrix is essentially free of sulfur in solid solution.

Figure 10 is a photomicrograph of the metal whose spectrographic analysis appears in Table 8. Although this metal

was analyzed to contain 100 ppm sulfur, microprobe analysis revealed that the large inclusions, in a sulfur-free metal matrix, contained about 27 wt % sulfur.

Table 8. Mass spectrographic analysis of uranium metal prepared by carbon reduction of U_3O_8

Element ^a	ppm	Element ^a	ppm
C	150	Ni	2
N	60	Mo	1
O	70	Hf	1
S	100	W	2
Si	20	S	0.1
P	1	Cd	N.D.
Mg	2	In	N.D.
V	1	Gd	N.D.
Fe	.2	Eu	N.D.

^a14 other elements detected contributed a total of 2 ppm; 36 other elements were not detected; 16 other elements (mostly rare) were not determined; 7 elements - Nb, Sc, Y, Dy, Ho, Er and Lu - had interference.

Metal prepared from the reduction of U_3O_8 derived from unsulfated UO_3 , on the other hand, was essentially sulfur free. It is obvious then that if it is desirable to exclude sulfur from the metal, an unsulfated oxide should be employed.

After the sources of the high nitrogen and sulfur contents in the metal were determined and means for their exclusion derived, metal with a total carbon, oxygen and nitrogen content of less than 400 ppm for these constituents was



Figure 10. Microstructure of uranium metal that analyzed mass spectrographically at 150 ppm carbon, 70 ppm oxygen and 60 ppm nitrogen. Cooled slowly to solidification. Large inclusions are mainly carbide. Mechanical polish, 1:1 HNO₃ etch for 30 seconds. 100X

typical. On a 200 g of metal scale, ingot yields of greater than 80% were obtained. Figures 10 and 11 show microstructures of two different samples of metal of this quality. The sample of Figure 10 was cooled at a slower rate near the temperature of solidification than that of Figure 11. Lower carbon and oxygen values can be obtained by continued heating of the metal at the maximum temperature; however, volatilization of the metal would result in a lower ingot yield. If it is assumed that the major factor involved in reducing the yield of metal in the ingot below theoretical is volatilization from the surface, a larger scale of operation could give higher ingot yields than those obtained on the laboratory scale.

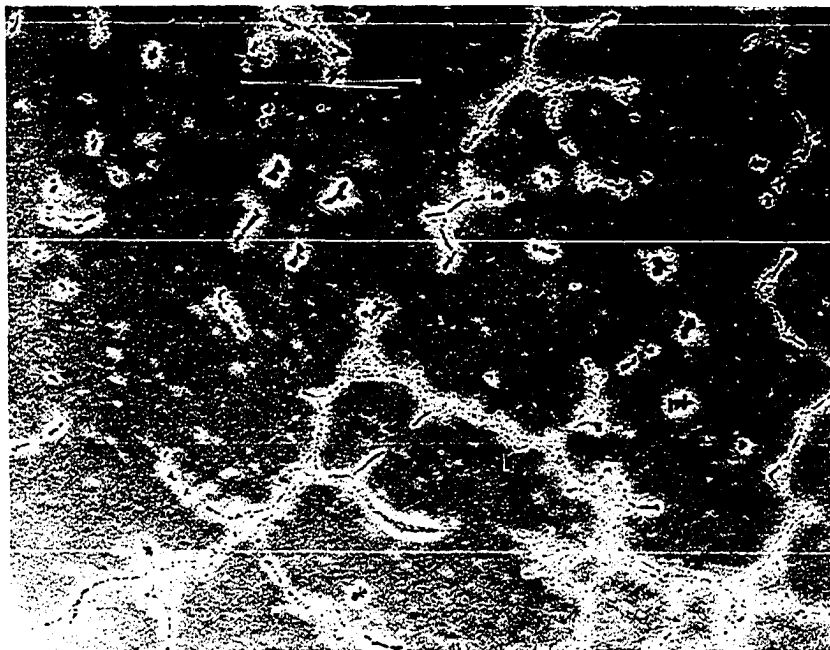


Figure 11. Microstructure of uranium metal which analyzed at 200 ppm carbon, 130 ppm oxygen and 30 ppm nitrogen. The finely divided inclusions are mainly carbide. Mechanical polish, 1:1 HNO₃ etch for 30 seconds. 100X

RECOMMENDATIONS FOR FURTHER STUDY

It is believed that the conditions are sufficiently well defined on a small scale (1/2 lb uranium) to warrant step-up in charge sizes. Consequently, the first recommendation suggested would be to study the previously derived process on a scale of at least 10 pounds of metal. One prerequisite to this study, however, would be the preparation of larger urania crucibles, 3 to 4 inches in diameter and 6 to 8 inches in height for the self-induction heating step. The procedure for crucible preparation should follow closely that employed for preparing the small crucibles to be described in Part II of this report.

The metal preparation process, as presently derived, allows the liquid uranium metal to solidify within the urania crucible after it has been prepared. Although the crucible is chemically inert to the metal, stresses set up due to the difference in contraction rates in the metal and oxide invariably causes the crucible to crack. As a result, the crucible in the experimental work was generally used for only a single run.

It appears, then, that the next step to be investigated further involves developing a means for removing the liquid

metal from the crucible before solidification occurs. One possible means for achieving this would be to use a crucible, with a pouring spout, that can be tilted after the reaction is completed to pour the liquid metal into a mold. Another possibility would be to use a crucible with a bottom plug that can be removed to allow the liquid metal to flow through an orifice in the bottom of the crucible.

SUMMARY OF METAL PREPARATION

The carbon reduction of uranium oxides has been successfully employed to yield high purity uranium metal in massive form by a laboratory-scale process that offers possibilities for expansion to a large-scale operation. This has been accomplished by using a two-step process.

The first step or operation consists of preparing an electrically conducting uranium intermediate product (oxycarbide) by partially reducing either UO_2 or U_3O_8 with the proper amount of carbon in a graphite crucible under vacuum conditions at temperatures between 1550° and $1950^\circ C$. The refining step consists of heating this product by self-induction under vacuum to yield liquid metal in a uranium oxide crucible assembly at temperatures up to about $2200^\circ C$.

When uranium dioxide was used as the source of uranium in the charge, no significant amount of reaction took place below $1300^\circ C$. The gas evolved in completing the reaction at higher temperatures was essentially all CO. A reaction of U_3O_8 with carbon under the conditions of operation employed initiates at about $750^\circ C$; consequently, some of the gas is evolved as CO_2 . It was found that 7.20 moles of carbon per mole of U_3O_8 would completely reduce this oxide to metal.

Uranium containing a total carbon, oxygen and nitrogen concentration of less than 400 ppm can be prepared by this process. The yield of metal in the ingot on a 200-g-of-metal scale is greater than 80%.

PART II. THE PREPARATION OF DENSE UO_2 SHAPES
BY THE CARBON REDUCTION OF U_3O_8

INTRODUCTION

After the development of the laboratory-scale process for the preparation of uranium metal by carbon reduction, a limited research study on the preparation of sintered UO_2 crucibles having greater density and strength was begun. A number of exploratory tests were made and a concentrated effort was undertaken on the more promising indications to realize this end. The process evolved in this study has also been extended to the preparation of dense uranium oxide in other shapes including those of nuclear fuel pellets.

LITERATURE REVIEW

Rather detailed work on the sintering of oxides of uranium was reported by Murray and Thackray (18), in 1950. Two standard oxides, the American Mallinckrodt oxide which analyzed to be $UO_{2.04}$ and the British Springfields oxide with a composition of $UO_{2.14}$ were used in this investigation. Pellets of the two oxides were cold compacted at 10,000 to 40,000 lbs/in² and sintered over a range of temperatures. Densities of 10 gm/cm³ were obtained for the Springfields oxide sintered at 1400°C, while the Mallinckrodt oxide sintered to only about 8.0 gm/cm³. However, the green densities of the two oxides were 4.7 gm/cm³ and 6.2 gm/cm³ respectively. Oxidation of the MCW oxide to $UO_{2.46}$ by heating in air at 300°C resulted in an improvement in its sintering properties, but it was still inferior to the Springfields $UO_{2.14}$.

When the Mallinckrodt oxide was sintered in hydrogen up to 1500°C, the density obtained showed little increase over the compacted green density.

Serious development of UO_2 as a nuclear fuel material for power reactors began in 1955 (19) when it was decided to load the Shippingport-Pressurized-Water Reactor (PWR) with Zircaloy-2-clad-fuel composed of UO_2 pellets.

Since then, numerous investigations have been conducted in an effort to better understand the factors which affect the sinterability of urania. A review of the published literature reveals that, although some of these studies have been broad in scope, the main characteristics studied and their effect on the final sintered density can be roughly divided (for discussion purposes) into a few general categories. They are: (1) the method used in preparing a ceramically active oxide, (2) the sintering atmosphere, (3) the oxygen to uranium ratio in the oxide and (4) the addition of small amounts of impurities.

The Method Used in Preparing a Ceramically Active Oxide

During 1957 and 1958, workers at Chalk River (20,21,22) reported that the density of sintered UO_2 pellets depended on the conditions under which the ammonium diuranate (ADU) was prepared. They concluded that in a batch precipitation of an ammonium uranate with ammonium hydroxide (NH_4OH), low uranium concentrations (less than 300 g U/l), high or excess ammonium hydroxide additions, solution temperatures of at least $60^{\circ}C$ and rapid precipitation all contribute to the development of a fine precipitate that yields a UO_2 which sinters to a high

density.

In 1962, Ainscough (23,24) reported that he had not observed any significant effect of precipitation parameters of polyuranate (temperature, rate of precipitation and final pH) on sinterability at 1650°C of UO_2 shaped by cold pressing. In his experiments, he calcined ammonium polyuranate to U_3O_8 at 700°C in an argon atmosphere and then H_2 reduced the octoxide to UO_2 . He found that the sintering behavior of the UO_2 depended on the calcining conditions used in converting the polyuranate to U_3O_8 since the U_3O_8 underwent free sintering at 600°C .

Dembinski et al. (25), in 1966, conducted a study wherein ammonium polyuranate was precipitated from a uranyl nitrate solution with ammonia (final pH - 8.5). The precipitate was then dried and calcined at 700°C where it was subsequently reduced to UO_2 in flowing hydrogen. The resulting UO_2 , which varied in oxygen to uranium ratio from 2.15 to 2.30, was then cold pressed and sintered in moistened hydrogen at various temperatures up to 1700°C . On the basis of their results, they concluded that high initial uranyl nitrate concentrations result in the formation of precipitates of large grain sizes. These larger grained materials did not sinter as well as the

finer grained material. They also found that the grain microstructure was dependent on the rate at which the precipitation step was carried out.

In an effort to prepare a sinterable dioxide from the trioxide, Niederkorn and Circo (26), in 1969, carried out a study to determine some of the conditions necessary in such a process. Solutions of uranyl nitrate containing from 50 to 200 g U/l were prepared by dissolving UO_3 in HNO_3 . A concentrated NH_4OH solution was then added to a pH of 8.5, while the time of addition ranged from two minutes to 30 minutes and the temperature varied from 20 to $80^{\circ}C$. They found that the highest sintered densities were prepared from uranyl nitrate solutions containing 50 g U/l at a precipitation time of 30 minutes at 60 to $80^{\circ}C$.

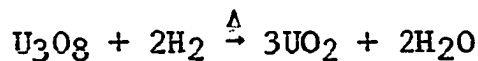
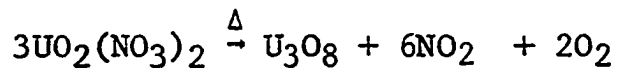
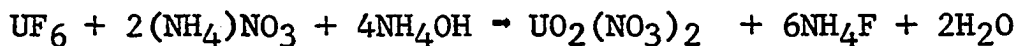
Communion has also been cited as a method of yielding an active uranium oxide. In 1957, Belle and Jones (27) and Simpson (28) reported that ball milling commercially prepared uranium dioxide prior to compaction resulted in increased final sintered densities.

Vaughn and coworkers, at about the same time, (29) found that wet ball milling commercial uranium trioxide increased the reactivity and sinterability of the resultant

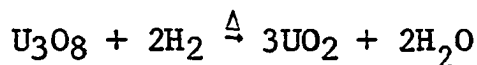
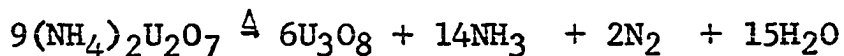
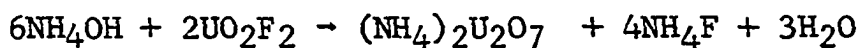
uranium dioxide. Compacts having densities of 95% of theoretical were obtained by pressing at 20,000 lb/in² and sintering for 1 hour at 1650°C in hydrogen.

Carlson, Root and Shane (30), in 1960, conducted a study in hopes of developing a practical process for the mass production of dense UO₂ bodies. The dioxide used in this work was prepared by either the uranyl nitrate precipitation method or the ammonium diuranate precipitation method. They reported the reactions for these two methods as follows:

(1) Uranyl Nitrate Precipitation Method



(2) Ammonium Diuranate Precipitation Method



Sintered pellets were then prepared from these UO₂ products by cold pressing between 25 and 100 tons/in² and sintered in

dissociated ammonia at temperatures between 1400 and 1700°C for 12 hours.

One area of this investigation involved the effect of ball milling on producing a more sinterable oxide. They found that the ball milling operation was effective in breaking down large agglomerates present in the dioxide samples. They also reported that short periods of milling were effective in lowering the sintering temperature required to reach a given density. Surface smoothness and the ease with which the pellets could be pressed was also enhanced by moderate milling. Chemical analyses of the oxides following the milling step revealed some contamination (~100 ppm) depending upon the grinding medium.

In 1961, Carpenter and Kuhlman (31) conducted a study on characterizing UO_2 powders. They found that, in general, high sintered density pellets were produced from powders having high surface area, small agglomerate and particle size, high O to U ratio and low bulk and tap densities. Prolonged ball milling was found to result in reduced agglomerate size and bulk density, increased O to U ratios, increased surface areas and improved sinterability of oxides which sintered poorly before milling.

More recently, Japanese researchers (32) reported that ball milling increased the specific surface area of uranium dioxide powders only slightly, but noted increases in the final sintered densities of the same oxides.

Another method that has been investigated to produce an active uranium oxide involves an oxidation-reduction sequence. Stenquist and Anicetti (33) reported that the oxidation-reduction cycling of an inactive oxide broke down agglomerates of particles that prevent compaction and densification, thus yielding a more sinterable oxide. This result was substantiated by Dayton and Tipton (34) in 1960.

In 1961, Gordon (35) at Olin Mathieson reported on developments for a more economical process for fabricating dense UO_2 pellets. Several commercial lots of UO_2 powder with varying sintering characteristics were activated by oxidation-reduction cycling followed by oxidation to an oxygen to uranium ratio of at least 2.25. Pellet densities of greater than 95% of theoretical were reportedly obtained by cold pressing this oxidized product at 38,000 lb/in² and sintering in nitrogen for 1 hour at 1300°C. Although it was previously thought that the oxidation-reduction cycle only broke down the coarse agglomerates, more recent results

revealed that the oxidation-reduction step also partially removed the fluoride impurities in the UO_2 .

The activation of normal ceramic grade UO_2 and 93.15 percent enriched UO_2 by either milling or milling and oxidation-reduction steps was reported by Barr (36), in 1970. Initially, ceramic grade normal UO_2 batches were calcined at 400, 600 and 800°C in air and nitrogen. The resulting powders were then pressed into pellets and sintered for 2 hours in an atmosphere of argon-8 v/o hydrogen at 1675 C.

