

UNIVERSITY OF ILLINOIS
THE GRADUATE COLLEGE

HOT PRESSING OF ACTINIDE OXIDES

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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ENTITLED * HOT PRESSING OF ACTINIDE OXIDES

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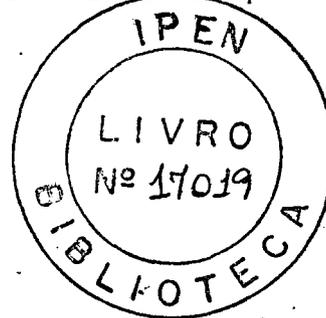
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I. INTRODUCTION

The continued demand for new types of nuclear ceramic fuels requires frequent reappraisal of existing fabrication processes.

The recent development of an entirely automatic system for oxide and ferrite hot pressing^{*} suggests the usefulness of evaluating the new possibilities introduced. Although the achievement of a solution for the hot pressing automation constitutes a technological breakthrough of decisive significance, the critical subject of production speed remains still debatable. In this context, the knowledge of the relations among temperature, time, pressure, density, microstructures and dimensional characteristics becomes a consideration of paramount importance, essential to define if the automated procedure is to compete with traditional cold forming processes.

The intent of this investigation is to determine the mentioned relationships for the actinide oxides currently being used as fuel, in nuclear power generation. The production variables of urania-thoria-plutonia hot pressed bodies will be analysed in the 300 - 1625 °C temperature range, for pressures up to 5,100 psi.

A substantial part of this study was developed as a contribution to the Argonne National Laboratory effort for the fabrication of the ZPPR reactor (U,Pu)O₂ fueled plates (Ref. 1). Many data presented here were obtained from papers written with the collaboration of this thesis author (Refs. 2,3) and published in the course of the investigation described here.

*Definitions in Appendix A.

II. LITERATURE SURVEY

A. Hot Pressing as a Fabrication Procedure

In the past, two main difficulties precluded an extensive utilization of hot pressing for the fabrication of oxide bodies. They were the problem of automating the process, to achieve high-speed production, and the unavailability of inexpensive long-life dies for high temperatures (Ref. 4).

In 1963 Zelms and McClelland (Ref. 5) had already foreseen the possibility of constructing a continuous hot press for oxides, and actually developed a semi-continuous apparatus. It became apparent that the automation of the process was feasible, originating eventually a new ceramic fabrication technique, competitive with classical methods both on the basis of technical performance and fabrication costs.

Such glistening perspective was changed to reality by Oudemans (Ref. 6), who described in 1968 a fully automatic equipment for the continuous hot pressing of urania, alumina and ferrites. This apparatus, assembled in Eindhoven, Netherlands, could be operated every working day for more than one year, at 1200 °C and 2280 psi, giving exceptional dimensional accuracy and excellent production rates. Densities as high as 98% of the theoretical could be attained for urania, and 99.9% for alumina. The last material could be sintered in one minute, at 1400 °C.

The use of liners inside metallic sleeves provides an economical die suitable for high temperature work. Moss and Stollar (Ref. 7) conceived a composite die in which the liner is subject to an external axial force as well as complete radial constraint. Important advantages

of this die design are the ease of liner replacement and the possibility of a wide variety of insert materials, such as graphite, "glassy carbon", oxide ceramics, boron nitride and intermetallics. One of their die assemblies, which contained a graphite liner with a wall thickness of 0.188 in. and an internal diameter of 0.5 in., was used at temperatures of 1000 °C and pressures up to 80,000 psi, without difficulty of removal of the formed material.

It will be shown in this paper that die insert materials particularly attractive for utilization with actinide oxides are "glassy carbon" (Ref. 8), and the now available ultra-high strength graphites. Such graphites at 70 °F have compressive and tensile strengths of 21,000 and 15,000 psi (Ref. 9), respectively; these values are substantially higher than those corresponding to the graphites currently used in hot pressing operations, which have maximum compressive and tensile strengths of 8540 and 1790 psi, respectively (ATJ grade graphite, Ref. 10). High density aluminas can be employed as liners, also; they are suitable for hot pressing UO_2 - ThO_2 compositions at temperatures up to 1400 °C.

For die-sleeves, molybdenum base alloys are very convenient. One of the most interesting is the molybdenum-0.5% titanium-0.1% zirconium alloy, known as TZM, which has a higher recrystallization temperature and better hot strength than unalloyed molybdenum and the molybdenum-0.5% titanium alloy (Ref. 11). At 1300 °C, the TZM tensile strength is 53,500 psi and the elastic limit 18,400 psi. The creep effects can be minimized by mounting the die under variable compression, using a device similar to that utilized by Oudemans for hot pressing of urania (Ref. 12).

For hot pressing in the temperature range 1300 - 1800 °C, a high-strength graphite sleeve, with "glassy carbon" liner, will be shown farther in this work to constitute an adequate combination, that can stand compacting pressures up to 7000 psi.

The foregoing observations, although emphasizing the solutions for the automation problem and long-life die design, suggest that a useful comparison between hot pressing and other ceramic forming methods, demands a comprehensive analysis of all the factors involved. A complete discussion of this matter is beyond the scope of the present study; moreover, the most pertinent features of such complex questions were considered in depth by Allen (Ref. 13) and Fulrath (Ref. 14) in their critical evaluation of ceramic forming systems. Nevertheless, many requisites not readily met by currently available production processes, can be attended by pressure sintering.

Some characteristics inherent in the hot pressing procedure are especially attractive for the fabrication of actinide oxides. The aspects that assume particular relevance are given next.

(1) Exceptional dimensional accuracy is obtained without any grinding and finishing operations, which cause loss of extremely valuable material and may originate a criticality hazard. Even large pieces, as for instance plates 2 x 2 x 1/4 in., can be fabricated within close tolerances (Ref.15). In relation to smaller bodies, Oudemans (Ref. 16) could make urania rods (approximately 1/2 in. diameter) with the required dimensional accuracy for use in nuclear reactors. Utilizing the same apparatus, he could produce ferrite rods whose diameter was found to

remain within a tolerance of 5 microns, over a production period of six months.

(2) Binder addition and its burnout are unnecessary. Thus, contamination with organic decomposition products is avoided.

(3) Where sintering can cause volatilization, decomposition or undesirable phase changes, hot pressing permits lower sintering temperatures and shorter sintering times. This is important for instance in the pressure sintering of PuO_2 , that can decompose to PuO_{2-x} and Pu_2O_3 (Ref. 17).

(4) Final densities can be made very high, in times much shorter than those corresponding to pressureless sintering. An application of such high densities can be found in the case of fuels for low burn-up thermal converter reactors.

(5) Reacting materials during the hot pressing is possible. The large dimensional distortions that generally accompany pressureless reaction sintering, can be avoided completely. Warren and Chakrader (Ref. 18), using reactive hot pressing of uranyl oxalate at 700°C , produced high density UO_2 pellets of good quality. Pressure calcining of UO_{2+x} in various atmospheres, described further in this paper, was successfully developed at Argonne National Laboratory by J. Handwerk and the author in January 1968, and is object of a patent request (Ref. 19).

(6) Hot pressing apparatus may be very compact in size. A small automated system, similar to that described by Oudemans (Ref. 20), is excellent for work to be carried out in glove-boxes or in hot-cells. Since all fabrication involving plutonium must be developed inside

glove-boxes, pressure sintering is a natural choice for plutonia ceramics.

In the past five years many papers on the use of pressure sintering have appeared in the technical literature. However, the fundamental reference works of Goetzl (Ref. 21), Jones (Ref. 22) and Murray (Ref. 23) are essential for an adequate evaluation of that forming technique potential, in the field of nuclear ceramics.

Recently, several detailed reviews of hot pressing of ceramics were published (Refs. 24-26). Considerable efforts have been made to extend the number of hot-forming techniques. Hot isostatic pressing (Ref. 27), hot extrusion (Ref. 28) and ultra-high pressure sintering (Ref. 27) constitute some successful examples.

Experiments with continuous processes (Refs. 29, 30) led to the highly efficient Oudemans' production apparatus, previously mentioned in the beginning of this study.

Pressure calcinering (decomposition pressure sintering) and reactive hot pressing deserve special attention, since they can simplify considerably the fabrication of nuclear ceramic fuels.

The term "pressure calcinering" was established by Morgan (Ref. 31) for chemically activated pressure sintering, where decomposable powders are calcined under pressure, decomposition products being allowed to escape. Densification effects occur as decomposition takes place. Morgan prefers to distinguish pressure calcinering from reactive hot pressing, that is, the pressure sintering in which phase change occurs without gas evolution (Ref. 27).

Very fine grained, submicron, highly dense, translucent refractory oxides have been prepared utilizing pressure calcining, at pressures of about 10,000 psi, in the temperature range 900 - 1200 °C. However, it is important to observe that the strength of the materials produced is not very high.

Chaklader and collaborators (Refs. 18, 32-34) have extensively studied reactive hot pressing which, in their interpretation, comprises all types of enhanced reactivity related to phase inversions, dislocation and decomposition reactions.

Pressure sintering is controlled essentially by the same factors that govern the behavior of conventional sintering, but with the added variable of applied pressure. The understanding of the interrelation of particle characteristics, time, temperature, pressure and atmosphere exists for some materials, but on an empirical basis only. The following generalizations are reasonably consistent (Ref. 24):

- (a) densification rate increases with decreasing particle size, all other factors being constant;
- (b) densification rate increases with temperature;
- (c) densification rate increases with pressure.

Table 1 (Ref. 14) shows a list of materials used or considered for use as uniaxial pressure sintering die components. The corresponding limits of temperature and associated maximum pressure are also given.

Graphite has been the material utilized most often in hot pressing, but it presents many shortcomings. In the case of nuclear ceramics, where high-purity is imperative, contamination due to corrosion

TABLE 1 (Ref. 14)

UNIAXIAL PRESSURE SINTERING DIE MATERIALS

<u>Die Material</u>	<u>Maximum Use Temperature (°C)</u>	<u>Maximum Pressure (psi)</u>
Graphite	2500	10,000
Al ₂ O ₃	1200	30,000
ZrO ₂	1180	*
BeO	1000	15,000
MgO	*	*
SiC	1500	40,000
TaC	1700	8,000
WC, TiC	1400	10,000
TiB ₂	1200	15,000
W	1500	3,500
Mo	1100	3,000
Inconel X, Hastelloy, Stainless Steels	1100	varies

* Not Known

and wear constitutes a serious problem. To overcome or decrease reaction between the material being pressed and the graphite die parts, die washes, coatings and spacers, sleeves of various compositions have been employed. Pyrolytic graphite punch coatings, boron nitride and aluminum oxide mold or die washes, spacers of noble and refractory metals (e.g., Pt, W, Mo, Ta), refractory compounds (SiC) and refractory oxide powders (ZrO_2) have attained some success (Ref. 24).

In pressure sintering, graphite must be operated in an inert atmosphere or vacuum; above $2200^{\circ}C$ an inert atmosphere is essential, due to the high vapour pressure. $CO-CO_2$ plus N_2 at equilibrium, caused by the reaction of air or residual oxygen with carbon black insulation and/or the graphite die material, forms the gaseous atmosphere, in many assemblies. Flushing with an inert gas such as argon is a current method. Many of the materials listed in Table 1 also demand the utilization of a controlled atmosphere. Vacuum pressure sintering has been applied successfully in several cases, but generally it does not seem to present significant advantages when refractory oxides are considered (Ref. 24).

Table 2 shows examples of maximum sizes of hot pressed ceramics (Ref. 14).

Density variations become severe for hot pressed shapes with length-to-diameter ratios above about 4 (Ref. 14). Cylindrical, square and rectangular cross sections can be fabricated by employing collapsible inner mandrels. It is also possible to form tubes and thin-walled cylinders.

TABLE 2 (Ref. 14)

EXAMPLES OF MAXIMUM SIZES OF PRESSURE SINTERED CERAMICS

<u>Material</u>	<u>Diameter</u> (inches)	<u>Length or Height</u> (inches)
Al ₂ O ₃	3	6
MgO	7	½
BeO	10	10
	12	2
TiB ₂	6	18
	8 ^b	8
BN	14	14
SiC	6	2

The degree of microstructural uniformity in pressure sintered ceramic compacts constitutes one aspect of the forming process which requires much additional work. It will be seen in the course of this thesis that microstructural heterogeneities can become a critical problem, principally in the case of pressure calcintering. Within a single hot pressed piece, considerable gradients in density and/or grain size may also occur, particularly in large flat pieces. Grain size variations from 12 μ at the center to nearly 100 μ at the edge were observed in a beryllia sample, 12 inches in diameter. In other pieces of the same material density variations of $\pm 0.2\%$ within a single body have been reported (Ref. 14).

Although Oudemans has demonstrated the effectiveness of a continuous production pressure sintering system (Ref. 6), batch processes still present much interest. The utilization of many die assemblies which are preheated, passed under a press, and then cooled has been described, but die costs can become a prohibitive factor. The stacked pressings of a number of pieces in a single die, used in the development of this thesis, as well as group pressing of a number of die assemblies, have been used successfully on a semi-continuous basis. These two techniques, combined into a single, multiple-layer and multiple-cavity die arrangement, were employed for the production of a large number of small (0.5" dia. x 0.2" long) thermoelectric elements (Ref. 35).

The application of pressures much larger than those indicated in Table 1 opened new perspectives for the hot pressing of ceramics. Before 1964, the majority of ultrahigh pressure research had been performed at pressures above 725,000 psi and, except for the now-classical synthesis of diamond and a few other cases, was limited to metallic systems. Vasilos and Spriggs (Ref. 24) described in 1964, a 1,000,000 psi pressure sintering apparatus capable of producing 0.5 inch in diameter by 1.0 inch long oxide samples. Densities in excess of 99%, with grain sizes below one micron could be achieved for Al_2O_3 , MgO, NiO and Cr_2O_3 . Although the strength of specimens prepared at very high pressures is low (probably due to the fact they are densely packed, but have weakly bonded grains), this does not indicate a drawback for applying the process in the case of actinide oxides nuclear fuels, because

for them, mechanical properties are not always critical. The potential utility of high pressure sintering for actinide oxides lies in decreasing pressing times. The pronounced effect of pressure on the times necessary to reach a certain density can be exemplified by considering NiO. At 2000 psi, and 1100 °C NiO attains 95% relative density only after 500 minutes. The time is decreased to one half minute (1000 times less) when pressure is increased only ten times (Ref. 36).

B. Hot Pressing of Actinide Oxides

Many references to uranium oxide hot pressing are found in the literature, but there is a dearth of information concerning thorium, plutonium and $UO_{2+x}-ThO_2-PuO_2$ compositions.

1. Urania

Murray and collaborators (Ref. 37) studied oxides of the composition $UO_{2.0}$ (particle size approximately 5 microns) and $UO_{2.13}$ (particle size not reported). Graphite dies were used.

$UO_{2.13}$ was produced by incomplete reduction of UO_3 . This oxide was utilized to study the influence of hyperstoichiometry, on densification, known to be pronounced for normal sintering (Ref. 38).

Fig. 1, based on data given in reference 37, shows hot pressing curves for $UO_{2.0}$, $UO_{2.13}$ and the results for cold pressed and sintered specimens of $UO_{2.13}$.

The pressing time at temperature was 10 minutes and the pressure used was 2000 psi, applied when the powder started to yield on heating. Before heating, the pressure applied was 1000 psi.

Curve A shows that the rate of sintering of $UO_{2.0}$ below $1700^{\circ}C$ is very slow. After $1700^{\circ}C$ the density increase is rapid to a maximum bulk density of 9.55 g/cc (87.1% theoretical density).

With $UO_{2.13}$ (curve B), sintering becomes appreciable at $1000^{\circ}C$. A maximum 96.5% theoretical density was reached at $1900^{\circ}C$. At temperatures above $1800^{\circ}C$ the samples were weak and brittle, usually breaking on extraction from the die.

Curve C represents the values obtained after sintering cold pressed $UO_{2.13}$ in argon for a period of 2 hours. The high values of densities, relative to curve B are tentatively explained by the non-reducing atmosphere allowing the increased rate of sintering to occur as a result of the hyperstoichiometric proportion of oxygen. In graphite-die hot pressing a reducing atmosphere exists, nullifying the increased rate of sintering usually resulting from the applied pressure.

From the work with urania and other oxides, it was concluded (Ref. 39) that there is a pronounced effect of particle size on the hot pressing characteristics. This is consistent with results of experiments developed more recently by Vasilos and Spriggs with NiO , for pressures in the 500-2000 psi range (Ref. 40). However, for pressures around 20,000 psi (time: 10 minutes) the influence of particle size is not very large.

One of the important observations presented by Murray in his hot pressing studies (Ref. 41) is that powders can be characterized by a particle size whose value lies between those obtained with air-permeability

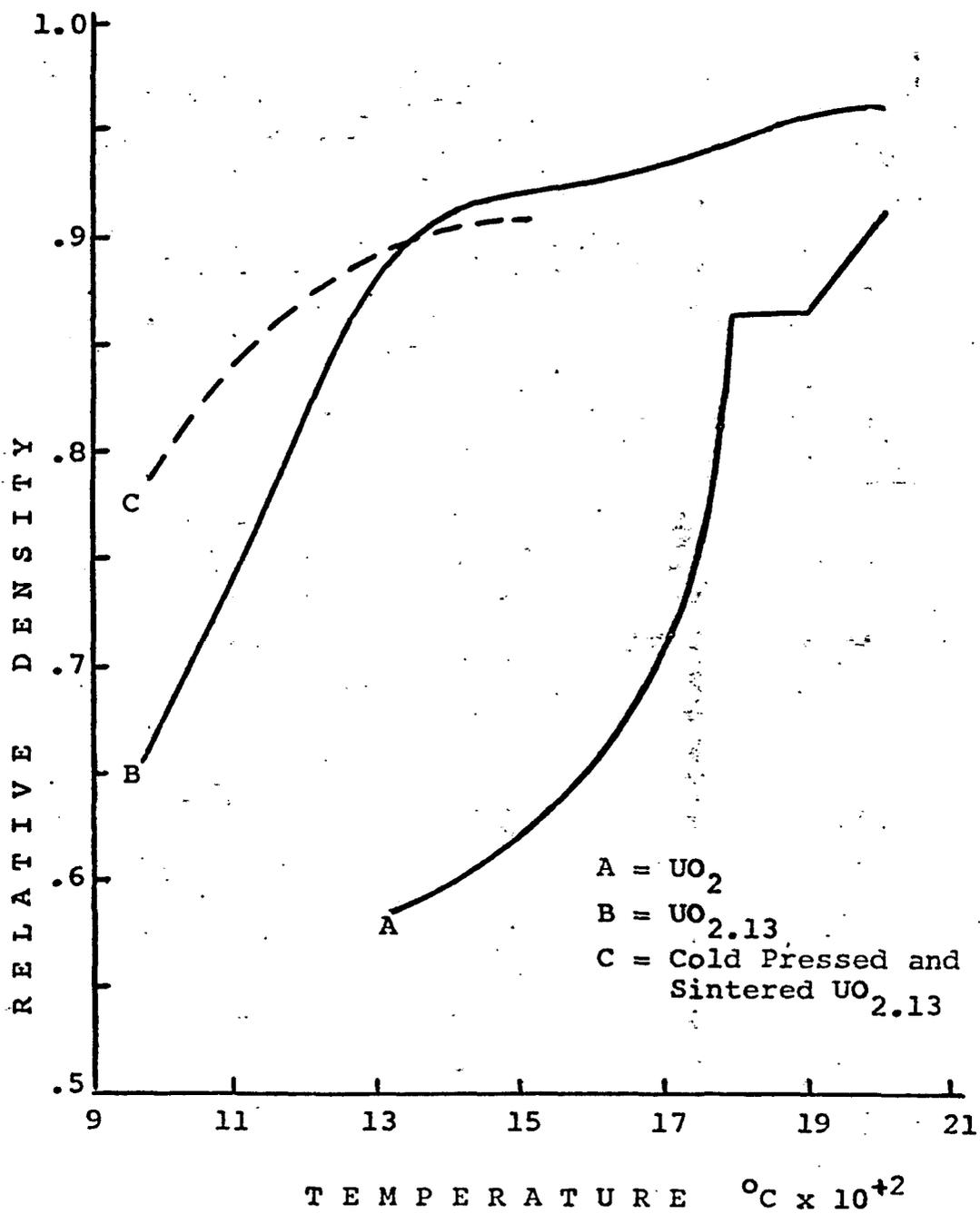


Figure 1. Hot Pressing Characteristics of Uranium Oxides
(Data from Ref. 37).

and gas-adsorption. These two methods give extreme limit values. The highest corresponds to air permeability, since in effect agglomerate size is being measured, whereas a low result originates from the other method, due to adsorption by morphological features like cracks and rough surfaces. As an illustration, air-permeability and nitrogen-adsorption measurements of particle size for the heavy magnesia, used in Murray's experiments, gave 1.6 and 0.04 microns respectively. This is an apparent size ratio of 40. According to Clayton (Ref. 42) the ratio determined from these two methods can be termed "roughness" or "porosity factor." The ratio may give some indication of the degree of roughness, porosity, irregularity and nonuniformity of the powder particles. When this ratio is unity, it can be assumed the powder is nonporous and smooth.

Table 3 (data from Ref. 43) gives the surface areas for UO_2 produced by different methods. S_G and S_p are the total and external surface areas, determined respectively by gas-adsorption and air permeability.

Considering the powders as spherical particles of known density d , it is easily shown that the surface area $S = \frac{6}{dD}$, D being the diameter of the equivalent sphere (Ref. 44).

Table 3 indicates that the values of S_G/S_p for UO_2 , although not so large as the one corresponding to the heavy magnesia previously mentioned, precludes the adoption of a single number as characteristic of surface area.

Amato and collaborators (Ref. 45), in their characterization of an urania powder for pressure sintering, gave both values of S_G and S_p .

TABLE 3*
SURFACE AREAS OF UO_2 POWDERS

Methods of Preparation	Surface Area (m^2/cc)		
	Total (S_G)	External (S_p)	S_G/S_p
1. High-pressure steam oxidation of uranium	12.9	3.1	4.2
2. Air pyrolysis of $UO_2(NO_3)_2 \cdot 6H_2O$ to U_3O_8 ; hydrogen reduction to UO_2 **	6.4	3.1	2.1
3. Hydrogen reduction of $UO_3 \cdot 2H_2O$	8.8	4.1	2.1
4. Hydrogen reduction of ammonium carbonate precipitated diuranate	40.7	4.1	9.9
5. Hydrogen reduction of ammonium hydroxide precipitated diuranate	37.4	13.9	2.7
6. Hydrogen reduction of urea precipitated diuranate	42.1	12.6	3.3

* Data from reference 43.

** Mallinckrodt Works material used in PWR (Pressurized Water Reactor) Core 1.

Such is also the criteria adopted in the development of this thesis, whenever the necessary instruments were available. However, it is felt that Murray's observations mentioned before, concerning the particle size effective in sintering, remain valid: the surface area characteristic of the powder in the densification process is really between S_G and S_p .

Murray makes (Ref. 37) a distinction between two types of uranium oxide powders prepared by reduction of UO_3 with hydrogen, depending on whether or not the reduction temperature is close to the point in which sintering of primary crystallites occurs. Category A comprises powders where the preparation temperatures did not cause primary crystallite sintering. The primary crystallites are separated and have residual vacant sites, therefore presenting high surface-energy. Subsequent hot pressing will be rapid. In category B the uranium primary crystallites agglomerate, forming relatively large regions containing closed pores. Consequently the rate of pressure sintering is slow and porosity is retained for a longer time. Apparently, these categories can be used for other oxides.

It will be seen later that the thorium powder, used in some of the experiments described in this thesis, seems to belong to category B.

Scott and Williams (Ref. 46) studied the warm pressing of UO_2 at $800^\circ C$ under pressures up to 20,000 psi. The hyperstoichiometric oxides $UO_{2.08}$ and $UO_{2.2}$ were warm pressed in the range 2000 - 20,000 psi, using a die of TiC bonded with Ni. The results are presented in Figure 2.