The enriched UO_2 , on the other hand, was first wet ball-milled in an Al_2O_3 medium with an Al_2O_3 /oxide weight ratio of 2/1 or a tungsten carbide medium with a WC/oxide weight ratio of 3/1. After milling, samples were oxidized in air at 500°C for 1 hour. Oxidized powder samples were then reduced in the argon-8 v/o hydrogen atmosphere for 1 hour at 1675°C. Pellets were then prepared and sintered as described above.

Barr found that the oxidation-reduction sequence employed increased the final sintered densities 2 to 3% in both the normal and enriched oxides that after the oxidation step had an O/U of 2.65. However, he concluded that the oxygen-to-uranium ratio by itself did not have a significant effect on sinterability.

The Sintering Atmosphere

The effect of certain furnace atmospheres on the final sintered density of UO_2 has been the subject of various studies. Williams and associates (37), in 1958, reported on the sintering of various oxides ranging in composition from UO_2 to U_3O_8 in argon, nitrogen, carbon dioxide, vacuum and hydrogen at various temperatures. The starting oxide used in this investigation was prepared by the pyrolysis of ammonium diuranate at $300^\circ C$ to produce UO_3 which was then reduced in hydrogen to UO_2 at $650^\circ C$. Hyperstoichiometric oxides were prepared by the room temperature oxidation of the dioxide. The method used for preparing U_3O_8 was not given. Pellets were formed by pressing at 10 ton/in^2 and a standard sintering time of 2 hours was used.

They found that argon, nitrogen, carbon dioxide and vacuum were all suitable sintering atmospheres for the production of high-density nonstoichiometric oxide pellets. When hydrogen was used as a sintering atmosphere, the temperatures needed to obtain similar densities was found to be about $400^\circ C$ higher. If, however, the specific surface area of the oxide was high enough ($\sim 10 \text{ m}^2/\text{g}$), essentially the same results were obtained with hydrogen as with the other atmos-

pheres.

The sintering of uranium dioxide prepared by reduction of an ammonium uranate precipitated from a uranyl nitrate solution with urea was the subject of a study of Runfors et al. (38), also in 1958. In one series of tests, steam and both moist and dry hydrogen were used as sintering media. Of these, they found that the samples sintered in steam yielded the highest densities. Later, they compared hydrogen and argon as sintering media. Unlike the results obtained by Williams, they found that compacts sintered in hydrogen had higher densities than those sintered in argon.

Hubert, Webster and Bright (39) in 1958 also presented results on the sintering of UO_2 . The dioxide used in their study was prepared by the hydrogen reduction of ammonium diuranate. This material had an oxygen to uranium ratio of 2.19 and sintered to a density of 9.47 g/cm^3 on firing in hydrogen at 1700°C for 30 minutes. Cold pressed compacts of the $UO_{2.19}$ material were also sintered in argon, wet argon, argon + oxygen, nitrogen, nitrogen + oxygen, nitrogen + hydrogen, hydrogen and steam over the temperature range 1200° to 1500°C . They found that at 1200°C , wet argon yielded the highest density at 9.74 g/cm^3 while at 1500°C compacts sin-

tered in steam yielded the highest density at 10.20 g/cm^3 .

Terraza and his associates (40), also in 1958, reported on the sintering of UO_2 . The uranium dioxide used in this study was prepared by precipitating uranium peroxide from a uranyl nitrate solution with hydrogen peroxide. The peroxide was then calcined to UO_3 and subsequently reduced to UO_2 with hydrogen at a temperature of 700°C . The purpose of this investigation was to obtain high density in vacuum at medium temperatures using water as an agglomerate. Sintered products having an apparent density of 10.43 g/cm^3 were obtained by heating in vacuum at 1200°C for various periods up to 11 hours. Sample weight losses, however were reported at about 0.3 w/o.

Amoto and Colombo (41), in 1962, conducted a study that compared the sintering of UO_2 in steam with sintering in hydrogen; three qualities of UO_2 powder were used. They were: (1) depleted ceramic grade UO_2 from Mallinckrodt Chemical Works (MCW), (2) normal UO_2 from the Commissariat a l'Energie Atomique (CEA) and (3) normal UO_2 from the Comitato Nazionale per l'Energia Nucleare (CNEN). Table 9 summarizes some of the properties of these three oxides before and after sintering in hydrogen.

Table 9. Properties of uranium oxide powders used in Amoto and Colombo's study

Property	Manufacturer		
	MCW	CEA	CNEN
Tap density, g/cm ³	2.18	2.87	4.62
Average particle diameter, μ	1.28	0.90	1.98
Specific surface area, m ² /g	3.45	4.60	3.60
O/U ratio	2.03	2.11	2.02
Fired density obtained by sintering in H ₂ at 1700°C for 3 hrs g/cm ³	10.1	10.3	10.1

In order to have strictly stoichiometric dioxides at the beginning and end of the sintering step, the following cycle was developed by these investigators for all tests in steam:

(1) heat the UO₂ to 800°C in an inert gas (argon or pure nitrogen)

(2) heat to the soaking temperature (800°C to sintering temperature) in hydrogen

(3) sinter in steam

(4) cool to 800°C in hydrogen and

(5) cool to room temperature in argon or nitrogen.

They discovered that higher densities were obtained through

steam sintering at 1398°C than through hydrogen sintering at 1700°C for the MCW and CEA powders. The CNEN powder on the other hand sintered poorly in steam. They concluded that, although better sintered densities were obtained in steam using lower soaking temperatures and times, they questioned that steam was actually cheaper than hydrogen for this operation.

The next year, these same investigators along with Protti (42) reported on the sintering of UO₂ in carbon dioxide. The oxide used in this study was the Mallinckrodt oxide whose properties are shown in Table 9. The same type of heating schedule was employed in this study as described in the previous report. However, CO₂ was used in the sintering step in place of steam. Their results showed that they obtained about the same degree of sintering in carbon dioxide as they did with steam.

In 1967, Kostic (43) carried out a study on the sintering of UO₂ in helium, hydrogen and vacuum. The dioxide used reportedly had a specific surface area of 5.2 m²/g with an O/U ratio of 2.05 ± 0.01. Experiments involved sintering pressed compacts of this material at 1300, 1400 and 1550°C for periods up to 8 hours. It was found that pellets sintered in helium

yielded the greatest sintered densities in all cases although those sintered in vacuum were similar. At 1400°C, for example pellets that were sintered in helium for 1 hour had a sintered density of about 10.50 g/cm³ while those sintered in vacuum had a sintered density of about 10.30 g/cm³. No mention was made regarding loss of UO₂ during sintering in vacuum at 1400°C. Increased sintering times up to 8 hours did not change their final sintered densities appreciably.

Samples sintered in hydrogen showed appreciable variations in the sintered densities at different temperatures. After 1 hour at 1400°C in hydrogen, the final sintered density was about 9.5 g/cm³, substantially less than the densities obtained in helium and vacuum. After 8 hours in hydrogen at 1400°C though, the final sintered densities were increased to 10.20 g/cm³, similar to those obtained in vacuum.

During the same year, Kolar et al. (44), reported on the effect that the atmosphere had on the sintering of uranium dioxide with high surface area. The UO₂ used in this study was prepared by decomposing and reducing active ammonium diuranate at 400 to 1000°C. The sintering atmospheres investigated included wet and dry hydrogen and wet and dry nitrogen. They found that all of the oxide samples sintered better in

the wet atmospheres as opposed to the dry ones, but varying results were obtained depending upon the specific surface area of the oxide starting material. When an oxide with a specific surface area of $7.5 \text{ m}^2/\text{g}$ was sintered in wet nitrogen at 1400°C for 3 hours, a density of 96.7% of theoretical was obtained while the UO_2 that had a specific surface area of $17.2 \text{ m}^2/\text{g}$ sintered to only $13.7 \text{ g}/\text{cm}^3$ in the wet nitrogen. On the other hand, when wet H_2 was used, the UO_2 with the higher specific surface area ($17.2 \text{ m}^2/\text{g}$) sintered to 93.2% of theoretical while the oxide with the lower specific surface area sintered to 90% of theoretical.

Miyazaki (45) in 1968 reported on the use of carbon monoxide in the low temperature sintering of UO_2 pellets. The materials were prepared at an elevated temperature by the simultaneous thermal decomposition and reduction of the ammonium diuranate (ADU) precipitate obtained from a purified nitrate solution. The reduction to the dioxide ($\text{UO}_{2.07}$ to $\text{UO}_{2.11}$) was accomplished using either hydrogen or carbon monoxide.

He reported that when the diuranate was reduced to the dioxide with carbon monoxide, pellets prepared from this dioxide gave densities exceeding $10.2 \text{ g}/\text{cm}^3$ after 4 hours

of heating at 1400°C in a carbon monoxide atmosphere. Slightly lower sintered densities were obtained for these pellets, however, when the sintering atmosphere was hydrogen and the sintering time was less than fourteen hours. Sintering times in excess of fourteen hours yielded higher densities in hydrogen. On the other hand, when the reduction step from ADU to UO_2 was carried out with hydrogen, all of the pellets sintered in hydrogen had higher sintered densities (10.3 to 10.6 g/cm^3) than those obtained when sintered in carbon monoxide (10.0 to 10.2 g/cm^3) irrespective of the sintering time.

In May 1969, Flipot, Glissen and Smolders (46) reported on a new manufacturing process for preparing UO_2 pellets with their final density controlled by a disactivation treatment. In their process, UO_2 of ceramic quality (specific surface area - $5 \text{ m}^2/\text{g}$) is deactivated by first heating it in CO_2 prior to the final sintering step. This thermal treatment involves heating either the powder or the pressed compact at 650°C to 900°C for about 3 hours in carbon dioxide. They reported that compacts prepared from the untreated oxide yielded sintered densities of 10.28 g/cm^3 after a 3 hour sintering at 1600°C in an argon-5 v/o hydrogen gas mixture, while

the treated oxide pressed to the same green density yielded a final sintered density of about 9.3 g/cm^3 . When the green densities of the untreated and treated oxide compacts were increased to 5.2 g/cm^3 , final sintered densities of about 10.5 g/cm^3 and 9.8 g/cm^3 respectively were obtained.

The Oxygen to Uranium Ratio in the Oxide

Hall et al. (47), in 1958, reported that the O/U ratio had an effect on the plastic deformation of uranium oxides. Three oxides with different oxygen to uranium ratios were employed. They were $\text{UO}_{2.06}$, $\text{UO}_{2.16}$ and stoichiometric dioxide. They found that $\text{UO}_{2.06}$ and $\text{UO}_{2.16}$ can be deformed plastically at about 800°C while the corresponding temperature for $\text{UO}_{2.00}$ was about 1600°C .

It was also reported that the creep characteristics of UO_{2+x} are similar to those of metals. The activation energy Q , for $\text{UO}_{2.06}$ was reported as 72 Kcal/mole while Q for $\text{UO}_{2.16}$ was 65 Kcal/mole. The activation energy for UO_2 was approximately the same as that determined for the self-diffusion of uranium in $\text{UO}_{2.00}$, i.e., 95 Kcal/mole.

In one phase of a broad study conducted at Olin Mathieson (35), in 1960, the effect of the initial O/U ratio to the final sintered density for 5 varied lots of dioxide was evalu-

ated.

The as-received materials were first oxidized to U_3O_8 in air at $500^\circ C$ followed by reduction in hydrogen at $525^\circ C$. The resulting oxides were then air roasted to introduce excess oxygen. After pellets were pressed at $38,000 \text{ lb/in}^2$, they were sintered in nitrogen for 2 hours and hydrogen for 1 hour.

Samples with an initial O/U ratio which varied from 2.13 to 2.16 sintered to a maximum density of 8.7 g/cm^3 . When the O/U was increased to 2.26, the sintered densities increased to about 10.4 g/cm^3 (~95% of theoretical). Increasing the O/U ratio further to 2.37 resulted in no density increase in 4 of the 5 batches tested and decreased the density obtained in one batch.

In 1961, workers at the United Nuclear Corporation (35) reported on a process they developed for fabricating uranium oxide fuel pellets by an inert atmosphere (nitrogen) and low temperature sintering method. Commercial ceramic grade dioxide prepared from ADU was first oxidized to U_3O_8 at $500^\circ C$ in air and then reduced back to UO_2 in hydrogen at $525^\circ C$. This treatment yielded a highly active nonstoichiometric oxide. When the oxide to U ratio was increased to greater than 2.25, sintered compacts of greater than 95% of theoreti-

cal were obtained. A comparison of these data with that obtained by Olin Mathieson in 1960, reveals striking similarities.

In 1968, Lay and Carter (48) reported that the O/U ratio has 'a direct bearing on the sinterability of uranium dioxide. Unlike previous investigators, however, they felt that the O/U ratio in the starting oxide was of little significance. What was considered important was the furnace atmosphere used since it fixes the O/U ratio at the sintering temperature.

They found that O/U ratios above stoichiometric UO_2 increased the uranium self-diffusion coefficient, and they concluded that the sintering of UO_2 was a volume controlled diffusion process.

The Addition of Small Amounts of Impurities

Sowman and Ploetz (49), in 1956, reported on the effect of additives on the sinterability of uranium dioxide. Six different lots of oxide were used. They included:

- (1) MCW UO_2 ,
- (2) UO_2 prepared by precipitating $UO_4 \cdot 2H_2O$ from uranyl nitrate at pH 2, followed by reduction with H_2 at $850^\circ C$ for 4 hours,
- (3) dioxide prepared by precipitating ADU with NH_4OH at

pH 7.5, followed by reduction with hydrogen at 850°C for 4 hours,

(4) UO₂ prepared by the steam oxidation of uranium chips at 350°C followed by reduction with hydrogen at 850°C for 4 hours,

(5) UO₂ prepared by the steam oxidation of uranium metal powder at 350°C followed by reduction with hydrogen at 850°C for 4 hours. The metal powder was prepared by passing H₂ over uranium chips at 250°C for 6 hours followed by hydride decomposition at 450°C, and

(6) UO₂ prepared by burning uranium metal to U₃O₈ in air followed by reduction with hydrogen at 850°C for 4 hours.

The additives investigated included CaO, NiO, MnO, Fe₂O₃, Al₂O₃, Ga₂O₃, Tl₂O₃, Y₂O₃, Nd₂O₃, TiO₂, CeO₂, V₂O₅, Nb₂O₅ and UF₄ in varying proportions with UO₂ up to 3 wt %. They found that Al₂O₃, CaO, Cr₂O₃, MnO₂, V₂O₅ and CaF₂ increased the final sintered density somewhat, but that TiO₂ was by far the most effective. They also found that small TiO₂ additions (0.25 w/o to 0.50 w/o) were more effective than the larger additions (1 w/o to 3 w/o). They concluded that the function of the sintering agent was probably one of increasing the surface activity.

Bright and his coworkers (50), in 1957, reported on the effect of carbon on the sintering behavior of uranium dioxide. UO_2 prepared by the hydrogen reduction of ammonium diuranate and the starch reduction of UO_3 were used.

Cold-pressed pellets of each oxide sintered to greater than 95% of theoretical at $1700^{\circ}C$ in hydrogen for 30 minutes. The addition of variable amounts of graphite to these oxides prior to cold pressing had a deleterious effect on the final sintered density. Compacts containing 1 wt % added graphite sintered to 90% of theoretical while green compacts that contained 10 wt % graphite sintered to only 58% of theoretical.

The effect of Nb_2O_5 , V_2O_5 and TiO_2 on the sintering of UO_2 was part of an investigation reported by Watson and Wilder (51), in 1960. Each of these materials was thoroughly mixed with production-grade MCW dioxide, pressed into pellets at $40,000 \text{ lb/in}^2$ and sintered in hydrogen at $1750^{\circ}C$ for various time periods. The mixed-oxide compositions studied included: $UO_2 + 0.4 \text{ w/o } Nb_2O_5$, $UO_2 + 0.1 \text{ w/o } V_2O_5$ and $UO_2 + 0.1 \text{ w/o } TiO_2$. Pellets of UO_2 were sintered at the same time for comparison purposes. On the basis of their results, they concluded the following:

(1) pure UO_2 sinters readily at temperatures below $1600^{\circ}C$ when

nonstoichiometric oxygen is available for diffusion and densification. In the absence of excess oxygen, sintering occurs at temperatures above 1600°C by self-diffusion of the stoichiometric oxygen in UO_2 .

(2) Additions of 0.4 w/o Nb_2O_5 and 0.1 w/o V_2O_5 to UO_2 aid densification at temperatures below 1500°C by forming interstitial solid solutions. Above 1500°C these additives melt, decompose and volatilize out.

(3) TiO_2 acts as an oxygen supplier during the early stages of sintering, increasing densification significantly by promoting nonstoichiometric oxygen diffusion. At higher temperatures, a ductile solid solution or liquid phase is formed that aids sintering by straining the lattice near the grain surface, permitting diffusion of stoichiometric UO_2 .

In 1964, Arthur and Scott (52), evaluated the effect of a large number of additives on the sintering of UO_2 . Springfield's oxide with an O/U ratio of 2.04 was mixed with variable amounts of CaO , NiO , MnO , Fe_2O_3 , Al_2O_3 , Ga_2O_3 , Tl_2O_3 , Y_2O_3 , Nd_2O_3 , TiO_2 , CeO_2 , V_2O_5 , Nb_2O_5 and UF_4 ranging from 0.2 wt % to 1.0 wt %, pressed into pellets at 10 tons/in² and sintered in dry hydrogen from 1300 to 1700°C for various time periods.

They found that only TiO_2 , V_2O_5 and Nb_2O_5 have an appreciable effect on the terminal densities of UO_2 after sintering in hydrogen. Unlike the results reported by Watson and Wilder, they found no evidence of TiO_2 in the liquid phase, but proposed no sintering mechanism.

In 1965, Manojlovic and associates (53) also reported on the effect of TiO_2 additions on the sintering of UO_2 in argon. The dioxide used in this study originated from ADU and had an O/U ratio of 2.07. After UO_2 - TiO_2 mixtures ranging from zero to 30 a/o TiO_2 were pressed into pellets at 4 tons/cm², they were sintered in argon for various time periods.

They found that no measurable quantities of a solid solution of TiO_2 in the cubic fluorite UO_2 phase was formed. They considered that possibly some chemical reaction between the TiO_2 and UO_2 was one of the main reasons for the beneficial effect of the TiO_2 additive.

In 1966, Matzke (54) reported another study on the effect of TiO_2 additions on the sintering of UO_2 . Reactor grade oxide was mixed with small amounts of TiO_2 and sintered in argon at 1950°C for various periods. Sintered densities of 96% of theoretical were obtained. On the basis of chemical analyses and quantitative metallography, it was concluded

that about 0.1 mole % TiO_2 is soluble in UO_2 at elevated temperatures and that a fraction of the titanium ions probably occupy interstitial positions. As a consequence, Matzke believed that the increased sintering was probably due to increased bulk diffusion due to the interstitial solution of titanium and an interstitial diffusion mechanism.

APPARATUS

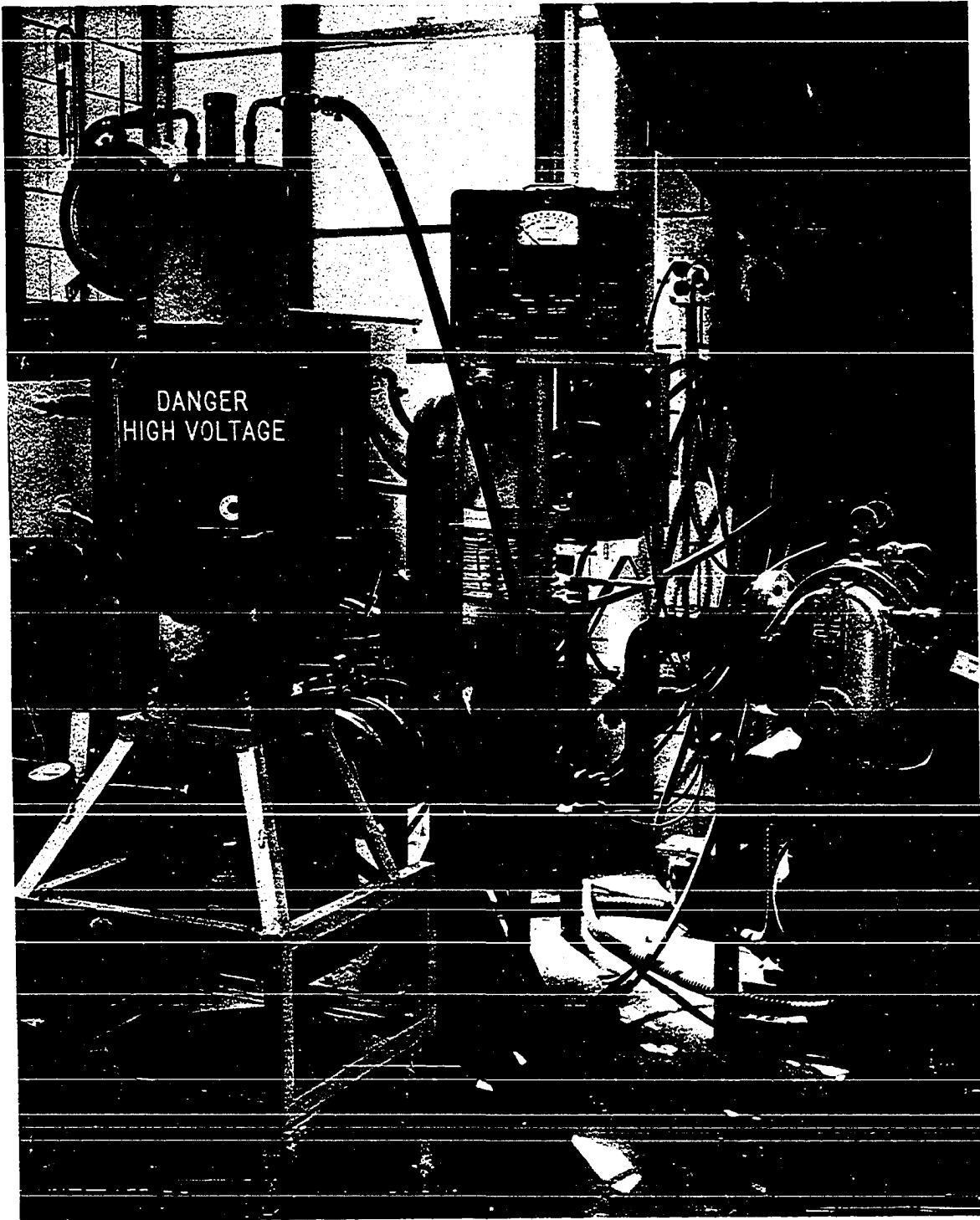
Some early exploratory tests on the preparation of dense UO_2 pellets and shapes were conducted in the vacuum induction furnace shown in Figure 12. Although this set-up used the same power supply (6 KW Ajax unit) and vacuum pumping system as described in Part I, the vacuum chamber, hoist-type induction coil and furnace assembly employed were larger.

The silica sleeve measured six and one-half inches inside diameter with a one-eighth inch wall thickness and was 26 inches in length. The induction coil used with this sleeve was seven inches inside diameter and consisted of 40 turns. The graphite crucible which served as a susceptor was four and one-half inches inside diameter and nine inches in height with a three-sixteenth inch wall.

Most of the compact sinterings using an atmosphere were carried out in a platinum wound electrical resistance tubular furnace Model J.M.C. K-26B manufactured by the Johnson and Matthey Co., Inc. This furnace was 15 inches in length with a bore of one and one-half inches. The length of the uniform temperature zone depended on the temperature. At $1000^{\circ}C$, it was three inches in length, while at $1400^{\circ}C$ its length was only two inches.

Figure 12. Photograph of vacuum induction furnace used in early exploratory tests

- A. Silica sleeve
- B. Thermocouple gauge
- C. Induction coil (hoist-type)
- D. Ionization gauge
- E. Roots-type booster pump
- F. Thermocouple and ionization gauge control
- G. Oil diffusion pump
- H. Pressure-vacuum gauge
- I. Wet test meter



The sintering chamber of this furnace was a sillimanite or an alundum tube 30 inches in length, one and three-eighths inches outside diameter with a one-eighth inch wall thickness. One end of this tube was tapered and served as the gas inlet port for the chamber. After the samples were positioned within the chamber, a rubber stopper fitted with a gas exit port and a Pt/Pt-13% Rh thermocouple was inserted into the open end of the furnace chamber. A photograph of this setup is shown in Figure 13.

A signal from either of two Pt/Pt-13% Rh thermocouples attached to the furnace windings served as an input to a Brown Potentiometer which controlled the furnace temperature. Temperatures within the furnace chamber were obtained periodically using the thermocouple inserted through the rubber stopper.

During the later phases of this investigation, another platinum wound furnace was acquired for use in crucible preparation. This unit was manufactured by the Norton Company and was designated as a Model No. 1352 Marshall Tubular Furnace. It was 16 inches in length with a three inch base. The uniform temperature zone measured 10 inches in length. This furnace was positioned vertically on an adjustable platform

Figure 13. Photograph of smaller platinum-wound resistance furnace used in investigation

- A. JMC Platinum Resistance Furnace
- B. Cooling coil (gas inlet)
- C. Cooling coil (gas outlet)
- D. Gas exit port
- E. Pt/Pt-13% Rh thermocouple
- F. Sillimanite furnace tube with reduced end

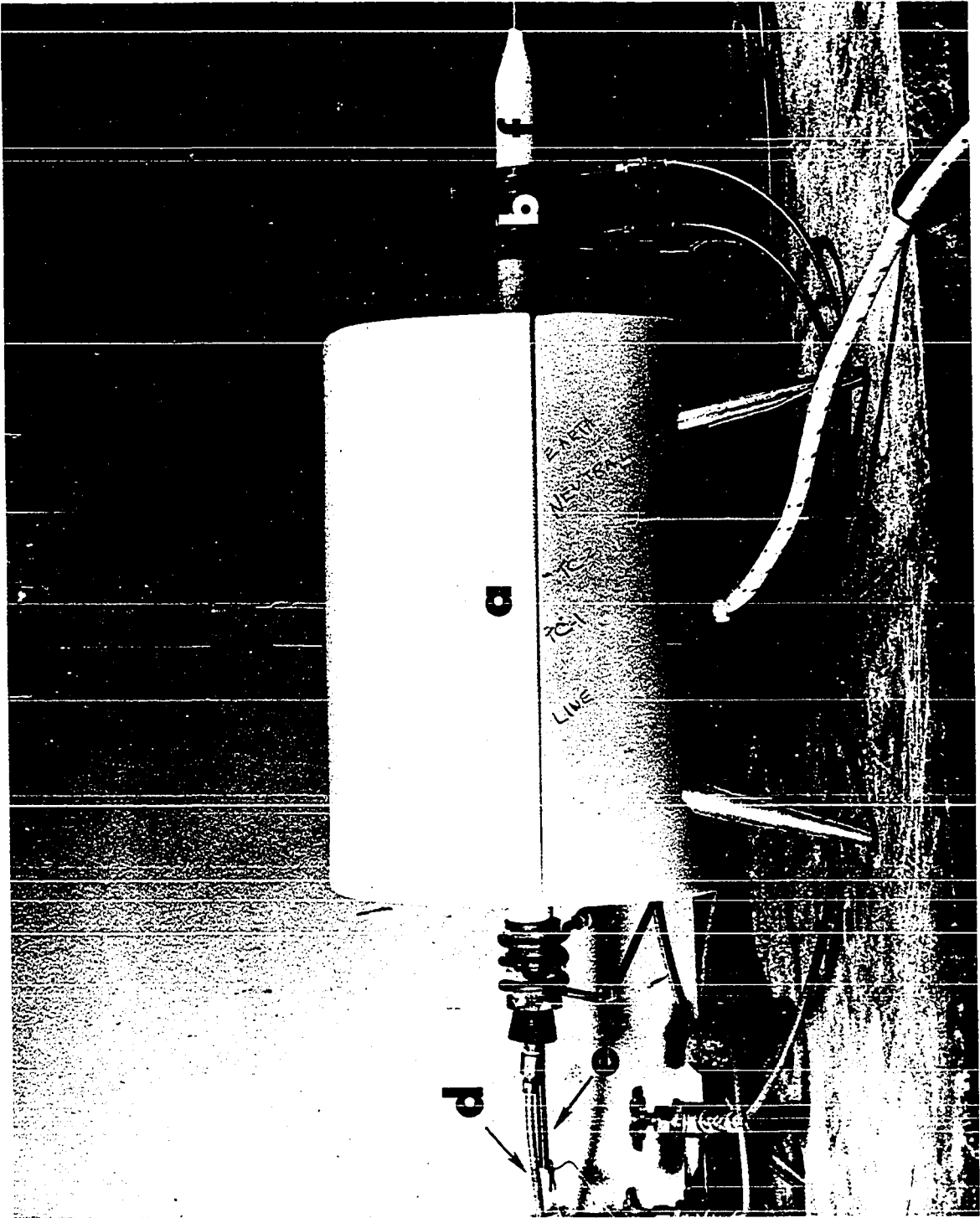
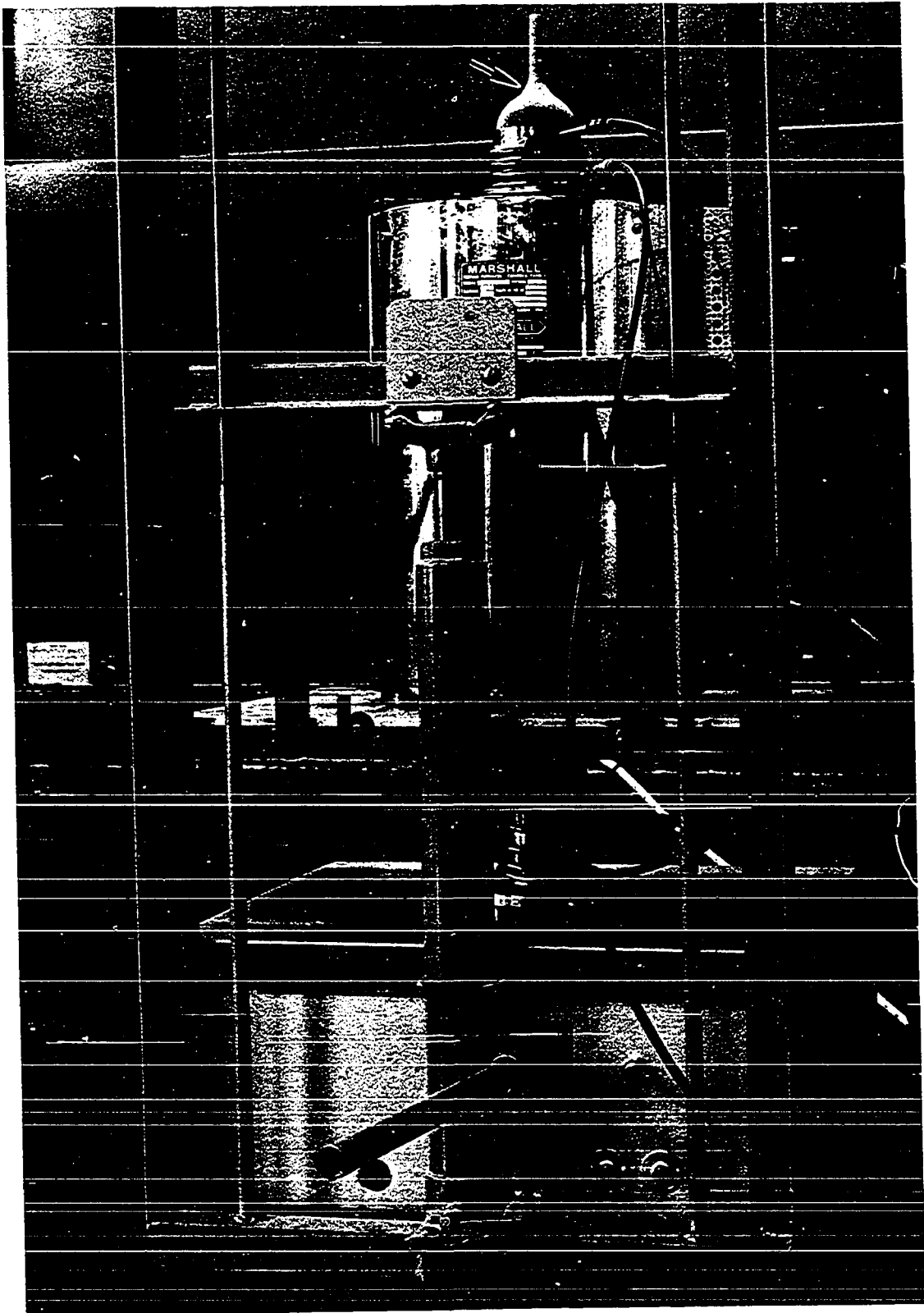


Figure 14. Photograph of larger platinum-wound resistance furnace used in investigation

- A. Model No. 1352 Tubular Furnace
- B. Adjustable platform
- C. Sillimanite furnace tube with reduced end
- D. Water-cooled flange (gas inlet)
- E. Hydraulic jack
- F. Cooling coil (gas outlet)



as shown in Figure 14. The sintering chamber used consisted of an alundum tube 30 inches in length, two and three-fourths inches outside diameter with a one-eighth inch wall thickness. The top end of this tube was tapered to about one-half inch outside diameter and was cooled with water in a copper coil. The bottom end of the tube rested on a neoprene gasket within a closed water-cooled flange. An alundum pedestal within the furnace chamber held the crucible in the hot zone during sintering.