$UO_{2.2}$ pellets were pressed in a Nimonic 80 die, but the resulting compacts fractured. This was attributed to dimensional change on cooling, due to the difference in the coefficients of expansion of $UO_{2.2}$ and the die material. Using a modified die, in which the compact was ejected in a protective atmosphere at the maximum operating

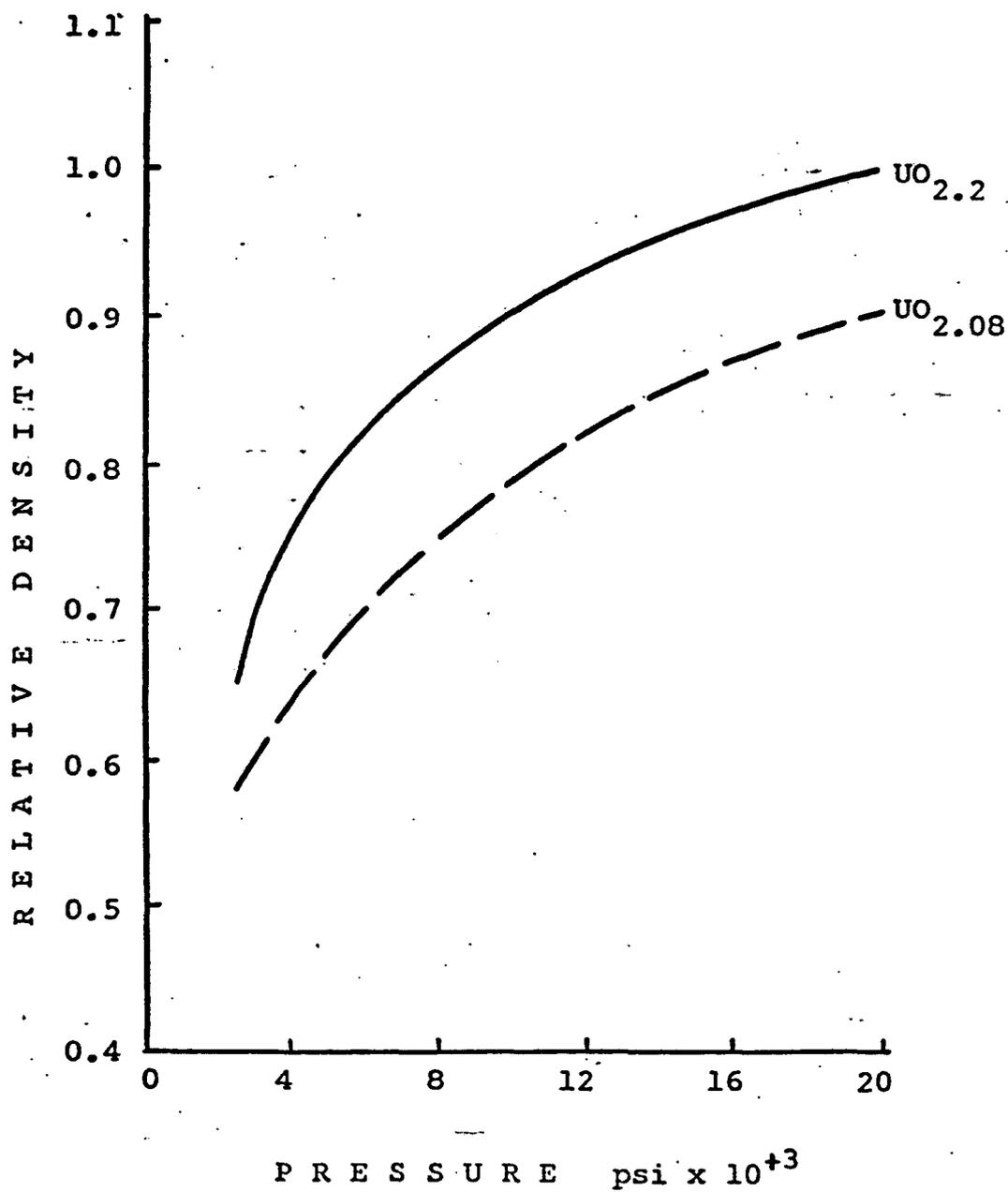


Figure 2. Densification of Non-Stoichiometric Uranium Oxide at 800 °C (Ref. 46).

temperature and cooled without the die, a sound piece could be obtained.

To avoid the problem created by differential expansion, a TiC die was employed in subsequent experiments. TiC has a mean coefficient of thermal expansion of about $10 \times 10^{-6} / ^\circ\text{C}$, practically the same at UO_2 :

The surface areas of $\text{UO}_{2.20}$ and $\text{UO}_{2.08}$ were 6 and 2 m^2/g , determined by N_2 adsorption, corresponding to equivalent spherical particle diameters of 0.1 and 0.25 μ .

Two 30 g loads of each material, separated by a TiC spacer $\frac{1}{8}$ " thick, were pressed simultaneously from opposite ends with a floating die body. The whole die assembly was heated to 800 $^\circ\text{C}$ in about twenty minutes and held at this temperature for ten minutes, the pressure being maintained constant during the experiment. The fall of pressure on the gauge attached to the press indicated that densification started at 600 $^\circ\text{C}$ and stopped after 2 or 3 minutes at the top temperature.

The oxygen: uranium ratio of both samples remained constant within ± 0.01 of the original value.

From figure 2 it can be concluded that the effect of pressure is pronounced in the range 2000 - 12,000 psi. This range is well above that utilized with common graphite dies. As far as densities are concerned, there is a definite advantage to using $\text{UO}_{2.2}$, instead of $\text{UO}_{2.08}$.

The constancy of the oxygen uranium ratio mentioned before demonstrates also the possibility of hot pressing uranium oxides in the absence of protective atmosphere.

Scott concluded that further work was needed to determine whether a plastic flow or a diffusional creep mechanism is responsible for the densification of $UO_{2.2}$ and $UO_{2.08}$. In a study of such nature, the determination of the effect of oxygen stoichiometry on plastic flow and diffusion rate of the cation was considered essential.

The most significant contribution of Scott's work was the demonstration that pressure sintering of uranium oxides is feasible in the temperature range where conventional automatic powder metallurgy equipment is currently available. However, the utilization of nonstoichiometric uranium compounds in nuclear power reactors does not constitute common practice. Therefore, a serious obstacle for industrial application of the warm pressing technique described still remains.

Amato and collaborators (Ref. 47), using an alumina-lined graphite die and $UO_{2.0}$ (whose characteristics are given in Table 4), hot pressed specimens at 4000 - 8000 psi for times ranging from 15 to 60 minutes and at temperatures of 1100 - 1200 °C. Figure 3 shows the relative densities they obtained. The results, consistent with those presented in figure 2, indicate again a pronounced effect of the applied pressure on the final density.

Amato concluded from his experiments that the plastic flow model developed by Mackenzie and Shuttleworth (Ref. 48) and modified by Murray and McClelland (Ref. 49) is more likely to hold than the Nabarro-Herring creep model (Ref. 50).

TABLE 4 (Ref. 47)

CHARACTERISTICS OF THE STOICHIOMETRIC URANIUM
OXIDE USED BY AMATO AND COLLABORATORS

Real density (CCl_4) (g/cc)	10.39
Tap density (g/cc)	2.12
Average particle diameter (Fisher), (micron)	2.80
Total surface area S_G (BET), (m^2/g)	3.69
External surface area S_p (m^2/g)	0.24
Roughness factor	15.37
DTA: 1st oxidation peak ($^{\circ}\text{C}$)	205
Temperature difference between 1st and 2nd oxidation peaks ($^{\circ}\text{C}$)	120
O/U ratio	2.00

Multispecimen hot pressing of UO_2 was developed at Argonne National Laboratory by the author. Part of the results are published in reference 3. Pressings of five to eleven plates 2" x 2" x 0.25" were made in graphite dies at temperatures from 1400 to 1625 $^{\circ}\text{C}$. It was shown the technique is amenable to close dimensional control. Density variation of specimens within one pressing was approximately 0.5%. Plates and discs were produced, the thickness being maintained within ± 0.005 " or better.

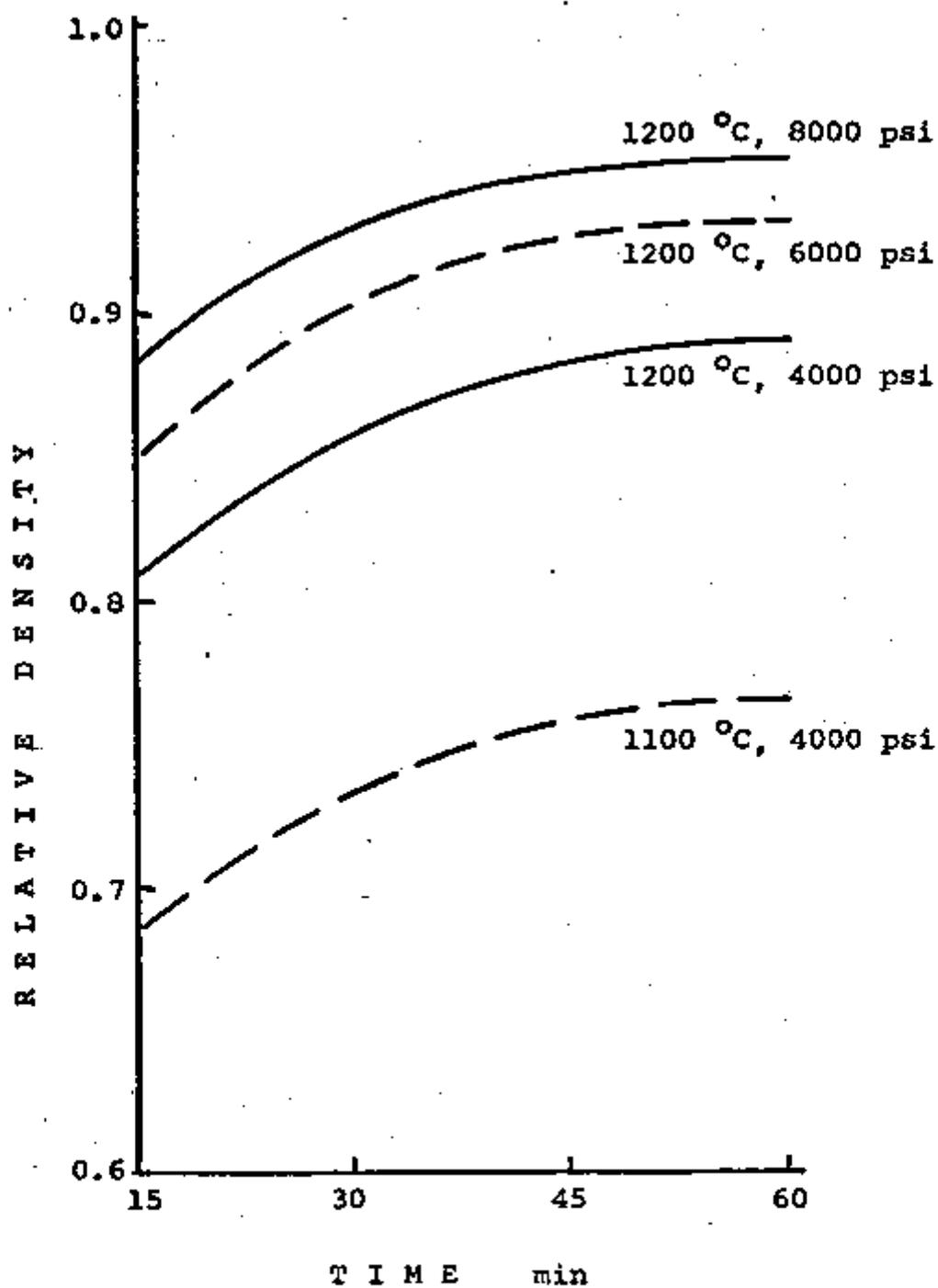


Figure 3. Densification of Stoichiometric Uranium Oxide. Effect of Time, Temperature and Pressure (Ref. 47).

Unexpectedly, carbon pickup apparently increased for lower hot pressing temperatures. An explanation of this will be presented further, in this paper.

The carbon contamination could be minimized by a hydrogen annealing treatment after pressing. This probably resulted from the presence of a small amount of H_2O in the hydrogen atmosphere.

Uranium carbide was observed in plates hot pressed at $1625^\circ C$, using CS grade graphite (Ref. 10); no carbide formation developed when the stronger ATJ graphite grade (Ref. 10) was employed.

The demonstration of the multispecimen hot pressing feasibility showed that a production process was possible for the fabrication of relatively large bodies of nuclear ceramic oxides. Such a process lends itself well to glove box operations, due to its compactness.

Reactive hot pressing of UO_2 was extensively studied by Warren and Chaklader (Ref. 18). UO_{2+X} obtained from calcination of uranyl oxalate in N_2 at $600^\circ C$, which was pressure sintered in N_2 at $700^\circ C$, for three minutes, produced a final density of 96 to 98% of theoretical. This exceptional result was attributed to the nonstoichiometry and sub-micron sized particles of UO_{2+X} produced by calcination. High density UO_2 pellets were also obtained using uranyl oxalate as starting material.

The kinetics of hot pressing of UO_{2+X} were studied in the temperature range $500 - 700^\circ C$. The process activation energy was 56 kcal/mole . Since this value corresponds to the creep activation energy of nonstoichiometric urania, Warren and Chaklader concluded that the rate controlling

mechanism for densification during the final stage and for the creep process are the same. For the creep process the rate determining step was considered to be cation self diffusion in urania.

The work of Dudemans (Ref. 6), previously mentioned, is possibly the first to describe an apparatus for the continuous hot pressing of urania. The characterization of the urania powders used is not given, neither are the specific operating conditions. Rods with a bulk density of 98% of the theoretical were obtained with the required dimensional accuracy for utilization in nuclear reactors.

2. Thoria

Murray and collaborators (Ref. 37), hot pressed thoria of 99.9% purity in the temperature range 1300 - 2000 °C, using graphite dies. The pressure was 2000 psi, applied when the powder started to yield. The time at maximum temperature was 10 minutes.

Figure 4 shows the densification of the thoria (curve A), for different temperatures. A rapid density increase exists up to 1700 °C; a maximum density of 9.78 g/cc is reached at 1900 °C. Curve B presents the densification for thorium carbonate (with decomposition to ThO₂). This is an indication of what was to be called "reactive hot pressing" some ten years later.

For these experiments the powder characterization was not established. This unfortunately decreases their value for the purpose of comparison with results presented in this paper.

The highest rates of densification for Th(CO₃)₂ were attributed to a larger proportion of vacant sites in the ThO₂ as formed, and these assisted the early removal of agglomerate pores.