The temperature of this furnace was controlled by a Brown Potentiometer that received a signal from a Pt/Pt-13% Rh thermocouple positioned in a well adjacent to the heating element.

MATERIALS

Charge and Refractory Oxide Crucible Materials

Carbon

The graphite used was the same (Grade 195) as that described in Part I (see pages 21 and 22) of this report.

Uranium oxides

The uranium oxides used originated from either production grade UO_2 or UO_3 . A detailed description of these oxides is given on pages 22-26, Part I.

Graphite Stock and Insulating Materials

The graphite stock used in preparing graphite ware and the insulating carbons used are the same as those described on pages 27 and 28, Part I.

Sintering Atmospheres

Carbon dioxide

The carbon dioxide used was obtained from the Mitchell Fire Extinguisher Service, Des Moines, Iowa. It was specified to be at least 99.9% CO_2 by volume. To evaluate the effect of impurities, if any, on the sintering of UO_2 , comparison tests were made with high purity CO_2 (Coleman Instrument Grade) supplied by the Matheson Company. Essentially the same results were obtained using either of these two

gases.

Argon, nitrogen and hydrogen

The argon, nitrogen and hydrogen used were obtained from the Air Products and Chemicals Company. Table 10 summarizes the impurity levels of these gases as supplied by the vendor.

Table 10. Analyses of the argon, nitrogen and hydrogen used in this investigation

Constituent	Analysis as volume percent		
	Argon	Nitrogen	Hydrogen
Ar	99.996	--	--
N ₂	0.0030	99.995	0.07
H ₂	0.0002	0.0010	99.92
O ₂	0.0007	0.0025	0.0005
CH ₄	0.0002	--	0.0001
CO ₂	0.002	--	0.0015
nitrogen oxides	-- ^a	--	0.0007
CO	--	--	0.0004
Cl ⁻	--	--	Trace

^aNot reported.

Binders

Polytran FS and L obtained from The Pillsbury Company were used in some experiments. Oxidation experiments on Polytran FS at 800°C showed it to contain about 9 wt % ash. Emission spectrographic analysis of this residue revealed that the major constituents were sodium and silicon.

Graphite Tray Support Materials

Uranium dioxide

The uranium dioxide used was production grade UO_2 described on pages 24-26 of this report.

Stabilized zirconia (ZrO_2)

The zirconium dioxide used is described on pages 26 and 27 of this report.

Yttria (Y_2O_3)

The Y_2O_3 used was prepared by calcining yttrium oxalate precipitated from an yttrium-rich fraction in the ion exchange separation of yttrium and rare earths. The purity of this material prepared at the Ames Laboratory was greater than 99% Y_2O_3 .

Titania (TiO_2)

The titanium oxide used was Fisher Certified ACS Titanium Oxide obtained from the Fisher Scientific Company. It had a purity greater than 99.9% as TiO_2 .

Hafnia (HfO_2)

The hafnium oxide used was prepared by calcining hafnium hydroxide $HfO(OH)_2$ obtained from the liquid-liquid extraction of zirconium-hafnium salts. This material reportedly contained 2 wt % zirconium.

FUNDAMENTAL VS. APPLIED APPROACH

Sintering, a process for consolidating powdered materials into a coherent mass under the influence of heat at temperatures below the fusion point, is the means employed to prepare dense UO_2 shapes. A number of mechanisms have been proposed to explain the sintering of nonmetallic materials; some of these mechanisms have been employed in discussing the sintering of UO_2 . These include:

- (1) Diffusion (movement of ions).
 - (a) Volume (movement through crystal lattices).
 - (b) Surface (movement on or near surfaces of crystallites).
- (2) Macroscopic Flow (movement of groups of atoms).
 - (a) Viscous (nonelastic movement where deformation requires a minimum yield stress).
- (3) Vapor Movement (vaporization-condensation).

The observed sintering behavior of UO_2 cannot be explained entirely on the basis of any one of these mechanisms. Rather, it appears that all of these mechanisms may be operative at some time during the sintering sequence. Although considerable insight might have been gained by seeking such a fundamental approach, the overall goal of this phase of the

investigation was to develop a process for preparing high density UO_2 crucibles for use in metal preparation. Consequently, a basic research study was bypassed in favor of a more applied approach in seeking a satisfactory solution to the immediate problem.

On the basis of previously reported results, there appears to be concurrence on the importance of a number of variables. However, the lack of agreement on the specification of other parameters that have been considered affective in the preparation of dense UO_2 bodies indicates there must be other unsuspected variables or synergistic effects that have not been considered.

Although the published literature did not supply adequate specifications for the total control of all factors, it was useful as a guide in defining major areas for consideration during the course of this study. Aside from temperature and time at temperature, it was evident from previous work that the history and origin of the starting material influenced the degree of sintering. Also, the state of division and the oxygen to uranium ratio of the oxide as well as the atmosphere had a bearing on the sintering of the uranium oxide.

EXPERIMENTAL

Procedures

The procedures employed during the second phase of this investigation included charge preparation, compact preparation, compact sintering in the platinum resistance furnace and evaluation of the product (sample). From the results of these experiments, conditions for the preparation of crucibles were devised, tested and evaluated. Since charge preparation, crucible preparation and control and evaluation techniques have been discussed in detail in Part I (pages 36-40), only a description of the compacting procedure and the sintering procedure used when the platinum resistance furnace (Figure 13) was employed will be presented here.

Compact preparation

The approximate weight of charge desired in a pelletized compact was pressed into the shape of a right circular cylinder in a double action steel die. The bore of the die was one-half inch in diameter. In order to avoid the possibility of side or unknown reactions with the charge materials, additives such as binders and special lubricants were generally not used for the compaction step. After the green compact was ejected from the die, it was measured with a micrometer

and weighed to the nearest one-ten-thousandth of a gram.

Compact sintering in the platinum resistance furnace

After the green compacts were positioned within the furnace and the end of the tube sealed, the heating chamber was purged for about 30 seconds with the sintering atmosphere to be employed. When the heating cycle was initiated, the gas flow rate was decreased to a slow rate in order to maintain the atmosphere over the samples during sintering. If the samples were sintered under reduced pressure, the system pressure was decreased to less than 50 microns before heating.

To reduce the stress on the furnace elements, the furnace temperature was increased slowly up to 600°C. About 1 hour was allowed to reach this temperature. Although temperatures above 600°C could be achieved quite rapidly, the heating rate used usually required an additional two hours to get to the top temperature (1400°C). When the sintering operation was completed, the compacts were allowed to furnace cool. About 3 hours were required to reduce the chamber temperature to 300°C. After the samples had cooled sufficiently, they were removed from the furnace, measured and weighed.

RESULTS AND DISCUSSION

Exploratory Tests

Urania crucibles used during the metal preparation phase, discussed in Part I of this report, were prepared by sintering jolt-packed production grade UO_2 in a graphite mold in vacuum at temperatures up to $1900^{\circ}C$ by induction using graphite. Although a usable crucible was produced, it lacked high strength.

Oxidation of pieces of the crucibles revealed that the oxygen to uranium ratio in the sintered oxide was usually less than two. The decrease in O/U ratio was probably the result of two influences. They were:

(1) reaction of the urania with the graphite mold at these temperatures and

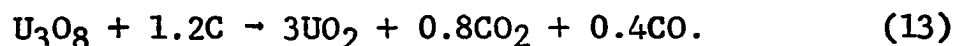
(2) instability of hyperstoichiometric urania under vacuum conditions.

In an effort to obtain more quantitative data, pellets of urania were cold pressed and then sintered in vacuum on a graphite tray under the same conditions as those used in crucible preparation. Analysis of these compacts revealed that the O/U ratios had been decreased to 1.99, weight losses exceeded five percent and the final sintered densities ranged

from 7.0 to 7.2 gm/cm³.

Since previous investigators generally agreed that a hyperstoichiometric oxide sinters to a higher density than sub-stoichiometric or stoichiometric oxide, a means for obtaining and controlling the oxygen to uranium ratio to give a slightly hyperstoichiometric oxide was devised.

Although air oxidation has been employed, in the past, for increasing the O/U ratio of UO₂, this method was bypassed in hopes of finding a more reproducible approach. During the first part of this investigation on metal preparation, it was reported that U₃O₈ could be reduced to UO₂ with carbon at 1000°C in vacuum according to Equation 13 given earlier (Part I) as:



On the basis of this reaction, it appeared that hyperstoichiometric urania compositions might be prepared from charges containing C/oxide mole ratios of less than 1.2.

As an initial test, 11 charges of U₃O₈ (from oxidized production grade UO₂) mixed with carbon in C/oxide mole ratios ranging 0.1 to 1.1 in one-tenth mole increments were prepared. Cold pressed compacts were then prepared from each of these charges and sintered on a graphite tray in vacuum at 1700°C,

for two hours. Table 11 summarizes the results obtained.

Although all of the sintered pellets analyzed to be $\text{UO}_{2.00}$, the final sintered densities varied from 7.28 gm/cm^3 to a maximum at 8.39 gm/cm^3 obtained with the charge containing a $\text{C/U}_3\text{O}_8$ mole ratio of 0.6. Since this ratio in each charge was less than 1.2, a hyperstoichiometric oxide would have been produced at 1000°C . The stoichiometric $\text{UO}_{2.00}$ product in all cases was probably due to thermal decomposition on heating to 1700°C .

It is not certain why the charges containing from 0.8 to 1.1 moles of carbon stuck to the graphite tray, but it appears that considerable carbide may have been formed at the areas of contact of these samples with the graphite. It should also be noted that the sample weight losses varied considerably depending on the initial $\text{C/U}_3\text{O}_8$ mole ratio. These data show that heating a charge with a carbon to U_3O_8 mole ratio of less than 0.6 under these conditions (1700°C for 2 hours, in vacuum) permits volatilization of an oxide species that results in a loss of nearly 10% of the UO_2 .

To eliminate the reaction between the graphite tray and the samples, a number of refractory oxides were tested for compatibility as support materials for the samples. Compacts

Table 11. Sintered densities obtained on compacts of C and U₃O₈ (from UO₂) by heating at 1700°C in a graphite susceptor under vacuum for 2 hours

Charge composition	Green compact wt.; gm.	Theo. UO ₂ wt. in pellet (gm.)	Oxide composition after sinter	Actual UO ₂ wt. after sinter, (gm.)	UO ₂ wt. loss %	Sintered density g/cm ³
U ₃ O ₈ + 0.1C	14.80	14.22	UO ₂ .00	12.90	9.28	7.28
U ₃ O ₈ + 0.2C	13.29	12.75	UO ₂ .00	11.54	9.49	7.30
U ₃ O ₈ + 0.3C	13.71	13.13	UO ₂ .00	12.00	8.60	7.36
U ₃ O ₈ + 0.4C	11.88	11.36	UO ₂ .00	10.30	9.33	6.78
U ₃ O ₈ + 0.5C	12.50	11.94	UO ₂ .00	10.80	9.54	7.06
U ₃ O ₈ + 0.6C	14.91	14.22	UO ₂ .00	13.90	2.25	8.39
U ₃ O ₈ + 0.7C	13.90	13.24	UO ₂ .00	12.97	2.03	7.79

Samples containing 0.8, 0.9, 1.0 and 1.1 moles of carbon per mole of U₃O₈ stuck to the graphite tray.

containing C/U₃O₈ mole ratios of 0.8 were placed on each of the powdered refractories that covered a small area of the graphite tray.

The refractories included ZrO₂, UO₂, TiO₂, HfO₂ and Y₂O₃. One pellet was also placed on the graphite and served as a blank. These samples were all heated in the same manner as described for the samples in Table 11 except that the sintering time was increased to six hours.

The addition of a support material between the graphite tray and the pressed compact reduced the loss in weight relative to the blank in all cases, but the loss still remained considerable. About a 23% weight loss occurred on the sample supported directly on graphite, while weight losses on the refractories ranged from 14 to 20%. Of the materials tested, no noticeable reaction occurred between the compacts and ZrO₂, Y₂O₃ and UO₂. However, considerable reaction occurred with the TiO₂ and HfO₂ support materials.

After a number of other related exploratory tests, the following observations were made regarding heating in graphite under vacuum:

- (1) sintering uranium oxide in vacuum at high temperatures, in the presence of graphite does not yield UO₂ shapes of high

strength and density

(2) the mixing of less than 1.2 moles of carbon per mole of U_3O_8 appears to have a beneficial effect on the sinterability of the oxide and

(3) the carbon to U_3O_8 mole ratio that yields the highest sintered density under these conditions was about 0.6. It is likely that the carbon required in the charge would be slightly higher for sintering in an environment free of graphite.

On the basis of these observations, subsequent experiments were carried out in a platinum resistance furnace. The initial exploratory test with this furnace was to determine what C/ U_3O_8 mole ratio for a charge yielded the highest sintered density in a graphite free environment. Four compacts prepared from charges containing different C/ U_3O_8 mole ratios were placed on a molybdenum tray, within an alundum tube and sintered in a nitrogen atmosphere at $1400^{\circ}C$ for two hours. Table 12 summarizes the results obtained.