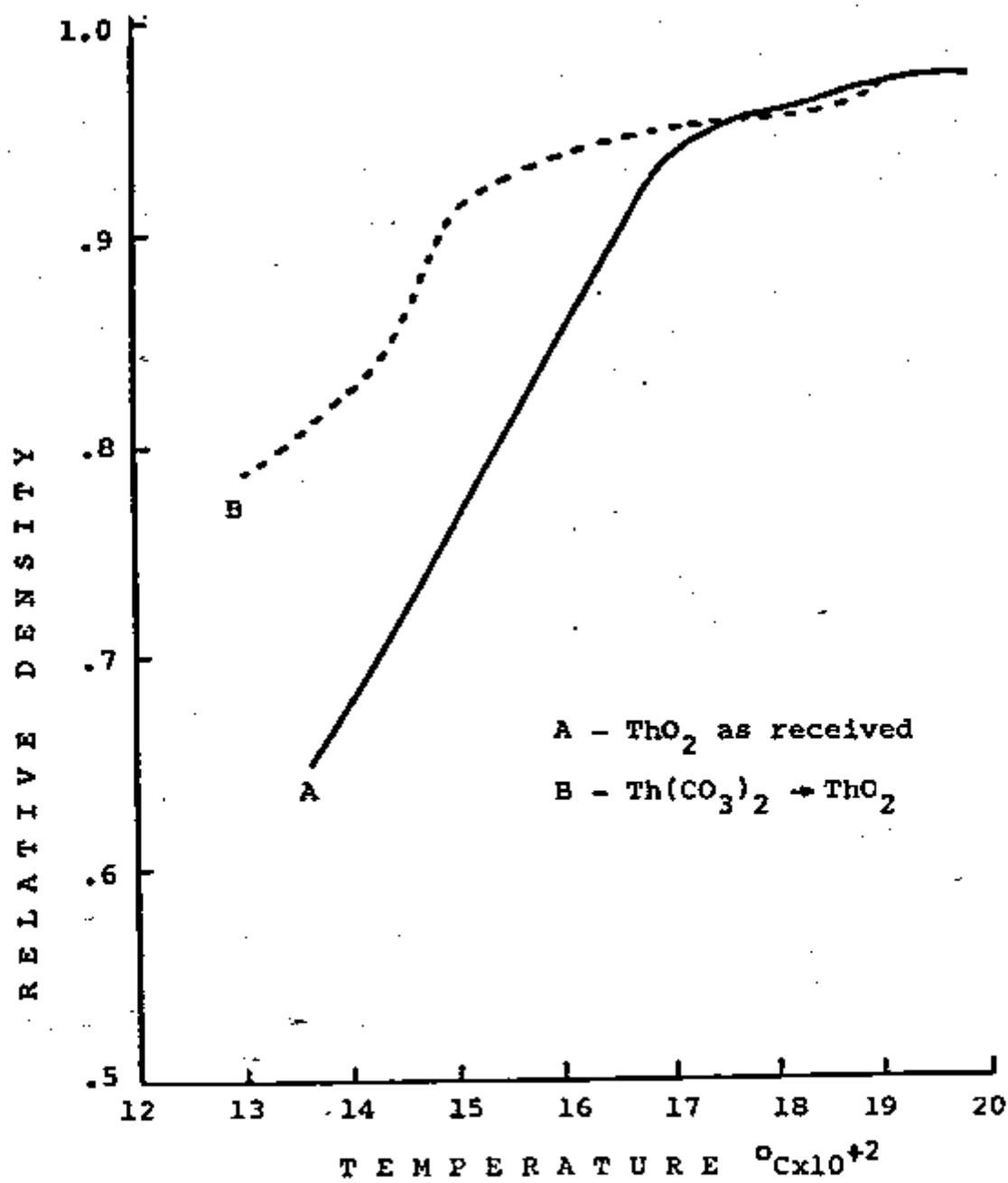


Figure 4. Hot Pressing Characteristics of ThO_2 (Ref. 37)

3. UO_{2+x} - PuO₂ - ThO₂ Composition

Hot pressing of these actinide oxide compositions seem to have been reported only by the author of this thesis and his collaborators, during the development of experiments corresponding to the investigation described in this paper.

III. EXPERIMENTAL PROCEDURE

A. Preliminary Work at Argonne National Laboratory

The preliminary results of UO_2 - ThO_2 compositions hot pressing were presented briefly in an Argonne National Laboratory internal report (Ref. 51), corresponding to work accomplished by C. T. de Freitas in cooperation with summer students. The investigation was developed in the Fuel Properties Group, managed by J. H. Handwerk. The significance of the results obtained consisted in the demonstration that the composition UO_2 - 20 w/o ThO_2 could be hot pressed to 90% of the theoretical density.

Pressure sintering of UO_2 - 15 w/o PuO_2 was investigated by C. T. de Freitas at the Argonne National Laboratory Plutonium Facilities. Most of the results were presented in reference 2, as part of the work developed for the completion of this thesis.

A significant part of the Liquid Metal Fast Breeder Reactor (LMFBR) development effort at Argonne National Laboratory (ANL) is directed toward reactor physics studies. To permit reactor physics studies of large LMFBR cores a Zero Power Plutonium Reactor (ZPPR) has been constructed. The bulk fuel for ZPPR consists of rectangular prismatic plates of U Pu Mo alloy jacketed in Type 304L stainless steel.

Present emphasis on oxide fuels for LMFBR application dictates the need for physics information specific to oxide compositions. Oxide effects will be determined in zoned experiments in ZPPR using plates geometrically similar to the bulk fuel but containing $(\text{U}, \text{Pu})\text{O}_2$. The

dimensional specifications on the required oxide fueled plates include a minimum gap between fuel and jacket, close tolerances on flatness, and controlled stoichiometry and total impurity content.

Although the fuel cores can be made by conventional cold pressing and sintering techniques, this process is composed of many steps and is not suited to conveniently meet the size and dimensional tolerance requirements. For this reason hot pressing was considered as an alternate fabrication procedure.

Because of the lack of published information on hot-pressing of $\text{UO}_2\text{-PuO}_2$, a parametric study was initiated to determine the effects of time (t), pressure (P), and temperature (T) on final compact density (D_E). In this manner, practical ranges of temperature and pressure to attain desired densities were defined.

The hot pressing unit used in this series of experiments is described in reference 2. In initial experiments, graphite dies and punches were used due to their high temperature resistance, easy machinability, and relatively low cost. For the determination of the function $D_E = f(T, P)$, single-sample hot pressing was performed in the temperature range 1000-1400°C. In further experimentation multispecimen hot pressing was developed using 1" diameter and 0.75" square dies, made of ATJ grade graphite. The layers were separated by ATJ graphite pieces. In this manner three samples were hot-pressed at one time.

A photograph of the hot pressing apparatus is shown in Figure 5. The hot press is capable of being controlled within $\pm 10^\circ\text{C}$. The pressure during an experimental run was maintained manually. Subsidence was measured to ± 0.001 ."

A typical hot pressing run on a single plate was conducted by filling the die with 40 g of UO_2 -15w/o PuO_2 . The assembled die was prepressed at 500 psi to permit ease of handling, and loaded into the furnace cavity. The press was then closed and a predetermined force exerted by manually pumping the hydraulic press. The dial indicator was set at zero and the furnace heating cycle started. All runs were made on a fixed temperature and time cycle. The pressure on the single-acting press was maintained at all times during the hot-pressing cycle. As the temperature increased any subsidence was noted. The specimen was maintained at maximum temperature and at fixed pressure for a predetermined period of time. It was found that only ten minutes at temperature was sufficient to reduce the subsidence to essentially zero.

After the specimen was held at maximum temperature and pressure for the desired period of time the furnace power was decreased. When the die had cooled to room temperature (in about one hour) the press platens were separated and the die was removed from the furnace. The specimen was ejected from the die and its thickness, width (or diameter), length and density were determined. Particular attention was paid to thickness variation and irregularities in surface. Samples for chemical analyses were taken after thorough mixing of crushed and powdered specimens.

The two types of depleted uranium oxides were used; UO_2 code TF-1, an oxidized-reduced oxide prepared at ANL, and UO_2 code TF-4, a commercial ceramic grade powder, from Kerr-McGee. The PuO_2 was produced by reduction of oxalate at low ($750^{\circ}C$) temperature. Table 5 gives the characteristics of these powders.

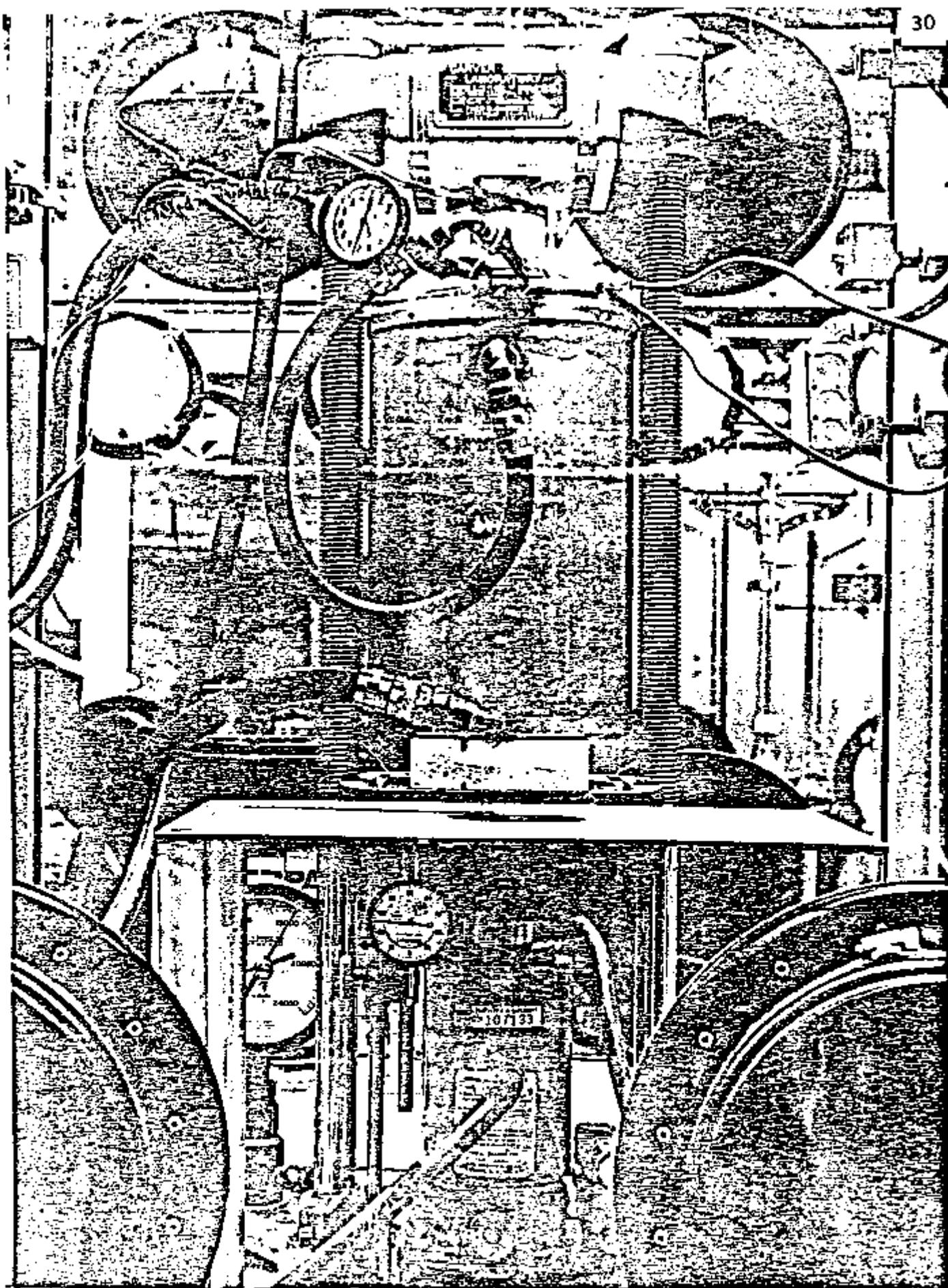


Figure 5. Hot Pressing Apparatus for the Study of UO_2 - PuO_2 Mixtures.

TABLE 5
 CHARACTERISTICS OF THE URANIUM OXIDES AND PuO₂
 USED IN THE HOT PRESSING OPERATIONS

<u>Characteristics</u>	<u>UO₂</u>		<u>PuO₂</u>
	<u>Code TF-1</u>	<u>Code TF-4</u>	
Particle size (Fischer) Microns	1.20	1.04	41
Oxygen w/o	12.49	12.42	12.38
Metal w/o	87.85	87.46	87.74
Oxygen/Metal (Atom ratio)	2.11	2.11	2.11
Nitrogen ppm	90	150	--
Carbon ppm	--	85	245

The oxides described above were blended using a manually operated V-blender on batches weighing about 70 grams. The results of chemical analyses performed on 0.5 gram samples taken from three different locations in one batch are shown in Table 6. The extremes in the reported analyses were 0.3% for uranium and 0.96% for plutonium. The extreme variation between samples were 0.43% for uranium and 0.68% for plutonium. The average ratio of uranium to plutonium was 5.73:1, which was the target blend. This result was considered adequate to justify manual blending of oxides for the parametric studies of immediate interest. They did not, however, satisfy the stringent homogeneity requirements placed on oxide plates for reactor physics experiments.