Under the conditions of this experiment, the charge with the C/ U_3O_8 mole ratio of 0.7 yielded the highest sintered density. It is to be noted that under an atmosphere of nitrogen and in the absence of graphite, the sintered densities

Table 12. Data obtained during the sintering of U_3O_8 + carbon compacts at $1400^\circ C$ in nitrogen for 2 hours

Charge composition	Pellet wt., (gm)	Theo. UO_2 wt. in pellet, (gm)	Oxide composition after sintering	Actual UO_2 wt. after sinter, (gm)	UO_2 wt. loss %	Density g/cm^3
U_3O_8 + 0.5C	10.50	10.03	$UO_{2.00}$	9.99	0.4	7.12
U_3O_8 + 0.6C	10.49	10.00	$UO_{2.00}$	9.95	0.5	7.56
U_3O_8 + 0.7C	10.50	10.00	$UO_{2.00}$	10.00	0	7.98
U_3O_8 + 0.8C	10.51	10.00	$UO_{2.00}$	9.99	0.01	7.42

obtained were essentially the same as those obtained earlier at a temperature 300°C higher and in a graphite environment under vacuum conditions. Furthermore, the UO_2 weight losses in nitrogen at 1400°C are insignificant compared to those obtained under vacuum at the higher temperatures.

The Effect of Certain Atmospheres on Sintering

Before evaluating the effect that certain atmospheres have on sinterability, preliminary tests were conducted to determine the initial reaction-densification temperature for compacts of U_3O_8 and carbon. Green compacts pressed at 30,000 psi and with C/ U_3O_8 mole ratios of 0.65, 0.70 and 0.75 were each placed on an alundum support at a number of specified positions in a sillimanite tube within the furnace and heated in nitrogen for four hours. The samples in the uniform temperature zone were heated to 1000°C , while the other sample temperatures depended on their position in the furnace. Since the temperature profile within the furnace was known, the initial reaction temperature could be correlated with the measurements obtained from the resulting compacts.

No noticeable reaction or measurable dimensional changes occurred below 600°C . At a temperature of about 600°C , the compacts began to swell although no definite weight loss

occurred; the noticeable reaction and densification began at approximately 780°C .

After the initial reaction temperature was determined, the effect of certain atmospheres on the sinterability of urania over a range of temperatures was compared. The atmospheres included a reduced pressure, argon (inert) and carbon dioxide (slightly oxidizing). Nitrogen was bypassed because earlier results showed that considerable cracking of production grade UO_2 pellets occurred in this atmosphere; hydrogen was not investigated at this point because of its reducing nature.

Two pressed pellets of production grade dioxide ($\text{UO}_{2.06}$) and compacts with $\text{C}/\text{U}_3\text{O}_8$ mole ratios of 0.65, 0.70 and 0.75 were used in each test. The pellets of $\text{UO}_{2.06}$ were placed at each end of the hot zone with the other compacts between them. This arrangement was used to determine if the conditions at each end of the hot zone were the same during a sintering test.

Since the first reaction in the ($\text{U}_3\text{O}_8+\text{C}$) pellets begins at about 780° , these samples were first sintered at 800°C for two hours. After the samples were cooled, they were measured, weighed and then heated to 900°C where they were maintained for two hours. This scheme was continued at 100 degree inter-

vals until the final sintering at 1400°C was completed. The data obtained when the compacts were heated under reduced pressure are shown in Table 13. The weights obtained after each heating through 1200°C revealed that all of the samples weighed the same as or greater than the calculated UO₂ weight in the green compact. The first weight losses below the theoretical UO₂ weights in the samples occurred during the 1300°C run with substantially more occurring during the 1400°C heating. Calculations, based on sample weights after the 1400°C treatment with the assumption that all the weight losses were due to oxygen volatilization, yielded final compositions ranging in O/U ratios from 1.51 to 1.71.

Calculations using data obtained several months later by oxidation analysis revealed O/U ratios ranging from UO_{2.10} to UO_{2.17}. The assumption that weight losses below the theoretical UO₂ weight were the result of oxygen volatilization seemed to be invalid. Instead, it appeared that a small amount of an oxide of uranium was vaporized from each of the samples during the heating step possibly leaving a residue of UO_{2.00}. On exposure to air, the "clean" sintered pellets had possibly picked up some additional oxygen over that contained in the UO_{2.00} residue to give the compositions obtained by

Table 13. Sintered densities and weights obtained in 2 hours at 100°C intervals from 800°C-1400°C under reduced pressure (~25 microns) for UO_{2.06} and charges containing C/U₃O₈ mole ratios of 0.65, 0.70 and 0.75

		UO _{2.06}	U ₃ O ₈ + 0.65C	U ₃ O ₈ + 0.70C	U ₃ O ₈ + 0.75C
sample wt., grams		9.98	10.50	10.50	10.52
theo. UO _{2.00} wt., g/cm ³		9.94	10.00	10.00	10.01
green density, g/cm ³		6.06	5.87	5.59	5.82
800°C	wt.	9.95	10.28	10.28	10.31
	density	7.36	6.10	5.92	6.01
900°C	wt.	9.95	10.12	10.13	10.15
	density	8.11	6.76	6.58	6.74
1000°C	wt.	9.95	10.10	10.12	10.14
	density	8.71	7.01	7.01	6.89
1100°C	wt.	9.95	10.08	10.11	10.14
	density	9.16	7.37	7.48	7.28
1200°C	wt.	9.94	10.04	10.08	10.11
	density	9.12	7.63	7.82	7.62
1300°C	wt.	9.89	9.98	10.01	10.03
	density	8.65	8.04	8.23	8.07
1400°C	wt.	9.66	9.71	9.83	9.83
	density	8.58	8.17	8.41	8.25
Calc. comp. assuming only oxygen wt. loss		UO _{1.52}	UO _{1.51}	UO _{1.71}	UO _{1.70}
Analyzed oxide comp. months later		UO _{2.10}	UO _{2.13}	UO _{2.17}	UO _{2.15}
Estimated comp. at 1400°C		UO _{2.00}	UO _{2.00}	UO _{2.00}	UO _{2.00}

oxidation.

In order to substantiate this belief, three pellets of $UO_{2.06}$ were heated under reduced pressure for two hours at $1400^{\circ}C$ and then cooled to room temperature. Weight losses in these samples averaged about three percent which would correspond to about $UO_{1.5}$ assuming the loss was due to oxygen only. About 20 minutes after the pellets were removed from the furnace some of the samples were analyzed by oxidation at $800^{\circ}C$ then, 12 hours later, a second group of the samples was oxidized. It was found that the average O/U ratio for the first set of samples was $UO_{2.03}$ while the average for the second group had increased to $UO_{2.07}$. The composition of the samples at completion of sintering then must have been very close to $UO_{2.00}$. Since the oxidation tests for the data shown in Table 13 were performed several months after the sintering it is conceivable that the O/U ratio in the uranium dioxide pellet could have increased to 2.10. Likewise, the other product samples in Table 13 no doubt had picked up oxygen on long standing and had compositions close to $UO_{2.00}$ at completion of sintering at $1400^{\circ}C$.

Sintered densities of compacts from U_3O_8 and carbon increased as temperature increased to $1400^{\circ}C$, while the dioxide

pellet density increased through 1100°C followed by successive density decreases at temperatures up to 1400°C. This decrease in the final sintered density may be the result of internal pressure from gas being trapped in closed pores formed during sintering at low temperature. At temperatures of 1200°C and above, then, the plasticity of the oxide may be sufficient to yield under this pressure and cause a density decrease.

Of the (U₃O₈+C) charge compositions tested, the maximum sintered density (8.41 g/cm³) was obtained at 1400°C when a C/U₃O₈ mole ratio of 0.7 was employed. This value, however, was not as high as the density obtained in the plain UO₂ compact at 1100°C (9.16 g/cm³) or at 1400°C (8.58 g/cm³) after some de-densification of the UO₂ had occurred.

Data obtained on heating compacts in argon at the various temperatures is shown in Table 14. Unlike the data obtained under reduced pressure, none of the samples decreased below their theoretical UO₂ weights calculated to be in the green compacts at any temperature.

Oxide compositions calculated from the sample weights at 1400°C ranged from UO_{2.00} to UO_{2.20}. These values are more in line than those obtained under reduced pressure since

Table 14. Sintered densities and weights obtained in 2 hours at 100°C intervals from 800°C-1400°C in argon for UO_{2.06} and charges containing C/U₃O₈ mole ratios of 0.65, 0.70 and 0.75

		UO _{2.06}	U ₃ O ₈ + 0.65C	U ₃ O ₈ + 0.70C	U ₃ O ₈ + 0.75C
sample wt., grams		9.99	10.45	10.50	10.50
theo. UO _{2.00} wt., g/cm ³		9.95	9.96	10.00	9.99
green density, g/cm ³		5.97	5.82	5.58	5.79
800°C	wt.	9.95	10.21	10.20	10.25
	density	7.91	6.10	6.41	6.51
900°C	wt.	9.95	10.10	10.12	10.15
	density	8.62	6.83	6.87	6.75
1000°C	wt.	9.95	10.10	10.12	10.15
	density	8.85	6.97	7.11	6.88
1100°C	wt.	9.95	10.09	10.12	10.15
	density	8.93	7.39	7.59	7.13
1200°C	wt.	9.95	10.09	10.11	10.15
	density	9.01	7.48	7.85	7.37
1300°C	wt.	9.95	10.09	10.11	10.15
	density	9.10	7.75	8.18	7.67
1400°C	wt.	9.95	10.03	10.09	10.11
	density	9.22	7.98	8.46	8.05
Oxide composition calculated from wt. at 1400°C assuming all wt. loss was all oxygen		UO _{2.00}	UO _{2.12}	UO _{2.15}	UO _{2.20}

there appeared to be no uranium volatilization. The uranium compositions calculated on the basis of oxidation data obtained several months after sintering, again demonstrated that some samples will pick up oxygen on standing in air. The maximum sintered densities increased in all samples of Table 14 at each higher temperature with the production grade dioxide yielding the highest density at all temperatures. Of the compacts prepared from U_3O_8 and carbon, the charge containing a C/ U_3O_8 mole ratio of 0.7 yielded the highest sintered density (8.46 g/cm^3).

Data obtained on compacts sintered in CO_2 (see Table 15) revealed that the pellets from charges of U_3O_8 and carbon did not decrease below the theoretical UO_2 weight in the green compact at any temperature. The compact of the dioxide ($UO_{2.06}$), on the other hand, decreased to slightly below the theoretical UO_2 weight in the green compact during the 900°C heating. A further weight decrease was noted after the 1100°C heating followed by two subsequent weight increases at 1200° and 1300°C . Although this observation has been substantiated in other experiments, a logical explanation other than volatilization of an oxide of uranium is not apparent, since otherwise a thermal decomposition or a chemical reduction in a

Table 15. Sintered densities and weights obtained in 2 hours at 100°C intervals from 800°C-1400°C in carbon dioxide for $UO_{2.06}$ and charges containing C/ U_3O_8 mole ratios of 0.65, 0.70 and 0.75

		$UO_{2.06}$	U_3O_8+ 0.65C	U_3O_8+ 0.70C	U_3O_8+ 0.75C
sample wt., grams		9.99	10.49	10.49	10.54
theo $UO_{2.00}$ wt., g/cm^3		9.95	10.00	9.99	10.03
green density, g/cm^3		6.06	5.80	5.61	5.75
800°C	wt.	9.95	10.15	10.13	10.19
	density	7.82	6.32	6.47	6.66
900°C	wt.	9.92	10.08	10.08	10.10
	density	8.44	6.80	6.74	6.73
1000°C	wt.	9.92	10.08	10.08	10.10
	density	9.07	7.12	7.35	7.07
1100°C	wt.	9.91	10.05	10.08	10.10
	density	9.17	7.59	7.87	7.50
1200°C	wt.	9.95	10.03	10.08	10.10
	density	8.78	7.97	8.39	8.10
1300°C	wt.	9.98	10.03	10.08	10.10
	density	8.57	8.30	8.74	8.42
1400°C	wt.	9.98	10.03	10.08	10.10
	density	8.57	8.50	8.91	8.66
Oxide composition calculated from wt. at 1400°C assuming wt. loss was all oxygen		$UO_{2.05}$	$UO_{2.05}$	$UO_{2.15}$	$UO_{2.12}$

slightly oxidizing atmosphere would be occurring.

Oxide compositions from the sample weights obtained following sintering at 1400°C in CO_2 ranged from $\text{UO}_{2.05}$ to $\text{UO}_{2.15}$. These samples also picked up oxygen on standing in air with maximum values of the O/U ratios at 2.18 which is in agreement with similarly exposed samples from Tables 13 and 14.

Sintering data obtained from production grade uranium dioxide at the various temperatures under an atmosphere of carbon dioxide revealed that the sintered density increased to 9.17 g/cm^3 at 1100°C followed by density decreases at 1200°C and 1300°C . These results are essentially the same as those obtained under reduced pressure. Again, it may be the result of gases being trapped within closed pores that are formed at lower temperatures, followed by the expansion of this gas in a more plastic UO_2 at the higher temperatures.

Sintered densities obtained on the compacts containing U_3O_8 and carbon in CO_2 at 1400°C revealed that the highest density (8.91 g/cm^3) was obtained when the C/ U_3O_8 mole ratio was 0.7. A comparison of the sintered densities obtained for these charges under reduced pressure, argon and carbon dioxide showed that CO_2 yielded the more dense compacts. On the basis

of these results and other related experiments, subsequent testing was limited to developing high density shapes from charges compacted at 30,000 psi containing a C/U₃O₈ mole ratio of 0.7 and sintered in CO₂ for 2 hours at 1400°C.

The Sinterability of Compacts Prepared from Charges of Carbon with U₃O₈ from Ammonium Diuranate

Although variations in final sintered densities were observed for charges of U₃O₈ and carbon in various atmospheres, the densities obtained were low relative to the theoretical density (UO_{2.00} = 10.97 g/cm³). To evaluate the sinterability under CO₂ of charges prepared from carbon (graphite) with oxides of various origins and histories, a batch of U₃O₈ was prepared starting with production grade UO₂. The general procedure used was as follows:

- (1) dissolve enough production grade dioxide in concentrated HNO₃ to yield a solution containing 100 g U/l,

- (2) heat the uranyl nitrate solution to about 60°C and precipitate the uranium as diuranate with NH₄OH. Excess ammonium hydroxide is added to increase the pH to 9,

- (3) filter, dry and powderize the diuranate.

Instead of reducing the diuranate in hydrogen to get highly sinterable UO₂, it was oxidized to U₃O₈ in air at 800°C.

Charges containing C/U₃O₈ mole ratios of 0.1, 0.3, 0.5, 0.7 and 0.9 were prepared using this oxide. After compacts were pressed at 30,000 lb/in², they were sintered in CO₂ for two hours at 1400°C. Table 16 summarizes the results obtained.

Table 16. Sintered densities obtained on charges prepared from ceramically active U₃O₈ and carbon in a CO₂ atmosphere at 1400°C for 2 hours

Charge composition	Sintered density	
	g/cm ³	% of theoretical
U ₃ O ₈ + 0.1C	8.66	78.98
U ₃ O ₈ + 0.3C	10.04	91.50
U ₃ O ₈ + 0.5C	10.47	95.40
U ₃ O ₈ + 0.7C	10.51	95.81
U ₃ O ₈ + 0.9C	10.37	94.51

As seen in the table, the highest sintered density was obtained with a charge containing a C/U₃O₈ mole ratio of 0.7. This maximum density mole ratio is the same as that obtained when U₃O₈ of lower sinterability was used. As expected, the sintered density (10.51 g/cm³) using the oxide of Table 16 is substantially greater than the density (8.91 g/cm³) obtained with the earlier U₃O₈ employed for the data shown in Table 15.

The diuranate method used for preparing the U₃O₈ was

chosen purposely to point out possible advantages to be gained by employing this type of an approach. First of all, the preparation of UO_2 as an intermediate could be avoided. As a result an air oxidation step replaces a hydrogen reduction step carried out at essentially the same temperature. Secondly, the U_3O_8 intermediate is quite stable at room temperature whereas ceramically active dioxide picks up oxygen relatively easily. Unless extreme care is taken following the hydrogen reduction step, ceramic grade UO_2 will ignite spontaneously and oxidize to U_3O_8 . Thirdly, essentially the same sintered densities using U_3O_8 can be obtained in CO_2 at $1400^\circ C$ as obtained with UO_2 in hydrogen at $1700^\circ C$.