TABLE 6

ANALYSIS OF METAL CONTENT IN UO_2 - PuO_2 MIXTURES BLENDED MANUALLY

Sample	U (w/o)		Pu (w/o)		Total Metal w/o	U/Pu
	Determination A	Determination B	Determination A	Determination B		
1	74.63	74.93	13.01	13.97	88.27	5.55:1
2	74.16	74.01	12.69	12.61	86.73	5.86:1
3	74.44	74.66	12.81	12.81	87.16	5.79:1
					AVG.	5.73:1

A total of 18 runs were made in an attempt to relate final plate density to the temperature and pressure employed during hot pressing. The results of seven of these runs are shown in Figure 6 which is a plot of D_E and T for a constant pressure of 3820 psi for 1" diameter single sample hot-pressing of $UO_2-15w/oPuO_2$. Densities as high as 93% of theoretical were obtained at $1400^\circ C$.

A triple layer hot pressing of square plates was performed at $1500^\circ C$ at a pressure of 3820 psi and a time of 30 minutes. The results of this run are shown as a square on the above figure. The tablets averaged 95.7% theoretical density and had an average thickness variation of $\pm 0.5\%$.

Some clues to the relative value of densification parameters can be obtained from studies of the subsidence of the compacts during pressing. Figure 7 is a curve of subsidence and rate of subsidence versus temperature for three hot pressing runs at 1000, 1200, and $1400^\circ C$. Since the temperature-time cycle during hot pressing was maintained constant for all runs the subsidence curves are common to each run. From this curve one can see that about 75% of possible densification has taken place at about $1000^\circ C$. The time derivative of the curve, which is rate of subsidence, yields the fact that the maximum rate of subsidence for the powders employed occurs at about $930^\circ C$. It is apparent from these curves that temperatures above $1100^\circ C$ yield diminishing returns. The importance of temperatures higher than $1100^\circ C$ are relative to the need for high density bodies approaching 95%.

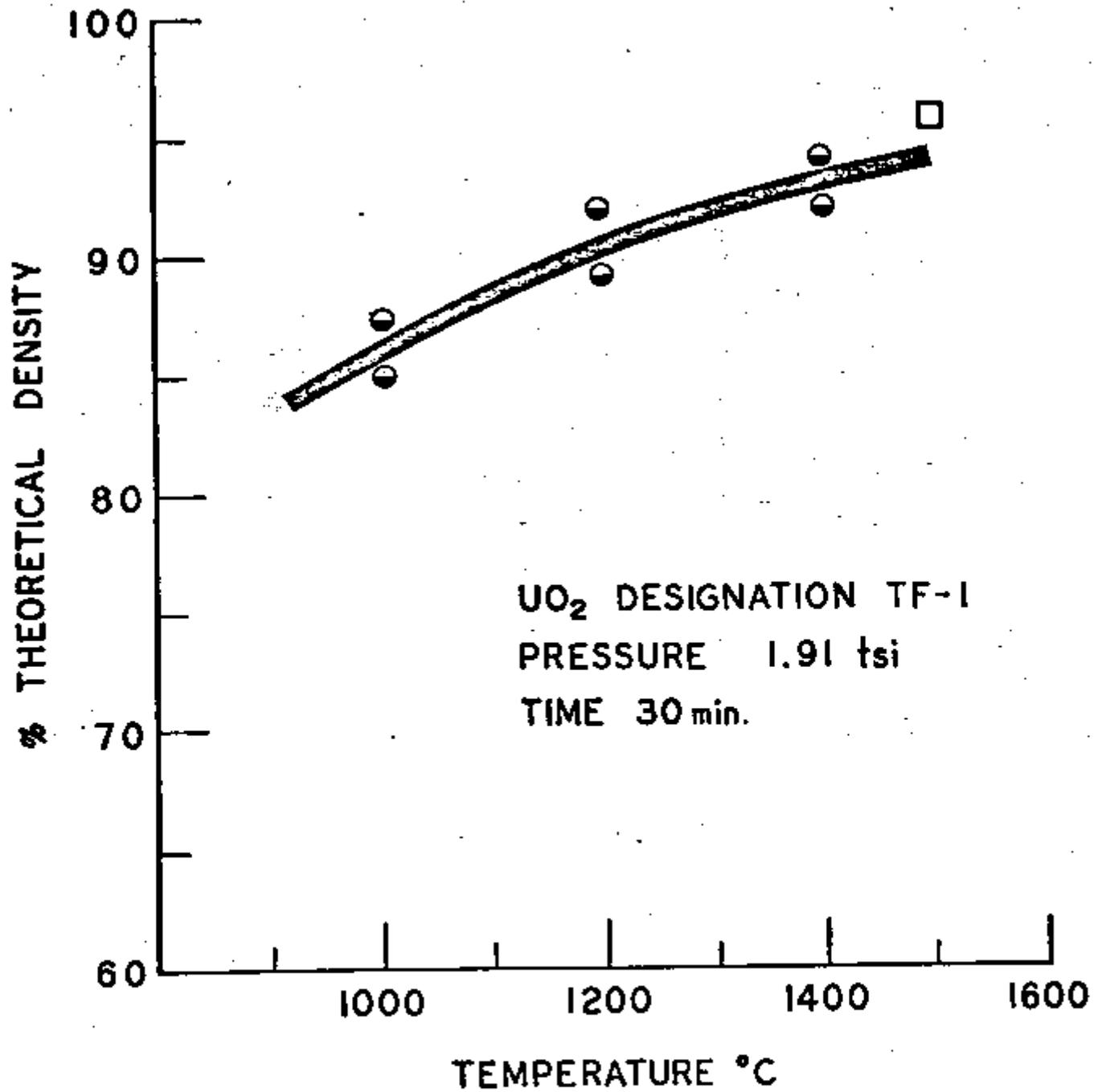


Figure 6. Density Versus Temperature for Hot Pressed UO₂-15w/o PuO₂.

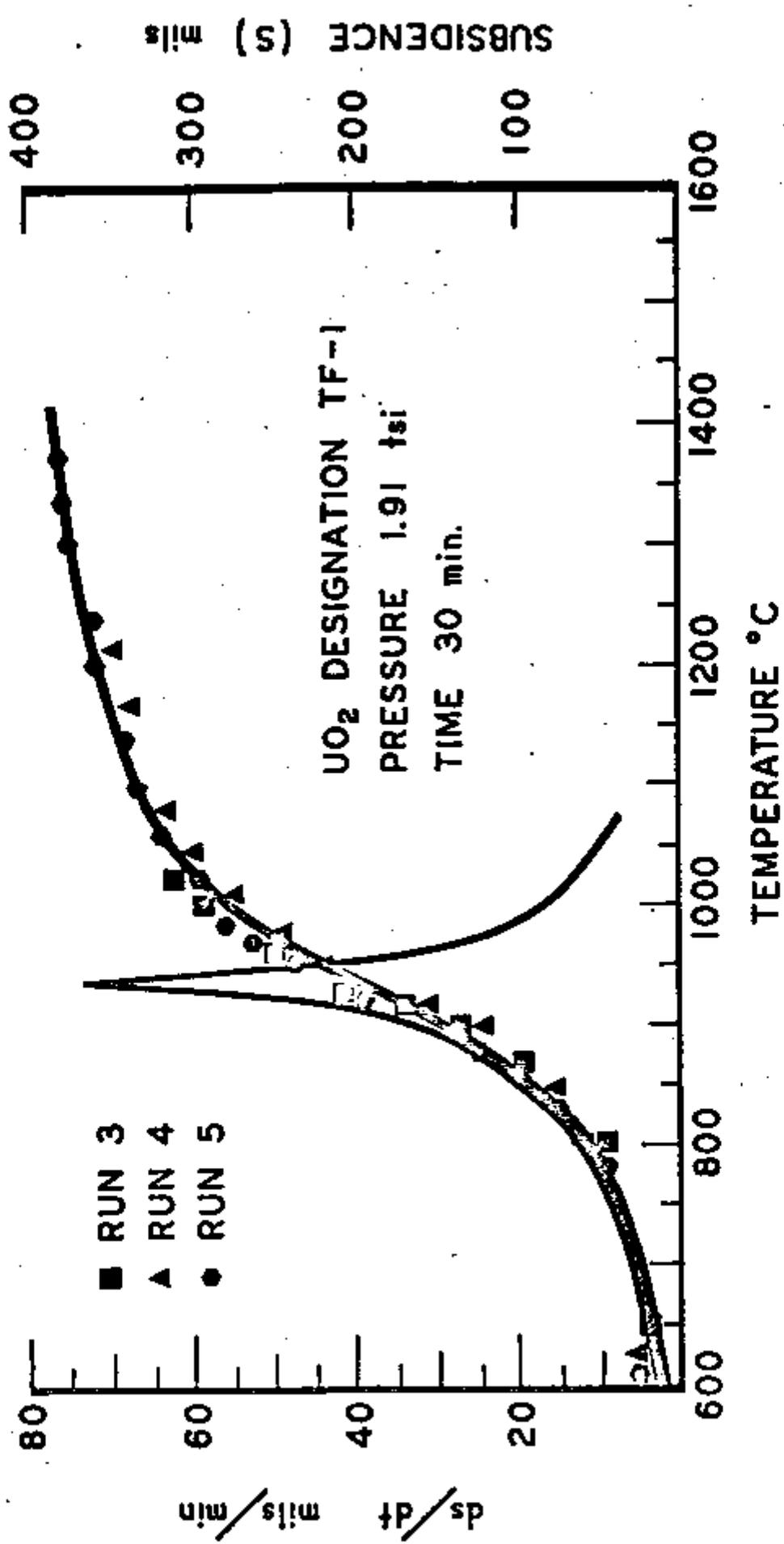


Figure 7. Subsidence Versus Temperature for Hot Pressed UO_2 - 15w/o PuO_2

Chemical analyses of samples from typical hot pressed plates are shown in Table 7. The effect of hot pressing upon the chemistry of the material is a change in stoichiometry and an increase in the carbon content. The change in stoichiometry is manifest as a reduction in the oxygen-to-metal ratio for hyper-stoichiometric material subjected to hot pressing at 1000 to 1400°C.

No attempt was made to distinguish between the effects of thermal decomposition and carbo-thermic reduction. The average carbon pickup in the hot pressed plates was 260 ppm. Although one would expect carburization to be influenced by temperature and time, no such trends were apparent.

B. Hot Pressing Equipment

1. UO₂ + X - ThO₂ Compositions

Most of the hot pressed UO_{2+X} - ThO₂ composition experiments utilized the apparatus shown in Figure 8. A slightly modified version of the same assembly, used for UO₂, is given in Figure 9.

A 25 KVA, 10 kilocycles induction heating unit was arranged to work in conjunction with a 20-ton hydraulic press.

Pressure and power were controlled manually. Temperature measurements were made with a disappearing-filament pyrometer sighted on a recessed hole on the top of the die. Calibration runs against a platinum/platinum-13% rhodium thermocouple inserted in the die, with the junction near the center of the compact, gave readings within $\pm 10^{\circ}\text{C}$ of those obtained optically.

TABLE 7

CHEMICAL ANALYSES FROM PLATES HOT PRESSED IN ALJ GRAPHITE DIES

Run No.	UO ₂ Code	Temp °C	Time Min.	Pressure tsf	U w/o	Pu w/o	U:Pu	O w/o	$\frac{U+Pu}{O}$ Molar	U+Pu+O	C ppm
3	TF-1	1000	30	1.98	74.8	12.93	5.77:1	12.00	2.04	99.7	460
4	TF-1	1200	30	1.98	74.6	12.84	5.80:1	11.90	2.02	99.3	460
5	TF-1	1400	30	1.98	74.5	12.75	5.85:1	12.26	2.09	99.6	580
6	TF-1	1200	30	1.28	74.9	12.87	5.83:1	12.20	2.07	100.0	
8	TF-4	1200	30	1.28	74.6	12.66	5.89:1	12.15	2.07	99.4	206
9	TF-4	1200	5	1.28	74.1	13.38	5.54:1	12.10	2.06	99.6	148
					Avg 74.6	12.9	5.78:1	12.1	2.06	99.6	370

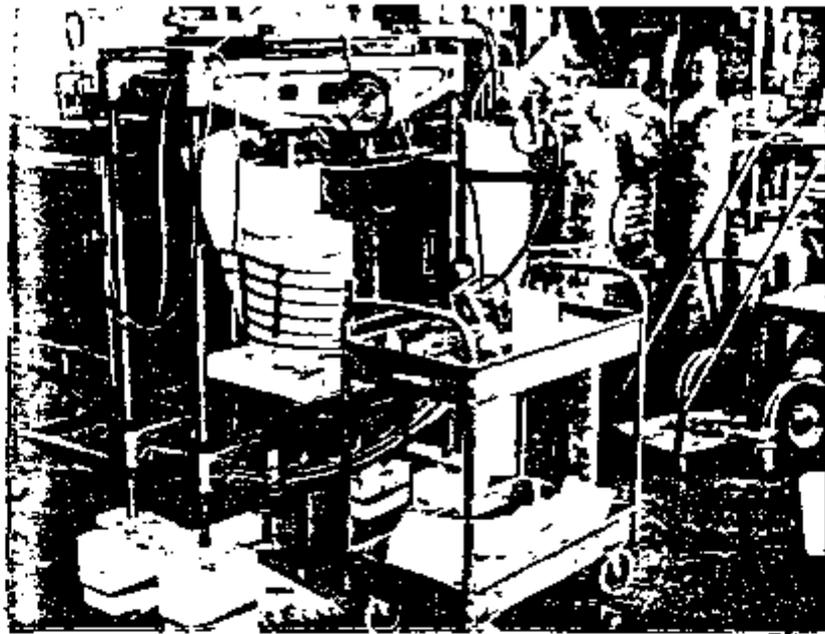


Figure 8. Induction Heated Hot Pressing Assembly Used with $UO_{2+x}-ThO_2$ Compositions.

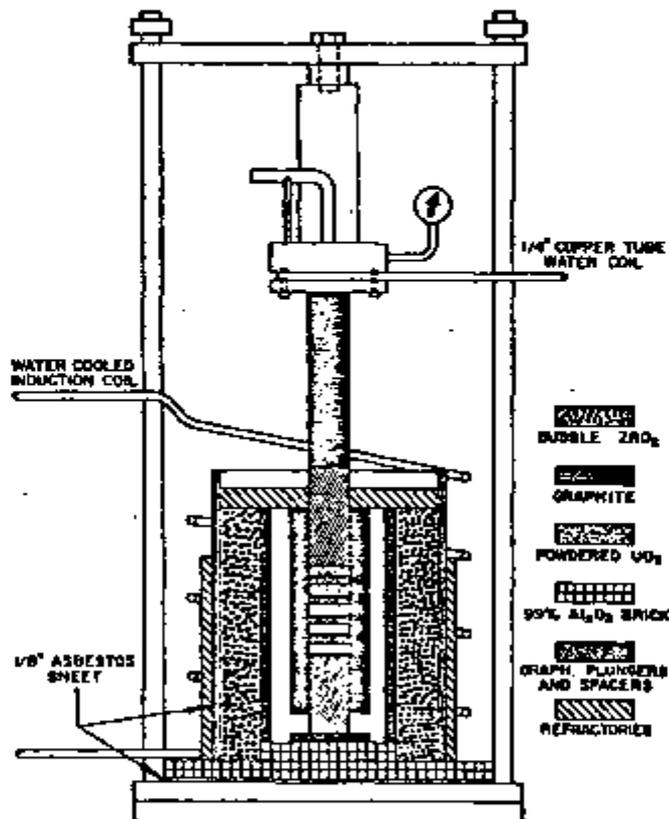


Figure 9. Cross Section of Apparatus Employed for UO_2 Hot Pressing.

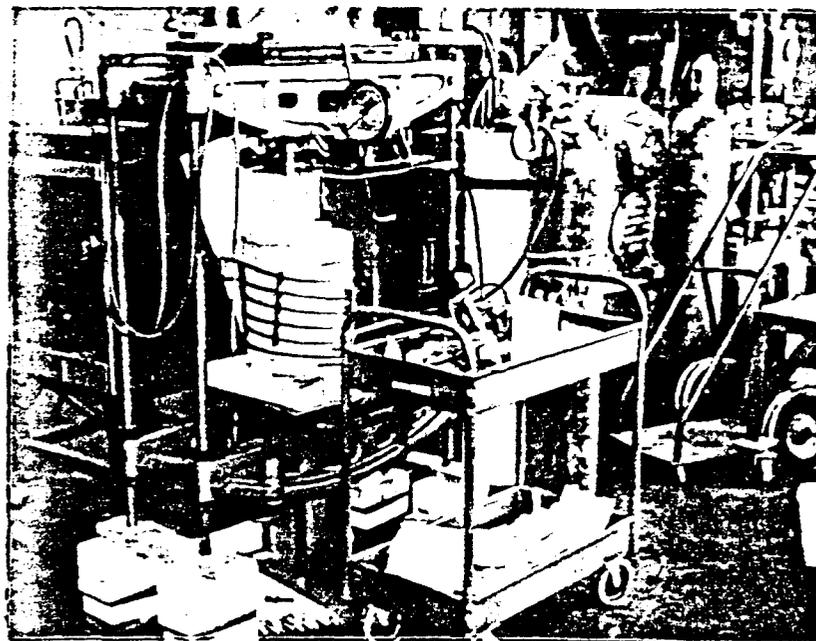


Figure 8. Induction Heated Hot Pressing Assembly Used with $UO_{2+X}-ThO_2$ Compositions.

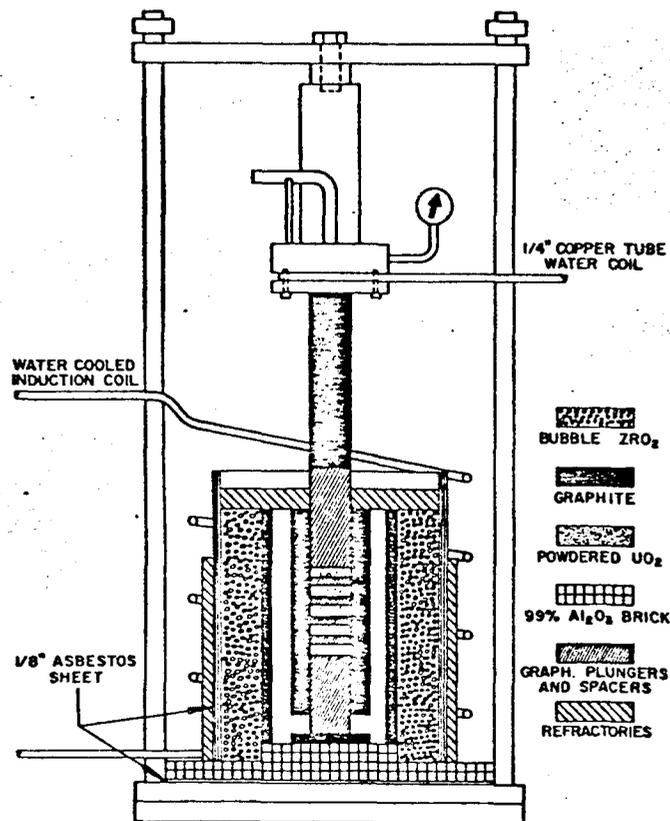


Figure 9. Cross Section of Apparatus Employed for UO_2 Hot Pressing.

The dies, approximately 5" diameter and 5" high in external dimension, were machined with square or circular cavity cross sections. The grade of graphite normally used was ATJ (Ref. 10); the softer, coarser grained and not so strong CS grade (Ref. 10) was also employed in a few experiments.

In Figure 9 it can be seen that the induced high-frequency field is restricted to the graphite susceptor; therefore, the die assembly is actually heated by radiation. The heating would be much faster if induction coupling was directly in the die body. Considering this fact, the author designed and supervised the construction of the induction-heated hot pressing apparatus shown in Figure 10. The 5" diameter graphite die is located very near the induction coils, inside a quartz vacuum chamber. Consequently, it can be heated much faster than in the assembly mentioned previously.

The single-action presses depicted in Figures 8 and 9 would require complicated floating die sets to get uniform compression from above and below. When floating dies were used with single-action presses for multispecimen pressure sintering, the compacts on the top of the stack had higher density. The variation reached 1.27% of theoretical density, for five specimens formed simultaneously at 1625°C. For this reason, the press shown in figure 10 was built to act in two opposite directions, with oleodynamically operated (Vickers system) water-cooled stainless steel double-action plungers. Of course, presses of this type lose some of the compactness of construction which has marked many of the most recent hydraulic-press creations. Presses applying high

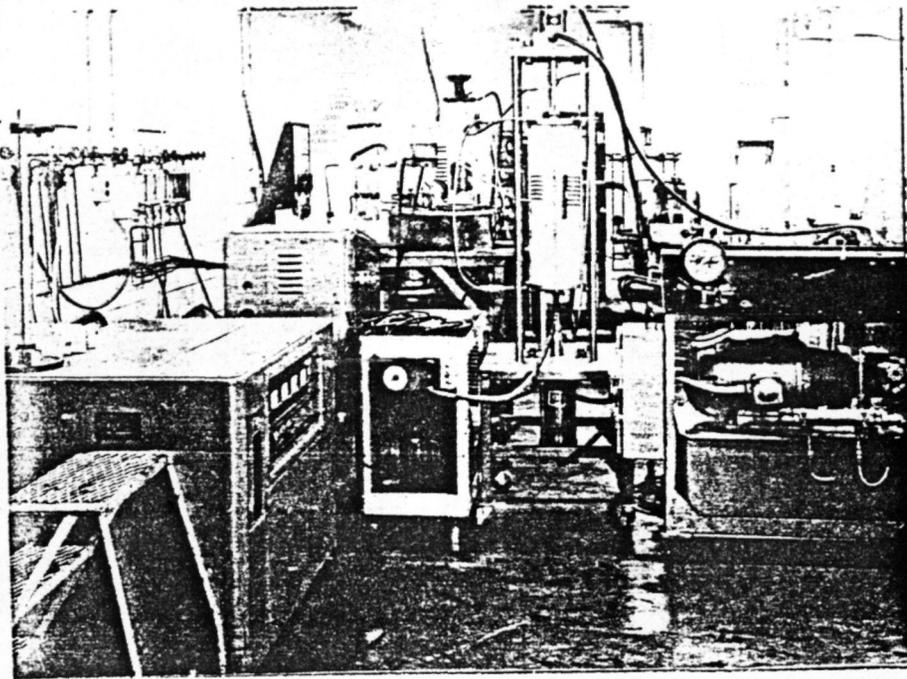


Figure 10. Hot Pressing Apparatus Using Double-Action Press and Vacuum Furnace, Induction Heated.

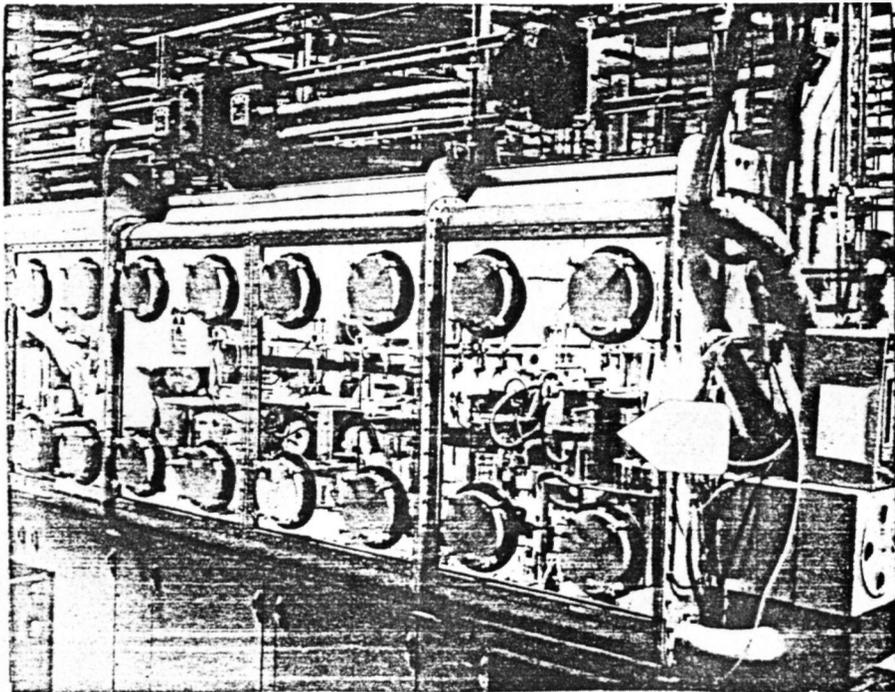


Figure 11. Platinum-Rhodium Resistance Furnace (indicated by arrow) Utilized for Hot Pressing Studies of $\text{UO}_{2+X}\text{-ThO}_2\text{-PuO}_2$ Compositions.

pressures from two opposite directions may be extremely tall, causing difficulties of installation if they are intended to work inside normal sized glove-boxes. The press might be installed in a horizontal position.

The double-action press and induction heated furnace operated quite well at temperatures in the 1000 - 1250 °C range, with a maximum load of 10 tons. In such conditions, the lowest pressure attained in the vacuum chamber was 0.2 mm Hg. The quartz chamber could operate also with inert or reducing gases. This hot pressing apparatus, designed primarily for the study of UO_{2+X} reactive pressure sintering, was completed only a short time before the termination of this research. Consequently, only preliminary experiments were developed with it.