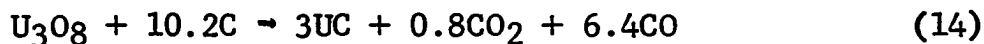
Attempts at Preparing a Ceramically Active Oxide

Although high sintered densities were obtained from charges using oxide prepared by the above method of UO_2 solution in HNO_3 followed by the ammonium diuranate precipitation, this acid dissolution step made it less attractive. Furthermore, since production grade UO_3 employed as the starting oxide is readily available, a treatment that employed this material with a minimal number of processing steps was desired.

Experiments being conducted by other investigators on the preparation of high purity ThO_2 showed that a very finely

divided oxide could be prepared by burning thorium carbide in oxygen. This approach was evaluated for preparing a finely divided ceramically active U_3O_8 .

Two charges calculated to yield 100 grams each of UC and UC_2 were prepared by heating mixtures of C and U_3O_8 in vacuum at $1800^{\circ}C$. The overall general reactions are shown in Equations 14 and 15.



After the reactions were essentially completed, the residual products were oxidized to U_3O_8 in flowing oxygen. The resulting oxides were then used in preparing charges for sintering studies that were carried out under the conditions set up above.

Density measurements on the sintered compacts revealed that the charge prepared from oxide obtained by oxidizing UC sintered to 7.66 g/cm^3 while that containing oxide from UC_2 sintered to 8.20 g/cm^3 . Even though this carbide formation-oxidation treatment yielded a more finely divided oxide starting material, microscopic examination revealed that the bulk of these materials was composed of shiny spheroidal particles.

In another group of tests, samples of production grade

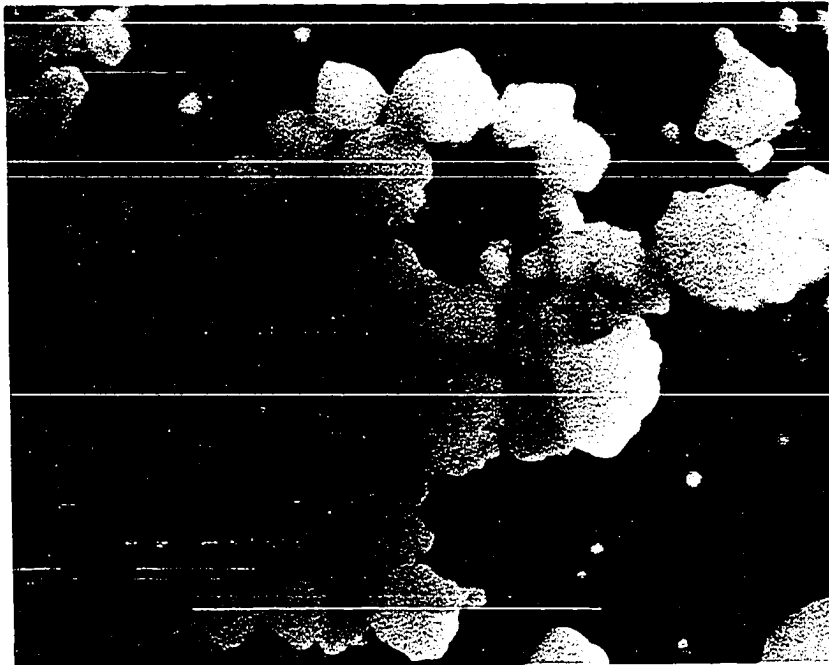
unsulfated and sulfated UO_3 were ball milled dry for extended periods of time up to 15 hours. The resulting oxide was then calcined at $800^{\circ}C$ to produce U_3O_8 for pellet preparation. Sintered densities obtained on pellets prepared from compacts of these oxides and carbon showed no appreciable density increases over compacts prepared from unmilled oxide.

Photomicrographs of these production grade trioxides in the as-received form are shown in Figure 15. Although the unsulfated particles were smaller in size, they exhibited the same general shape as the sulfated trioxide. Dry ball-milling produced substantial decreases in particle size, but had no noticeable effect on the particle shapes. Calcination of these oxides to U_3O_8 also did not appear to affect the particle shapes. Since the trioxides contained residual nitrate that was converted to U_3O_8 during heating, it appeared that wet ball-milling the trioxide to dissolve the nitrate might warrant study.

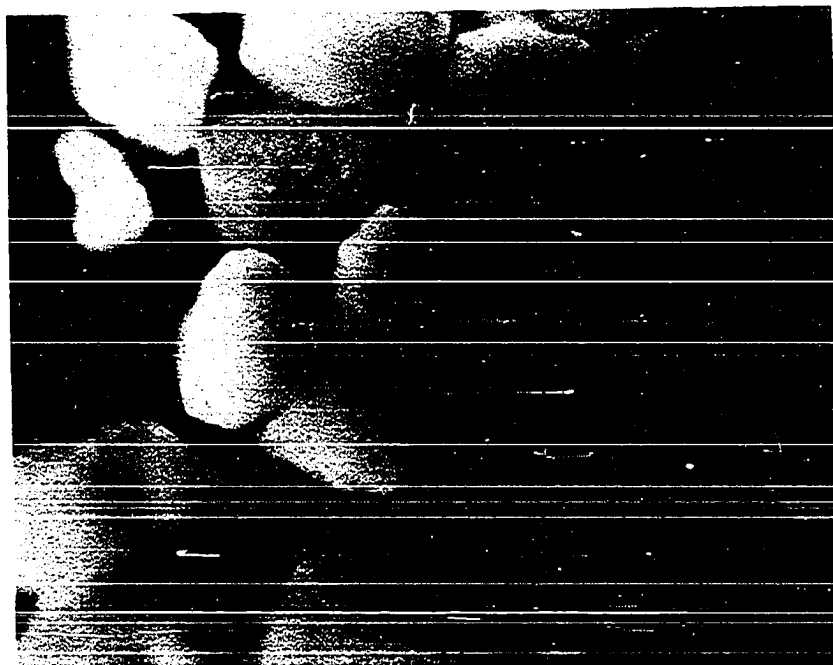
The Preparation of a Ceramically Active Oxide by Wet-Ball Milling Production Grade Trioxides

In the first exploratory test conducted, 200 grams of sulfated UO_3 was wet ball-milled in an alundum ball jar having a capacity of 1.25 liters. After about 100 alundum stones and

Figure 15. Photomicrographs of production grade unsulfated (A) and sulfated (B) uranium trioxides in the as-received form; 250X



A. Production grade unsulfated UO_3



B. Production grade sulfated UO_3

600 ml water was added with the UO_3 to the jar, the mill was operated for two hours. The $UO_3-UO_2(NO_3)_2$ -water slurry was then filtered and the filter cake was dried and calcined to U_3O_8 at $800^\circ C$. Although the filtrate contained residual nitrate as evidenced by its yellow color, no attempt was made, at that time, to combine it with the UO_2 filter cake. Furthermore, any residual nitrate retained in the filtercake was converted to U_3O_8 since the UO_3 filtercake was not washed following filtration.

Compacts prepared from charges of this U_3O_8 with 0.7 mole of carbon on sintering at $1400^\circ C$ yielded densities to 9.3 g/cm^3 or about 85 percent of theoretical. This represents about an 11% increase in density over that obtained on charges of U_3O_8 prepared by calcining production grade UO_3 directly. However, this density of 85% theoretical was still substantially lower than that obtained on pellets prepared from U_3O_8 obtained by way of the diuranate precipitation method.

In another exploratory test, essentially the same milling operation as described above was employed. The resulting slurry however was not filtered. Instead, it was placed in a beaker and the oxide allowed to settle. After the aqueous solution containing residual nitrate was decanted, another

400-500 ml of water was added and thoroughly mixed. This mixing-decanting step was employed until the aqueous solution was essentially free of nitrate. After the resulting nitrate-free UO_3 slurry was filtered, dried and calcined, pellets were prepared and sintered as before. Pellet densities exceeding 94 percent of theoretical were obtained. On the basis of these results, it appeared that a critical step involved the elimination of nitrate or other soluble compositions from the filtercake, or UO_3 , prior to conversion to U_3O_8 .

Although high sintered densities were obtained from the trioxide that was washed free of nitrate, such an approach would have limited applicability on anything larger than a laboratory scale. As a consequence, two other approaches were examined for eliminating the nitrate. In the first one, the water used in the ball-milling step was made alkaline by the addition of NH_4OH . It was hoped that the nitrate or soluble part would be converted to ammonium diuranate (ADU) during the milling step. Then, the filtercake containing UO_3 and ADU could be calcined to U_3O_8 . Even though it appeared that the soluble uranium was converted completely to diuranate, sintered compacts prepared from U_3O_8 from this material never exceeded 79 percent of theoretical.

In the second approach, the trioxide was ball milled in water as previously described. Instead of decanting the nitrate, after the mixing step it was precipitated as diuranate with excess ammonium hydroxide. After the UO_3 -ammonium diuranate mixture was filtered, washed, dried and calcined to U_3O_8 , charges with C/ U_3O_8 mole ratios of 0.7 were mixed, pressed and sintered. The sintered densities obtained exceeded 90 percent of theoretical. These values were lower than those obtained from the ball-milling and decanting procedure earlier (94%), but were substantially higher than the densities by milling in an alkaline solution (79%).

Subsequent experiments were then conducted to determine if the final sintered density could be increased above 90 percent of theoretical by evaluating the affect that certain variables had during the ball-milling step, the precipitation step and the calcination step.

The ball-milling step

The first tests were conducted to determine the affect that different water/ UO_3 weight ratios had during the milling step on the final sintered density. Three mill jars, each with a capacity of 1.25ℓ, were loaded as follows:

(A) 200 g UO_3 -200 ml distilled water-77 Al_2O_3 stones

(B) 200 g UO_3 -200 ml distilled water-154 Al_2O_3 stones

(C) 200 g UO_3 -200 ml distilled water-411 ZrO_2 stones

The alundum stones used were cylindrically shaped and had an average volume of $1.6 \text{ cm}^3/\text{stone}$ and an average weight of 52 g/stone. The ZrO_2 stones, also cylindrical in shape had an average volume of $0.6 \text{ cm}^3/\text{stone}$ with an average weight of 3.2 g/stone. Milling was accomplished by rotating the ball jars at 144 rpm for two hours.

Next, excess ammonium hydroxide was added to the slurry to precipitate the soluble nitrates. The resulting oxide-ADU mixture was then filtered, washed, dried and calcined to U_3O_8 at 800°C . In the second and third sets of experiments, these same steps were performed using 200 g of UO_3 , however the water to oxide weight ratios were increased to 2 and 4 respectively. The pellet densities obtained after sintering charges of the calcined oxides with 0.7 mole of carbon for two hours are shown in Table 17. The density decreases at the higher water/oxide weight ratios were probably the result of two affects. First, increasing the volume of water used decreased the oxide density in the slurry. Consequently, the surfaces of the stones saw less oxide per unit time. And second, the increased volume of slurry served as a cushion for the falling

stones causing a reduction in their momentum resulting in decreased grinding.

Table 17. Effect of different water to UO₃ weight ratios during ball-milling for 2 hours on final sintered density of the dioxide

No. and kind of stones used	Water to oxide weight ratio		
	1	2	4
77 Al ₂ O ₃	90.10	88.80	83.64
154 Al ₂ O ₃	91.07	89.78	85.22
411 ZrO ₂	91.95	90.03	88.23

When the water to oxide weight ratio was reduced to 1/2, the resulting mixture was too dense to produce any grinding. Instead the balls became stuck throughout the thick mud-like mixture. On the basis of these results, subsequent ball-milling steps were carried out using a water/oxide weight ratio of 1 and grinding with 411 ZrO₂ stones.

The parameters adopted up to this stage of development of an overall process for high density UO₂ shapes included:

1. 200 grams of production grade UO₃ with 200 grams of water,
2. ball mill in 1.25ℓ jar using 411 of the ZrO₂ grinding cylinders,

3. grind for a suitable period,
4. wash the slurry from the ball mill with a minimum of water, add ammonium hydroxide in excess to precipitate any soluble uranium,
5. filter and wash the filtercake (insoluble uranium compounds) to remove nitrate,
6. dry and powderize the uranium compounds (mostly UO_3),
7. thermally decompose the UO_3 to U_3O_8 ,
8. mix U_3O_8 with graphite powder to form a charge with a C/ U_3O_8 mole ratio of 0.7,
9. press about 10 grams of the mixture at 30,000 lb/in² into a right circular cylinder one-half inch in diameter,
10. sinter on an alundum support in CO_2 at 1400°C for two hours,
11. cool, weigh, measure and evaluate.

Some of the above steps have been evaluated while others are to be investigated further. For example, the period of grinding in step three and the temperature of precipitation need further study.

The affect of the ball-milling time on the final sintered density was evaluated next. After batches of UO_3 and water were milled for 1, 3, 5 and 15 hours, respectively, the re-

sulting oxide-nitrate mixtures were processed and sintered as previously described. The results obtained are shown in Table 18.

Table 18. Effect of ball-milling time on final sintered densities obtained

Ball-milling time, hr.	Sintered density	
	g/cm ³	% of theoretical
1	8.88	81.00
3	10.18	92.80
5	10.31	94.00
15	10.43	95.11

An increase in the final sintered density of greater than 11 percent was obtained by increasing the ball-milling time from one hour to three hours (81 to 92.80). When the milling time was increased to five hours, an additional one percent increase in the density was obtained (94.00). However, 10 additional hours of ball milling was required to increase the final density another percent (95.11). On the basis of these data and since UO₂ density specifications on light water thermal reactors of current design lie between 93 and 96 percent of theoretical, a five-hour ball-milling time was used in subsequent experiments.

The precipitation step

In another series of tests, the effect of the slurry temperature during the ammonium diuranate precipitation step on the final sintered density was evaluated. In the first series of tests, four batches of UO_3 and water were each ball-milled for five hours as previously described. After removing the slurries from the mill, three of the four batches were heated for precipitation at 50° , 75° and $\sim 99^\circ C$ respectively. Excess ammonium hydroxide was added in each case to precipitate the soluble uranium. Table 19 summarizes the results obtained on sintered pellets prepared from these four batches after processing according to the subsequent adopted steps.

Table 19. Effect of slurry temperature during the ammonium hydroxide precipitation step on the final sintered density of UO_2 pellets

Slurry temperature, $^\circ C$	Sintered density	
	g/cm^3	% of theoretical
Room (~ 25)	10.31	94.01
50	9.29	84.71
75	8.89	81.04
~ 99	8.62	78.66

When the slurry temperature was increased for the precipitation, final sintered densities decreased. At about $99^\circ C$, the final sintered density had decreased about 15 percent to 78.66

percent of theoretical. Microscopic examination of the powdered materials from the ammonium hydroxide precipitation revealed that the samples heated to the higher temperatures contained many very fine grains of material not present in the sample treated at room temperature. Although the proportion of grains appeared to be about the same in each of the three samples, they increased in size as the precipitation temperature increased.

From an analysis of these results, a subsequent experiment was conducted wherein the slurry temperature was reduced to about 4°C before the ammonium hydroxide addition. Even though microscopic examination revealed the absence of the fine grains as observed in the powders from the higher treatment temperatures, the final sintered density was only 83 percent of theoretical. As a consequence, subsequent precipitation steps were carried out at room temperature.

The calcination temperature

In the last series of tests concerned with preparing a ceramically active oxide from UO_3 , the effect of the calcination temperature (UO_3 to U_3O_8) on the final sintered density was evaluated. In this sequence of tests, three batches of UO_3 and water were ball milled for five hours as previously

described. After the room temperature precipitation step, the slurries were filtered, washed, dried and calcined at 700°, 750° and 800°C respectively until conversion was completed. The sintered densities of UO₂ pellets prepared from U₃O₈ calcined at these three temperatures are shown in Table 20.