According to Goetzel (Ref. 21), the main advantage of induction heating lies in quicker heating and cooling of the die, eliminating the necessity for ejecting the hot-pressed compact. In certain types of experimental work this is especially advantageous, since the danger of oxidation during cooling, after ejection from the hot die, must be avoided. In an inert atmosphere glove box this problem would be less acute. However, the same author states that "resistance heating is, perhaps, the most interesting method." In this case, heat is generated either by passing a current of high amperage through the powder or preformed compact, or by passing the current through the die.

Resistance heating seems also to be particularly adequate, when continuous processes are considered.

In his continuous hot pressing apparatus, Oudemans (Ref. 6) used an alumina die, heated to the required temperature by a resistance wire (platinum-rhodium) wound in a helical groove ground in the outer surface of the die wall.

For this investigation of UO_{2+x} reactive hot pressing, it was decided to utilize a resistance furnace. This would facilitate the future possibility of developing a continuous hot pressing system. Figure 12 shows the reactive hot pressing apparatus.

The pressure was applied by a 50 ton Wabash* hydraulic press. This press could maintain a pressure of ± 200 psi of the desired value throughout the entire operation. It was calibrated against a known hydraulic pressure.

The dies were the same used with the induction heated furnace previously described.

A schematic of the assembly is shown in Figure 13.

For the temperature control two Pt - Pt 10% Rh thermocouples were utilized. One was inserted in a 3/8 inch diameter hole drilled in the die wall, parallel to the die axis; it was positioned at the same height in the mold as the sample, and was connected to a Honeywell** Elektronik strip chart controller. The other thermocouple, used to prevent any temperature excursions, was near the resistance wire, in the

*Wabash Metal Products Co., Wabash, Ind.

**Minneapolis-Honeywell, Philadelphia, Pa.

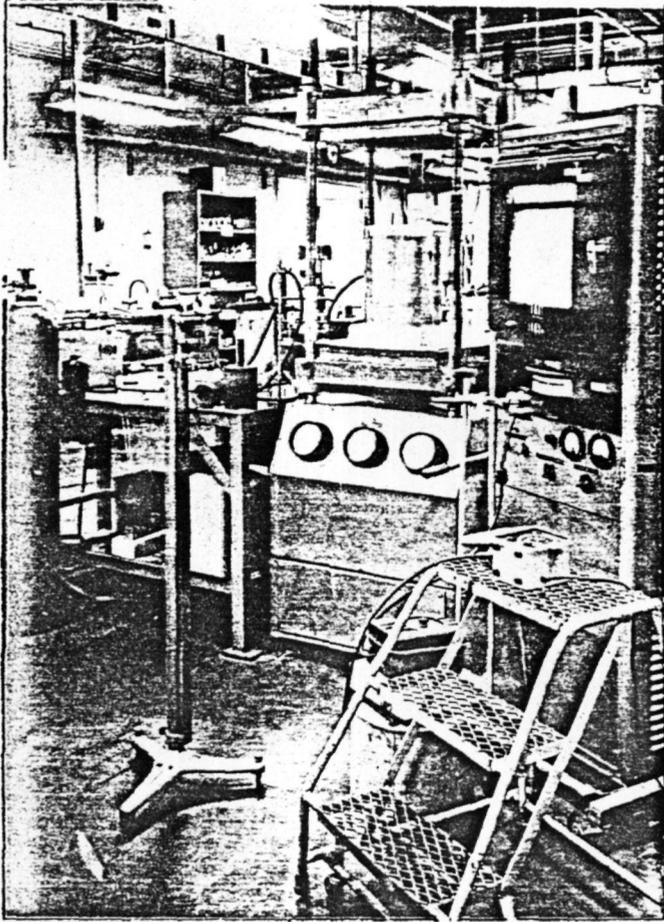


Figure 12. Reactive Hot Pressing Apparatus.

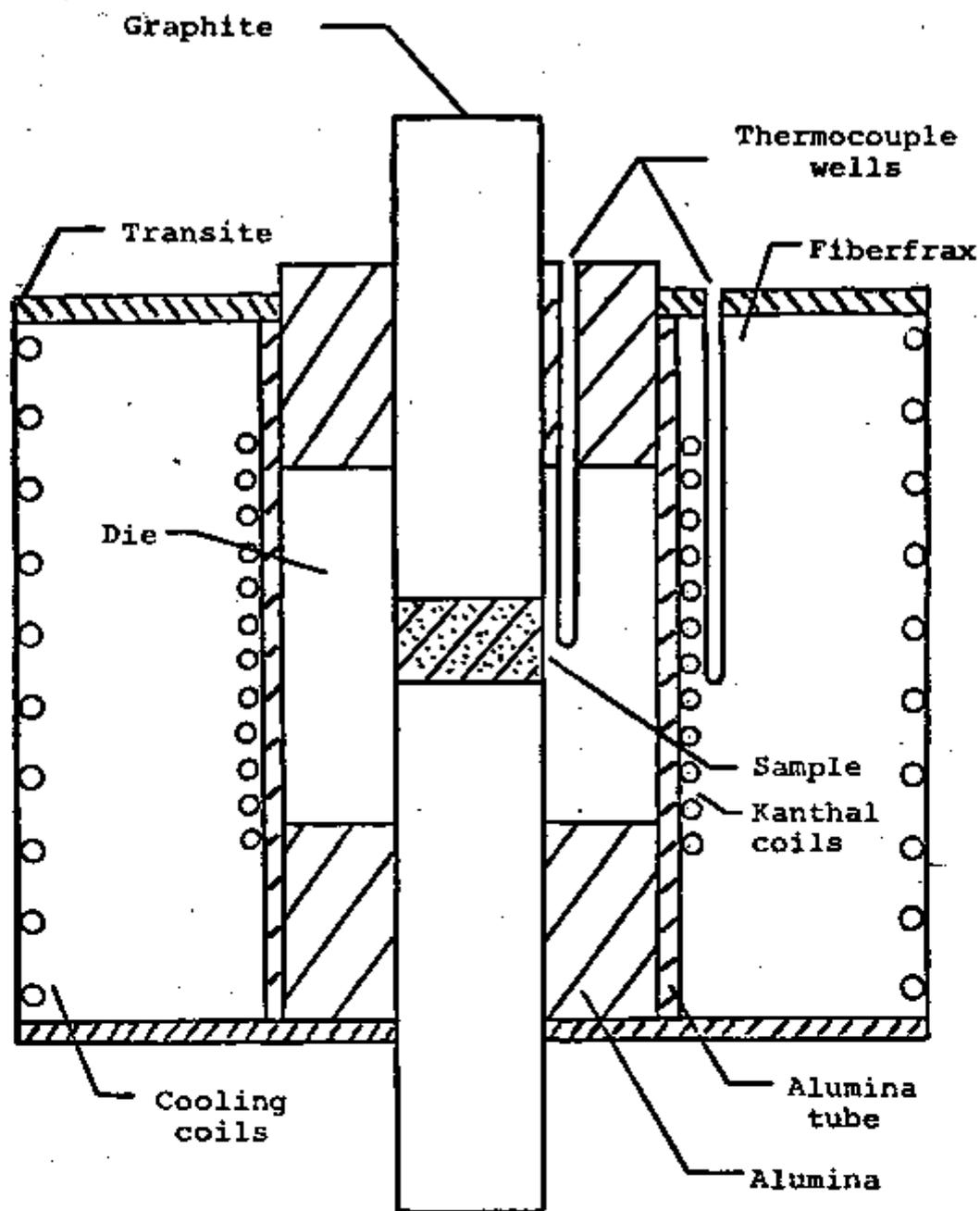


Figure 13. Cross Section of the Hot Press Assembly Used for Reactive Pressure Sintering.

position indicated in Figure 13. Temperature variations during the operation were estimated to be smaller than 5°C . In the range $700\text{--}1150^{\circ}\text{C}$, a thermocouple embedded in a UO_2 sample indicated differences of temperatures smaller than 15°C , in relation to the die wall temperature.

Some UO_2 and ThO_2 hot pressing experiments were developed using equipment described in the next section, designed for plutonia work. This was necessary to standardize the conditions of operation to compare the hot pressing characteristics of UO_{2+X} , ThO_2 , PuO_2 and $\text{UO}_{2+X} - \text{ThO}_2 - \text{PuO}_2$ compositions.

2. $\text{UO}_{2+X} - \text{ThO}_2$ Compositions Containing PuO_2

Since the maximum permissible limit of plutonium in air is only $3.2 \times 10^{-11} \text{ g/m}^3$ (Ref. 52), complete physical separation from such material is essential for the protection of operators or personnel working in the vicinities. Plutonium compounds have been commonly handled in windowed enclosures by means of arm-length neoprene gloves with gauntlets attached to flanges of glove ports through the walls of the enclosures. These housings are currently referred to as glove boxes, when they are used for process enclosure only.

All the hot pressing operations of $\text{UO}_{2+X} - \text{ThO}_2$ compositions containing PuO_2 were developed at the Argonne National Laboratory Plutonium Facilities. Figure 11 shows the Argonne Building 350 glove box PF-6 where the first pressure sintering experiments took place. PF-6 operates with negative pressure nitrogen atmosphere.

Two hot pressing assemblies had to be designed by the author for plutonium glove box operation. The drawings were based on the experience obtained with the $UO_{2+X} - ThO_2$ compositions hot pressing apparatus (Figures 8, 9, 12) then in successful operation for about six months.

The possibility of developing a continuous hot pressing system later was again one of the reasons why resistance furnaces were chosen for the pressure sintering operations. Necessary water cooling of the furnace outer shell to avoid excessive temperature rise of the glove boxes nitrogen and helium atmospheres, was much easier with resistance heating. Induction heated furnaces were also considered for the job, but metallic water cooled jackets would be larger than in the previous case, to avoid the effect of induced currents.

The construction, testing, installation and preliminary operations of those apparatuses took a considerable length of time. The installation was especially delicate since it was essential to utilize gloves during the entire job. It was estimated that the assembly of hot pressing equipment inside a glove box, already in operation, requires at least triple the time of a similar job performed outside the enclosure. It became apparent that a much more efficient procedure would be to include the protection facility in the original design of the entire pressure sintering system.

Figure 14 shows the hot pressing apparatus utilized for the fabrication of the actinide oxide compositions containing plutonia.

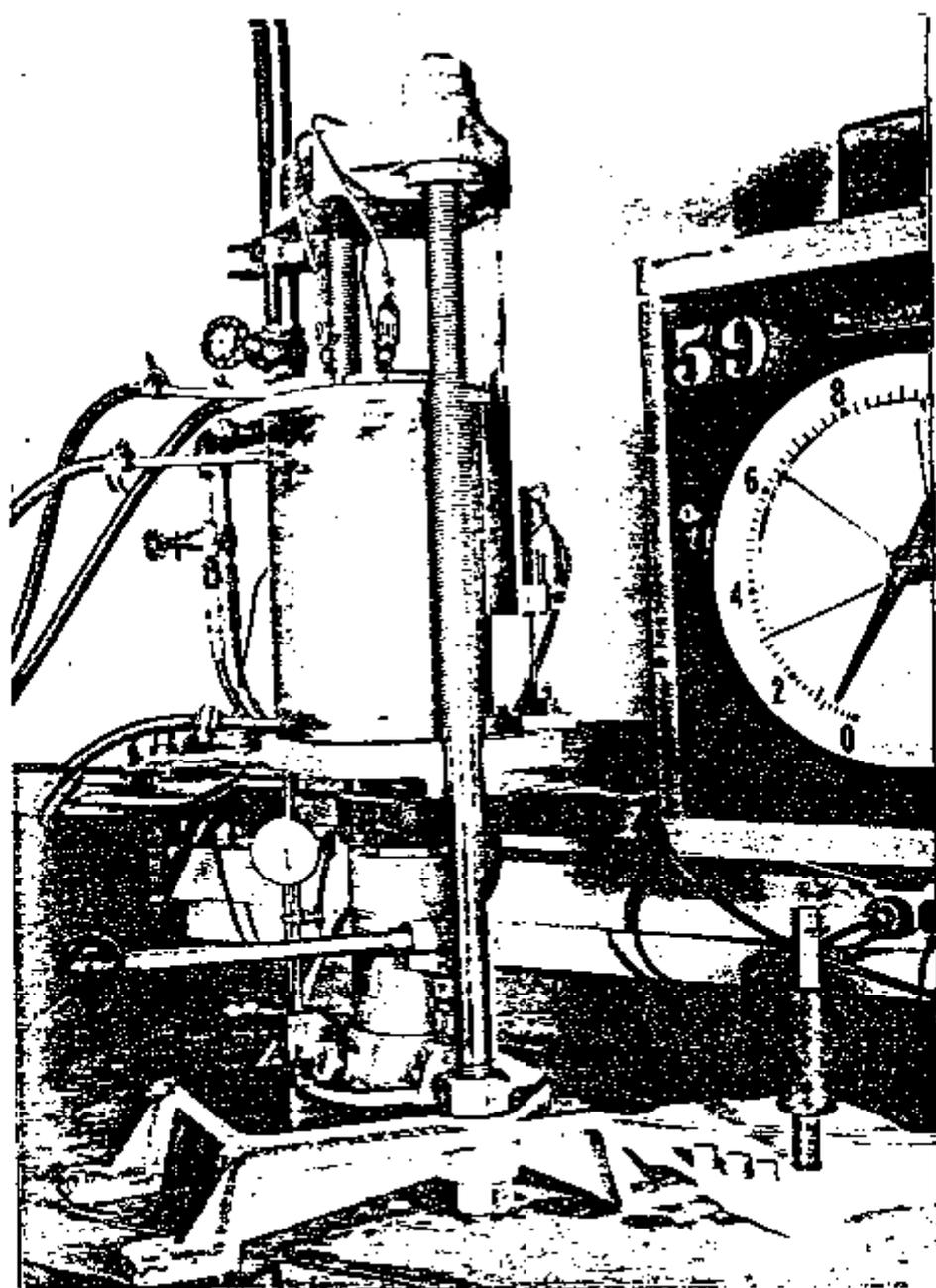


Figure 14. Apparatus used for the Study of $\text{UO}_{2+X} - \text{ThO}_2 - \text{PuO}_2$ Compositions Hot Pressing.