Table 20. Effect of calcination temperature on the final sintered density of UO₂ pellets

Calcination temperature, °C	Sintered density	
	g/cm ³	% of theoretical
700	10.43	95.10
750	10.38	94.30
800	10.32	94.10

Although these data show an increase in the final sintered density with a decrease in calcination temperature, the observed change between 700° and 800°C is open to conjecture. A possible reason for the decreased sintered density for material calcined at 800°C over that at 700°C might be attributed to free sintering at 800°C which is known to occur in other materials. Calcination at temperatures of 650° and 600°C required extended times for complete conversion to U₃O₈. Subsequent experiments, therefore, involved calcination at 700°C.

With reference to the general procedure outlined earlier,

the process developed for preparing a ceramically active U_3O_8 from production grade UO_3 on a laboratory-scale is as follows:

1. ball mill UO_3 and water as previously described for 5 hours,
2. precipitate the ammonium diuranate with excess ammonium hydroxide at room temperature,
3. filter, wash, dry, powderize, then calcine the filtercake at $700^{\circ}C$.

Figure 16 is a photomicrograph of U_3O_8 prepared by this method. Although the oxide shown in the figure was derived from unsulfated trioxide, essentially the same fine sizes and irregular shapes of U_3O_8 particles were obtained when sulfated trioxide was similarly treated.

When production grade UO_3 is directly calcined to U_3O_8 , the particle sizes and shapes of the trioxide are retained in the U_3O_8 . A comparison, then, of Figure 16 with Figure 15 demonstrates a marked change in the characteristics of the U_3O_8 particles as a result of the additional processing of the UO_3 starting material. The processing presented here has definitely resulted in the preparation of much finer and exceedingly less regular U_3O_8 particles. These observed changes in the oxide particles could be important factors in

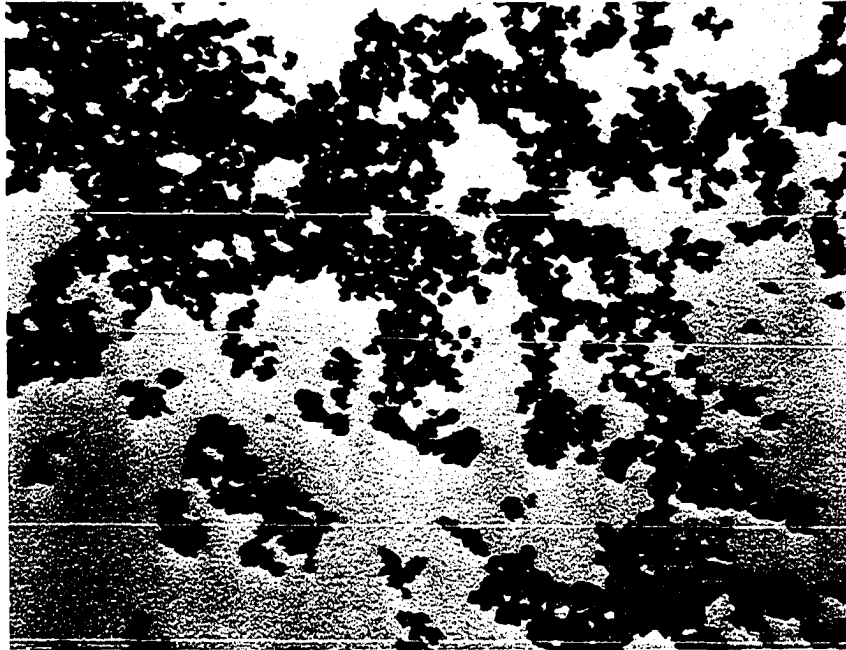


Figure 16. Photomicrograph of U_3O_8 powder prepared from unsulfated production grade UO_3 by the activation treatment derived in this investigation. Bright Field Illumination. 250X

obtaining the high sintered densities of the UO_2 product.

Figure 17 is a macrograph of three typical compacts obtained during the course of this investigation. The A pellet was prepared by heating a pressed compact of production grade $UO_{2.06}$ in nitrogen at $1400^{\circ}C$ for two hours. The resulting pellet has a poor surface texture and no observable sintering has occurred. Pellet B was made from a charge of carbon and U_3O_8 , prepared by calcining as-received UO_3 at $800^{\circ}C$; this pellet was sintered in CO_2 at $1400^{\circ}C$ for two hours. Although the surface texture is good, only slight densification has occurred. Sample C is a pellet prepared by sintering a charge of carbon and U_3O_8 , prepared by the activation treatment derived; this pellet was also sintered in CO_2 at $1400^{\circ}C$ for two hours. This sample is substantially more dense than the other two since all three were molded at the same pressure in the same die and had approximately the same diameter prior to sintering.

Figure 18 shows two micrographs of a sintered UO_2 pellet prepared by the process developed in this study. The upper micrograph (A), shows the as-mechanically-polished surface; the dark areas are voids. The lower micrograph (B) is the same sample after etching. The ultrafine grains formed during

Figure 17. Photograph of sintered urania compacts of different qualities

- A. Poor surface texture and low sintered density
(75% of theoretical)
- B. Good surface texture, but low sintered density
(76% of theoretical)
- C. Good surface texture and high sintered density
95% of theoretical

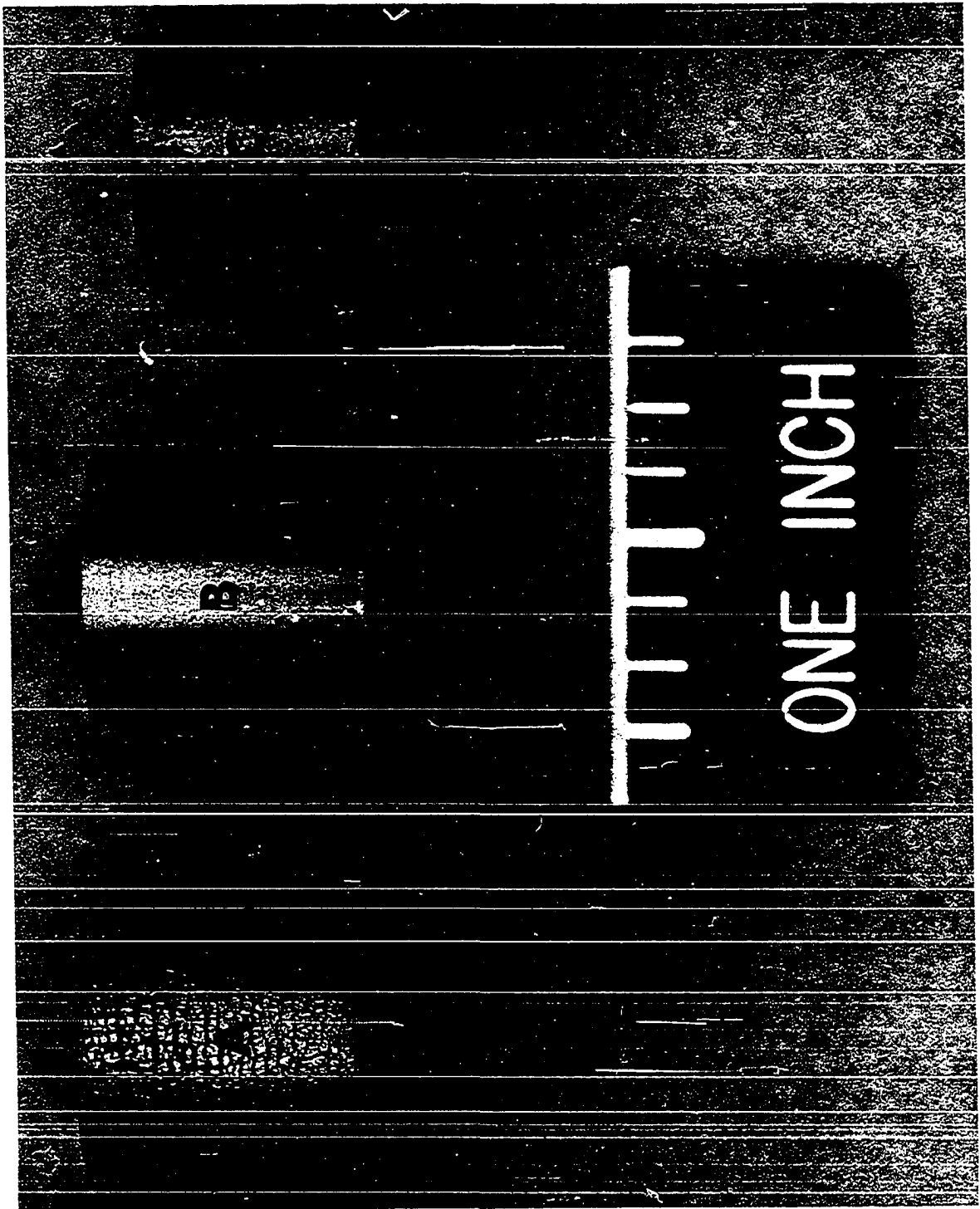
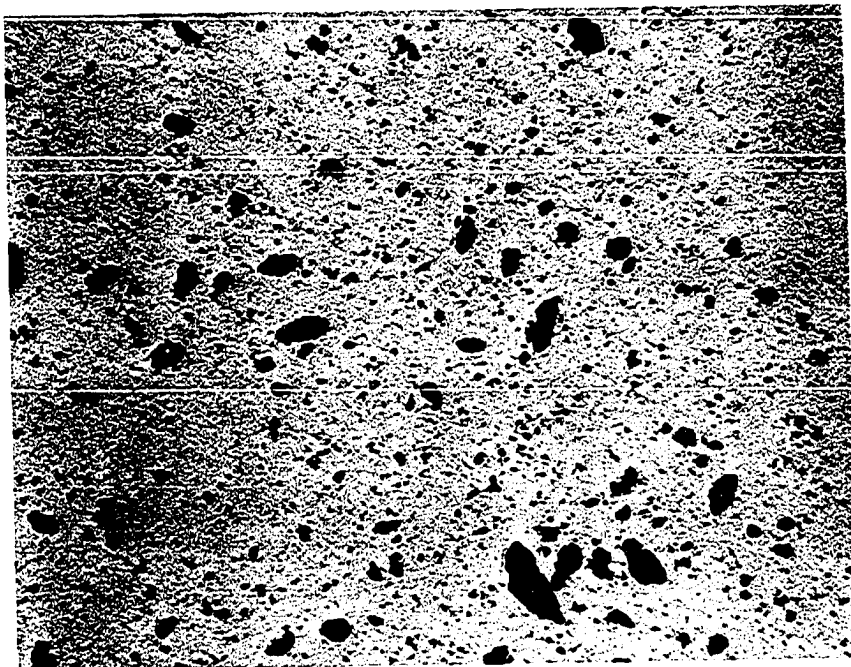
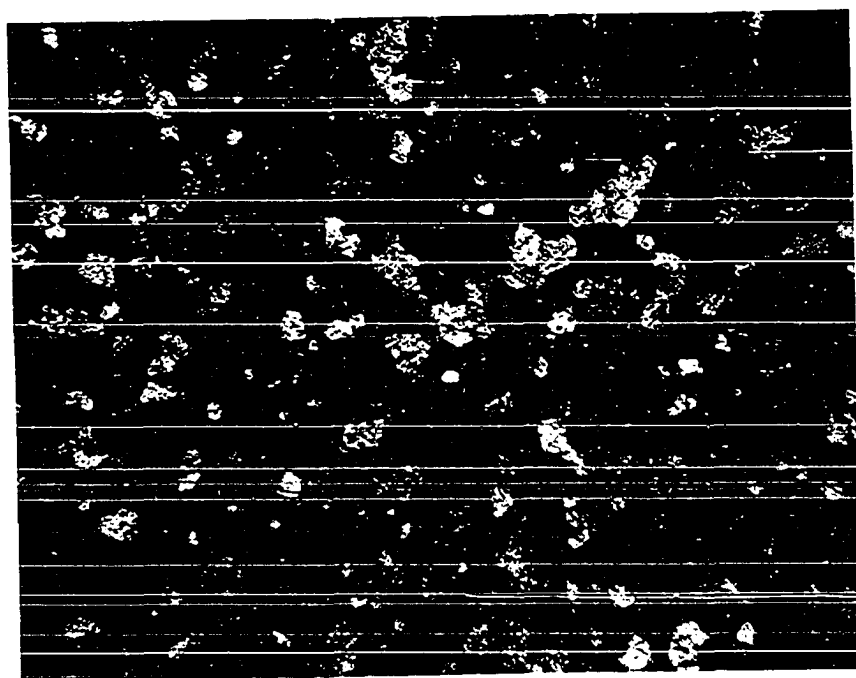


Figure 18. Photomicrographs of sintered UO_2 pellet prepared by process derived in this investigation before and after etching

- A. As mechanically polished; dark areas are voids; 250X
- B. As mechanically polished; etched for ~5 seconds in $\text{HF-H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$ solution; 750X



A



B

the sintering step are often desirable in pellets used as nuclear fuel; such fine grain structures in sintered UO_2 are associated with better irradiation stability of the UO_2 than larger grain sizes.

The Preparation of UO_2 Pellets with Varying Densities

Fuel specifications established during the design of certain nuclear reactors sometimes requires that the sintered UO_2 pellets have densities that are far from theoretical and may be as low as 80% of theoretical. Sintered compacts of varied density can be obtained by altering the C/ U_3O_8 mole ratio in the initial charge. However, another approach was evaluated wherein the C/ U_3O_8 mole ratio in the charge was maintained at 0.7 while the percentages of octa-oxides with different sintering characteristics was varied. The two oxides used were U_3O_8 prepared by the activation treatment derived in this study (A) and U_3O_8 prepared by calcining UO_3 directly (B). Table 21 summarizes the results obtained when charges containing various percentages of these oxides and 0.7 mole of carbon were sintered in CO_2 at $1400^\circ C$ for two hours.

While a density of 95.10 percent of theoretical was obtained from the charge containing U_3O_8 prepared entirely from the treated oxide (A), lower densities were obtained as

Table 21. Sintered densities obtained when mixed charges with varying percentages of (A) U_3O_8 prepared by the activation treatment derived in this investigation, and of (B) U_3O_8 prepared by calcining UO_3 directly, with 0.7 mole of carbon were sintered in CO_2 at $1400^\circ C$ for 2 hours

Composition % of A and B	Sintered densities		
	Calc. g/cm ³	Meas. g/cm ³	% of theoretical
100% A 0% B	10.43	10.43	95.10
70% A + 30% B	10.00	10.00	91.20
40% A + 60% B	9.58	9.60	81.51
0% A + 100% B	9.01	9.01	82.22

the fraction of the untreated oxide increased. When the charge was composed of 30 percent (B), the final sintered density was decreased to 91.20 percent of theoretical, while the sintered density of a charge containing 60 percent (B) was further decreased to 87.51 percent of theoretical. The calculated density values in the table are based on the contribution each of the species of U_3O_8 would independently contribute to the density of the mixture. It is seen that the relationship between composition and sintered density under the conditions used is quite linear. Lower densities could no doubt be derived by varying other parameters of the process.

This method of preparing normal UO_2 pellets with various

densities might offer reductions in costs in the fuel preparation phase of the nuclear fuel cycle. Instead of using all oxide that has been processed to yield a given density, a less sinterable oxide is used as a diluent with a highly sinterable oxide like that prepared in this investigation to obtain the desired sintered UO_2 density.

The Affect of an Additive (Polytran) on the Final Sintered Density

The use of common organic binders and sintering aids (stearic acid, carbowax, etc.) was not generally employed in this investigation. However, some tests were performed using Polytran FS as a binder. This material is a water soluble biopolymer composition containing scleroglucan, a high molecular weight polysaccharide produced by fermentation. Rheologically, Polytran L (6 wt % Polytran FS in water) solutions are strongly pseudoplastic which provide exceptional suspending and flow properties (55).

To evaluate the effect that Polytran L had on the green density and the final sintered density, charges of U_3O_8 (prepared by the treatment derived in this study) and 0.7 mole of carbon were mixed with Polytran L in the following proportions:

- A. ($\text{U}_3\text{O}_8 + 0.7\text{C}$) + no Polytran L
- B. ($\text{U}_3\text{O}_8 + 0.7\text{C}$) + 1 wt % Polytran L
- C. ($\text{U}_3\text{O}_8 + 0.7\text{C}$) + 2 wt % Polytran L
- D. ($\text{U}_3\text{O}_8 + 0.7\text{C}$) + 3 wt % Polytran L
- E. ($\text{U}_3\text{O}_8 + 0.7\text{C}$) + 3.5 wt % Polytran L

After compacts of these mixtures were prepared by cold pressing at 30,000 lb/in², they were sintered in CO₂ at 1400°C for 2 hours. The results obtained are shown in Table 22.

Table 22. Green densities and final sintered densities of the UO₂ pellets obtained on charges containing C/U₃O₈ mole ratios of 0.7 with 0, 1, 2, 3 and 3.5 wt % additions of Polytran L and heated in CO₂ for 2 hours at 1400°C after cold pressing

Charge composition	Polytran L addition to charge wt %	Green density of compact	Sintered density g/cm ³	% of theo
A. ($\text{U}_3\text{O}_8 + 0.7\text{C}$)	0	4.70	10.43	95.10
B. ($\text{U}_3\text{O}_8 + 0.7\text{C}$)	1	5.04	10.65	97.08
C. ($\text{U}_3\text{O}_8 + 0.7\text{C}$)	2	5.12	10.66	97.18
D. ($\text{U}_3\text{O}_8 + 0.7\text{C}$)	3	5.57	10.66	97.20
E. ($\text{U}_3\text{O}_8 + 0.7\text{C}$)	3.5	5.78	10.64	97.00

The first addition of Polytran L (1 wt %) produced a substantial increase in the green density and a notable increase in the final sintered density. Additions of 2, 3 and 3.5 wt % Polytran L produced further increases in the green density, but resulted in negligible increases in the final sintered density.

When production grade $UO_{2.06}$ was mixed with 1 wt % Polytran L, cold pressed at 30,000 lb/in² and sintered for two hours at 1400°C in CO₂, a final sintered density of 91.02 percent of theoretical was obtained. This is about a seven percent increase over that (84.04) obtained by sintering the untreated dioxide under the same conditions. As with the charges of U₃O₈ + carbon, further weight percent increases of Polytran L to these green compacts produced increased green densities, but no noticeable increase in the final sintered density. Although a very small addition of Polytran is affective in increasing the final sintered density, the nature of this effect is not certain.

Since the chemical specifications placed on reactor fuel materials is quite stringent, the added impurities by the addition of Polytran should be considered. Analysis of Polytran FS reported earlier (page 105) revealed that it contained

9 wt % ash. Thus, for a sample that contains 1 wt % Polytran L (which is a 6 wt % solution of Polytran FS) a maximum of 54 ppm increase in the impurity level would result assuming no volatilization of these impurities, which are mostly sodium and silicate, occurs during the sintering operations.

The Preparation of a Dense UO_2 Crucible

After the conditions for preparing a ceramically active U_3O_8 (from production Grade UO_3) were defined and it was demonstrated that UO_2 pellets of high sintered density could be prepared directly from cold compacted pellets of the U_3O_8 , attention was directed toward preparing a dense UO_2 crucible using this material in a charge having a C/ U_3O_8 mole ratio of 0.7. (All further testing on the development of a dense crucible employed only this oxide).

The fabrication of UO_2 crucibles during the metal preparation phase of this study was described earlier (page 37, Part I). Basically, it involved jolt packing production grade $UO_{2.06}$ in a graphite mold and sintering it in vacuum at temperatures up to $1900^{\circ}C$. Although these crucibles had a sintered density of less than 60 percent of theoretical, they were sufficiently strong to contain the small amounts of

metal obtained in the experimental reductions in that phase of the investigation. Exploratory tests during the early phases of Part II of the overall investigation have shown, however, that the sinterability of urania is greatly reduced in the presence of graphite. Thus, it appeared that either an entirely new method for crucible preparation would have to be developed or suitable alterations made in the earlier method. Since graphite is relatively inexpensive, easily fabricated and has high strength, further tests were conducted in hopes of altering the method of crucible preparation rather than seeking an entirely new approach.

Although graphite has a deleterious effect on the sinterability of urania, it had not been determined what influence the presence of graphite had on sinterability during the primary reaction-densification step which occurs well below 1200°C . In an effort to better understand and evaluate this behavior, five compacts ($\text{U}_3\text{O}_8 + 0.7\text{C}$) were cold-pressed at 30,000 lb/in² and treated as follows:

- Sample A. 1. heat at 800°C for two hours in nitrogen on a graphite tray; cool, weigh and measure
2. sinter in CO_2 at 1400°C for two hours on an alundum tray; cool, weigh and measure.

The B, C, D and E samples were treated the same except that the lower temperature heatings were increased to 900°, 1000°, 1100° and 1200°C respectively. In an effort to reduce volatilization which would occur in vacuum, the primary densification was performed under an inert atmosphere. Since CO₂ would have reacted with the graphite forming CO, nitrogen was employed in the first heating step for each sample. Table 23 summarizes the results obtained.

As the temperature of the heating, in the presence of graphite was increased, the final sintered density of the resulting UO₂ compact after the 1400°C treatment decreased somewhat. Since the sample receiving the 900°C treatment had shown some densification over that of the green compact and the final sintered density obtained after 1400°C was about 94 percent of theoretical, an initial densification temperature of 900°C was chosen.

To evaluate these findings, a crucible was first jolt-packed from a charge of U₃O₈ and carbon and heated by induction in a graphite susceptor to 900°C under a nitrogen blanket within the furnace chamber shown in Figure 12. Instead of maintaining this temperature for two hours, however, heating was stopped after 20 minutes when noticeable shrinkage of the

Table 23. Densities obtained following initial densification steps at 800°, 900°, 1000°, 1100° and 1200°C for 2 hours on a graphite tray in nitrogen followed by sintering in CO₂ for 2 hours at 1400°C on an alundum tray

Sample	Green density		Densifi- cation temp, °C	Density after densification at temperature		Final sintered density (1400°C)	
	g/cm ³	% of theo.		g/cm ³	% of theo.	g/cm ³	% of theo.
A	4.84	44.12	800	4.80	43.75	10.42	94.98
B	4.84	44.12	900	5.94	54.14	10.31	93.98
C	4.84	44.12	1000	6.87	62.62	9.81	89.42
D	4.84	44.12	1100	7.21	65.72	9.75	88.87
E	4.84	44.12	1200	7.28	66.36	9.61	87.60

For comparison purposes, a blank was sintered on a graphite tray at 1400°C for two hours in nitrogen. A density of 7.28 gm/cm³ (66.36% of theoretical) was obtained.

crucible was observed through the sight glass. After the crucible had cooled to room temperature, it was removed from the graphite mold and examined. In addition to the shrinkage, which made it readily removable from the graphite mold, the crucible was relatively strong and could be handled easily without fracture.

Next, the crucible was sintered at 1400°C for two hours under CO_2 on an alundum pedestal in the furnace shown in Figure 14. The resulting crucible appeared to be quite dense and very strong. When stroked on the side with a pencil, the crucible responded with a clear high pitch sound. Dunk densities, determined later, on pieces of crucibles prepared in a similar manner exceeded 85 percent of theoretical. Although this density is below the densities obtained by cold-pressing and sintering pellets of the same charge material, it is considerably above the dunk densities obtained for crucibles prepared by jolt packing and sintering in vacuum at 1900°C (57 percent of theoretical). A photograph of a crucible prepared in the above manner is shown in Figure 19. Crucibles of this size will hold sufficient uranium oxycarbide to prepare one-half pound of uranium metal by the process described in Part I of this report.

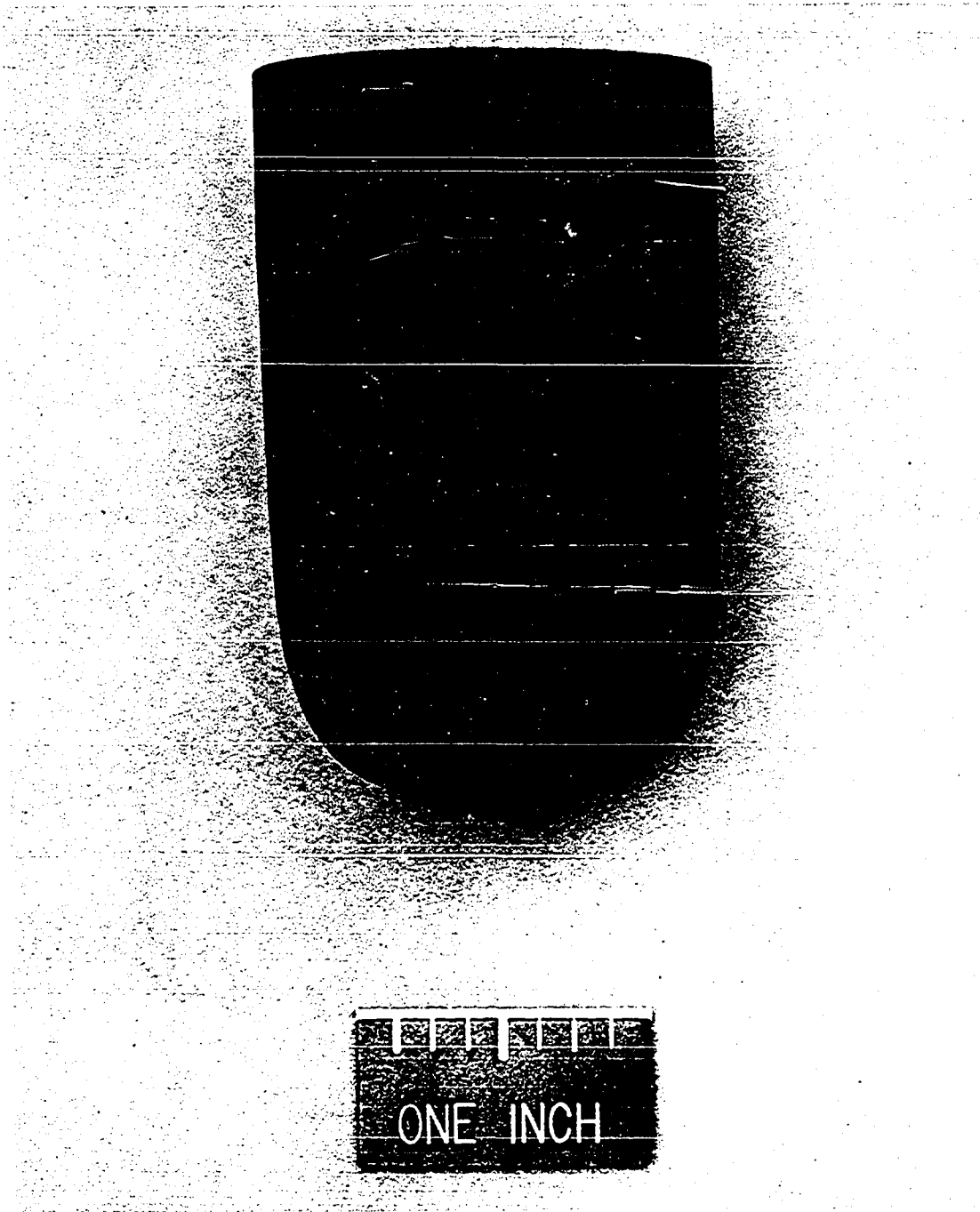


Figure 19. Photograph of a high density sintered UO₂ crucible prepared by the process derived in this investigation

SUMMARY OF DENSE UO₂ SHAPES PREPARATION

The preparation of dense UO₂ shapes by the carbon reduction of U₃O₈ in a preshaped compact has been studied. After charges of U₃O₈ (prepared by calcining production grade UO₃) and carbon were mixed to give different C/U₃O₈ mole ratios, cold pressed pellets of these mixtures were sintered under vacuum, in argon and CO₂ at temperatures up to 1400°C. It was found that charges with a C/U₃O₈ mole ratio of 0.7 sintered the best regardless of the atmosphere, but that CO₂ yielded the highest sintered densities.

Since the sintered densities of the UO₂ pellets obtained with the U₃O₈ prepared from as-received UO₃ were substantially less than theoretical, a method of preparing a more sinterable U₃O₈ was devised. This laboratory-scale process included:

1. wet ball-milling production grade UO₃,
2. precipitating the soluble uranium compounds with excess ammonium hydroxide,
3. filtering, washing, drying and powderizing the filter cake, and
4. calcining the filter cake (mostly UO₃ with some ammonium diuranate) to U₃O₈.

Compacts prepared from charges of this U₃O₈ with 0.7 mole of

carbon by cold pressing at 30,000 lb/in² sintered to greater than 95 percent of theoretical after two hours in CO₂ at 1400°C. The addition of a binder to the charge for compacting increased the sintered density of the pellets to 97 percent of theoretical.

Results of the study on the preparation of dense UO₂ pellets were then applied to preparing dense UO₂ crucibles by jolt packing. To avoid the deleterious effect that graphite has shown with respect to the sinterability of urania at temperatures above 1000°C, a two step process resulted. In the first step, the mixed charge of U₃O₈ and carbon is jolt-packed in the form of a crucible within a graphite mold and then heated to 900°C under nitrogen. Enough densification is produced so that the crucible can be removed and sintered under a CO₂ atmosphere in a graphite-free environment at 1400°C. Although these crucibles were compacted by simply jolt-packing the charge without binder in a graphite mold, they exhibited high densities and high strength.

RECOMMENDATIONS FOR FURTHER STUDY

During the course of scientific investigations, new ideas and interesting exploratory results that are not of immediate concern will often develop. Since these ideas and results may have a minor bearing on the main objectives of the investigation, they usually do not warrant full consideration at the time. During the second phase of this study on the preparation of dense UO_2 shapes the following items fell into this category.

1. Although the highest sintered densities were obtained with CO_2 , other sintering atmospheres should be investigated.

2. Since there appears to be a direct correlation between the sinterability of the oxide and its particle sizes and shapes, a more detailed investigation might be conducted on determining this correlation. Due to the unavailability of equipment to measure the surface areas of particles, this type of an investigation was bypassed.

3. Methods, other than jolt-packing, should be explored in crucible preparation. Alternate methods might include tamping or ramming the charge into a graphite mold; also hydrostatic pressing into a special mold should be applicable. During the same investigation, the employment of Polytran FS,

that was so beneficial in pellet preparation, should be evaluated in crucible preparation.

4. The preparation of a larger urania crucible should be investigated. Further, development of a removable plug in the bottom of this crucible for use in bottom pouring in the larger scale preparation of metal should be evaluated.

5. The irradiation stability of UO_2 pellets prepared by the process derived in the report should be evaluated. Since the microstructure of these pellets showed a very fine grain structure, the irradiation stability of these pellets might show improvement over most present day urania fuel pellets.

6. The process developed here for the preparation of dense UO_2 pellets and shapes might be extended. The process as presently derived involves only the oxide prepared from normal uranium (0.7 wt % U-235). However, oxide fuels in most reactor systems usually contain oxide that has been enriched several percent in the uranium-235 isotope. Consequently, the preparation of dense UO_2 shapes by the carbon reduction of U_3O_8 that is derived from UF_6 warrants further consideration.

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