Figure 15 presents the large platinum-rhodium resistance furnace employed in the production of 2" x 2" x 1/4" UO₂ - 0.2 w/o PuO₂ plates.

Both furnaces shown in Figures 14 and 15 used the same basic design presented in Figure 13, with major modifications only in the cooling system and type of resistance wire.

The smaller furnace (Figures 11 and 14) had a stainless steel water cooled jacket, while the other unit (Figure 15) employed a system of cooling coils. Both used platinum-10 w/o rhodium wire wound in the outer surface of alumina tubes 2" and 5" diameter respectively. The temperature control and its calibration were similar to those adopted in the case of the reactive hot pressing furnace described in the foregoing section (Figure 13).

A Carver* laboratory press was used for the experiments developed with the small furnace (Figure 14). The accuracy of this press was estimated to be \pm 50 psi. Pressure calibration was done against a calibrated strain gauge.

In some experiments, a pressure transducer capable of measuring up to 3500 psi, was installed on the press hydraulic line, the output recorded on a dual channel recorder. A low voltage differential transformer (LVDT) measured the displacement of the material under compression. The output of the LVDT was used to drive a second channel on the two channel recorder. In the preliminary testing of this hot pressing

*Fred S. Carver, Inc., Summit, N. J.

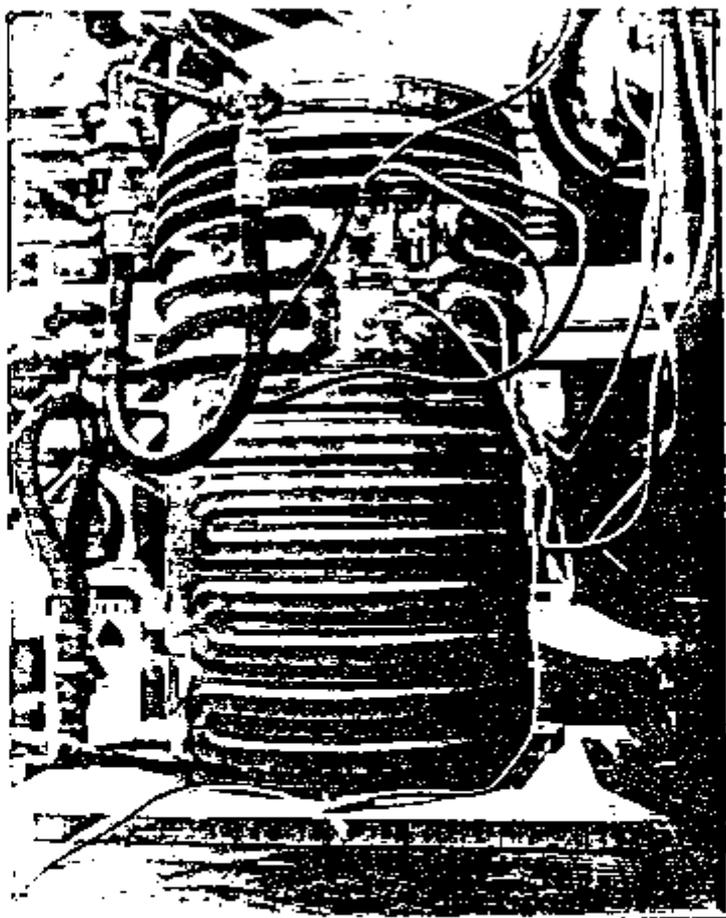


Figure 15. Hot Pressing Furnace Used for the Production of 2" x 2" x $\frac{1}{4}$ "
 $UO_2 - PuO_2$ Plates.

apparatus, it was shown that a 2" subsidence could be measured with an absolute accuracy of ± 0.01 inch. This was accomplished by a combination of two LVDT's, one having a range of 0 - 2.0", the other having a range of 0 - 0.1" with an accuracy of one microinch. The subsidence was recorded with the first LVDT, until the deformation was within approximately 0.05" of the required deformation. Then the second LVDT was used to indicate subsidence. By using this precise measurement technique, density could be controlled accurately.

Most of this equipment was built or modified at the Argonne National Laboratory electronic shops.

In most of the hot pressing runs developed with the Carver press, the subsidence was measured with a Starett dial indicator, accurate to ± 0.001 ". It was fixed to the press base and measured displacements of the press platen and hence subsidence. Calculations of the corrections to be introduced in the measured subsidence values to determine sample shrinkage, were made by considering thermal expansion and deformation of the system under variable load.

The large hot pressing furnace shown in Figure 15 was operated with a 50 ton single-action hydraulic press, substantially modified at the Argonne National Laboratory mechanical shops and assembled in the ANL Plutonium Facilities building 350 PF-5 glove box. Since PF-5 operates with helium atmosphere, special attention was given to the problem of cooling the furnace shell, in order to avoid excessive heating of the glove box. The much larger sized furnace and the higher

thermal conductivity of helium produced operational procedures different than the previously mentioned smaller pressure sintering system, installed in the nitrogen filled glove box PF-6.

In the 50 ton press the pressure was maintained manually and read from a Bourdon gauge, calibrated with a strain ring. Subsidences were measured with a Starett dial indicator, accurate to $\pm 0.001''$.

C. Materials Preparation

1. UO_{2+X}

U₃O₈ was prepared by calcining for 5 hours at 650°C a commercial ceramic grade nuclear purity depleted urania powder, from Kerr-McGee (TF-4, see page 29). UO_{2+X}, with X between 0.03 and 0.67 was prepared by partial reduction of U₃O₈ in hydrogen at 700 °C or by mixing the proper compositions of the powders obtained in the reduction operations. The mixtures were wet-milled 24 hours with ½" diameter alumina balls and benzene, in porcelain vessels rotating at 75 rpm.

UO₂ code TF-1 (page 29) was a powder obtained by successive oxidations and reductions of UO₂ produced at Argonne National Laboratory, with expected very good sintering characteristics. With a final oxidation treatment, the oxygen:uranium ratio in this powder was adjusted to 2.11, the same value of UO₂ code TF-4.

No binders were added to the uranium oxide powders.

For the UO₂ TF-1 and UO₂ TF-4 powders, a 325 mesh U. S. Standard sieve was employed to separate the finer fraction to be utilized in the hot pressing experiments.

2. ThO₂

Ceramic grade nuclear purity ThO₂ from Lindsay Corporation was utilized in the pressure sintering operations. Only the -325 mesh fraction was used, with no binder addition.

3. PuO₂

The plutonium oxide utilized was produced by reduction of oxalate at 750°C. This low temperature is adequate for the formation of small particle size plutonia powder. This material was not sieved.

4. UO_{2+X} - ThO₂ - PuO₂ Compositions

UO_{2+X} - 20 w/o ThO₂ compositions were produced by wet or dry milling for 24 hours, UO₂ code TF-4 with ThO₂, using ½" diameter alumina balls and porcelain vessels rotating at 75 rpm. Xylene was the liquid utilized in the wet milling operation. It was observed microscopically that dry milling promoted the formation of urania and/or thoria agglomerates as large as 500 microns; no agglomeration could be noted in wet milled powders.

Two methods were used for mixing UO_{2.11} - 15 w/o PuO₂. One of them, previously mentioned (page 31), utilized a "V" - blender operated at about 80 rpm for 2 minutes, on batches weighing 70 grams. The other employed a Spex* No. 8000 Mixer/Mill.

For mixing, a polystyrene vial was available with plexiglass balls. With this system, metallic contamination became impossible.

*Spex Industries, Inc., Metuchen, N. J.

100 ml of material could be handled in each vial. When grinding action was necessary, a tungsten carbide vial could be used with two tungsten carbide balls.

Due to the previously mentioned tendency of the UO_2 to agglomerate in dry mixing conditions, it was judged convenient to use the Spex not only as a mixer, but also as a grinder, to assure better homogeneity of the $UG_2 - PuO_2$ mixtures. Compositions prepared in this way had exceptionally high densities when hot pressed.

The mixture of ThO_2 and PuO_2 was made also using the "V" blender. This same device was employed again to prepare some of the $UO_2 - ThO_2$ compositions. In this way the mixing conditions were standardized and the $UO_2 - ThO_2$, $UO_2 - PuO_2$, $ThO_2 - PuO_2$ results could be compared.

The "V" blender is evidently of very low efficiency when compared with the Spex mixer. The "V" blender was used for some batches to relate mixing to final results.

Wet milling of $UO_2 - PuO_2$ mixtures with liquids such as water, xylene or benzene was not recommended, since the hydrogen and/or carbon present in their molecules are good nuclear moderators, creating special problems of criticality control.

D. Powders Surface Area Measurements

The surface areas of the UO_2 and ThO_2 powders utilized in the hot pressing experiments were measured by an air permeability method using a Fisher Sub Sieve Sizer.* This apparatus had a rated accuracy

* Fisher Scientific, Chicago, Ill.

of 5% in the particle size range of 0.2 to 50 microns. Various experiments developed by the author on -325 mesh depleted UO_2 indicated also a reproducibility of about 5%.

The surface areas of ThO_2 , UO_2 codes TF-1 and TF-4 powders were determined by a gas-adsorption technique. A Strohlein Area Meter* was used. This apparatus employs a greatly simplified method based on the time consuming and highly complex BET process. A single point evaluation was made, since experience had shown that surface areas obtained in this way were only about 10% below the values obtained with multiple measurements. The reproducibility of the surface area results were within $\pm 3\%$.

According to the discussion presented on page 15, the Fisher method gives a value corresponding to the external surface S_p of the particle, while the Strohlein method determines its total surface S_G .

The surface area values S_p and S_G were converted to particle size D_p and D_G (page 15).

Table 8 gives the particle sizes of the UO_{2+X} and ThO_2 powders utilized in this investigation. In this table F is the porosity of the packed powder sample in the Fisher method determination.

* Strohlein & Co., Dusseldorf, Germany.

TABLE 8
PARTICLE SIZES AND ROUGHNESS OF UO_{2+x} AND ThO_2 POWDERS

Material	Particle size (micron)			Roughness D_p/D_G
	Method		D_G	
	Fisher D_p	P		
UO_2 code TF-1	1.20	0.79	0.45	2.7
UO_2 code TF-4	1.04	0.76	0.18	5.9
U_3O_8	0.71	0.82	0.22	3.2
$UO_{2.33}$	0.75	0.82	0.23	3.3
$UO_{2.16}$	0.81	0.80	0.16	5.0
ThO_2	1.95	0.77	1.15	1.7

From Table 8 it is seen that the ThO_2 particle size is considerably larger than the values corresponding to the other oxides.

Microscopic observation showed that the ThO_2 powder contained large agglomerates. This suggests the ThO_2 belonged to the category B of Murray's classification (page 17).

No equipment was available at the Argonne National Laboratory Plutonium Facilities for surface area determination of the plutonia powders utilized in this investigation. However, the Argonne National

Laboratory Special Materials Section indicated the plutonia powder particle size to be smaller than one micron.

E. Hot Pressing Experiments

1. UO_{2+X} , $X < 0.67$

As an extension of the work described in reference 6, UO_{2+X} multispecimen hot pressing was developed using W, Mo, Ta, "glassy carbon" and Poco graphite pieces to separate the specimens inside the die. Of these materials, only "glassy carbon" and Poco graphite did not react with the UO_{2+X} samples. ATJ and CS graphite, employed in previous work (Ref. 3) reacted strongly, principally with UO_{2+X} hyperstoichiometric powders; such interaction could be decreased substantially when filter paper liners were put between the graphite separators and the urania powder. From these experiments it was concluded that the utilization of "glassy carbon" or Poco graphite die inserts and separators would decrease the sampled carbon pickup significantly.

Due to the long delivery time of die inserts and separators considered as the most adequate to avoid carbon contamination, it was decided to use paper liners between the ATJ graphite separators, since the life of those pieces was definitely increased in this manner.

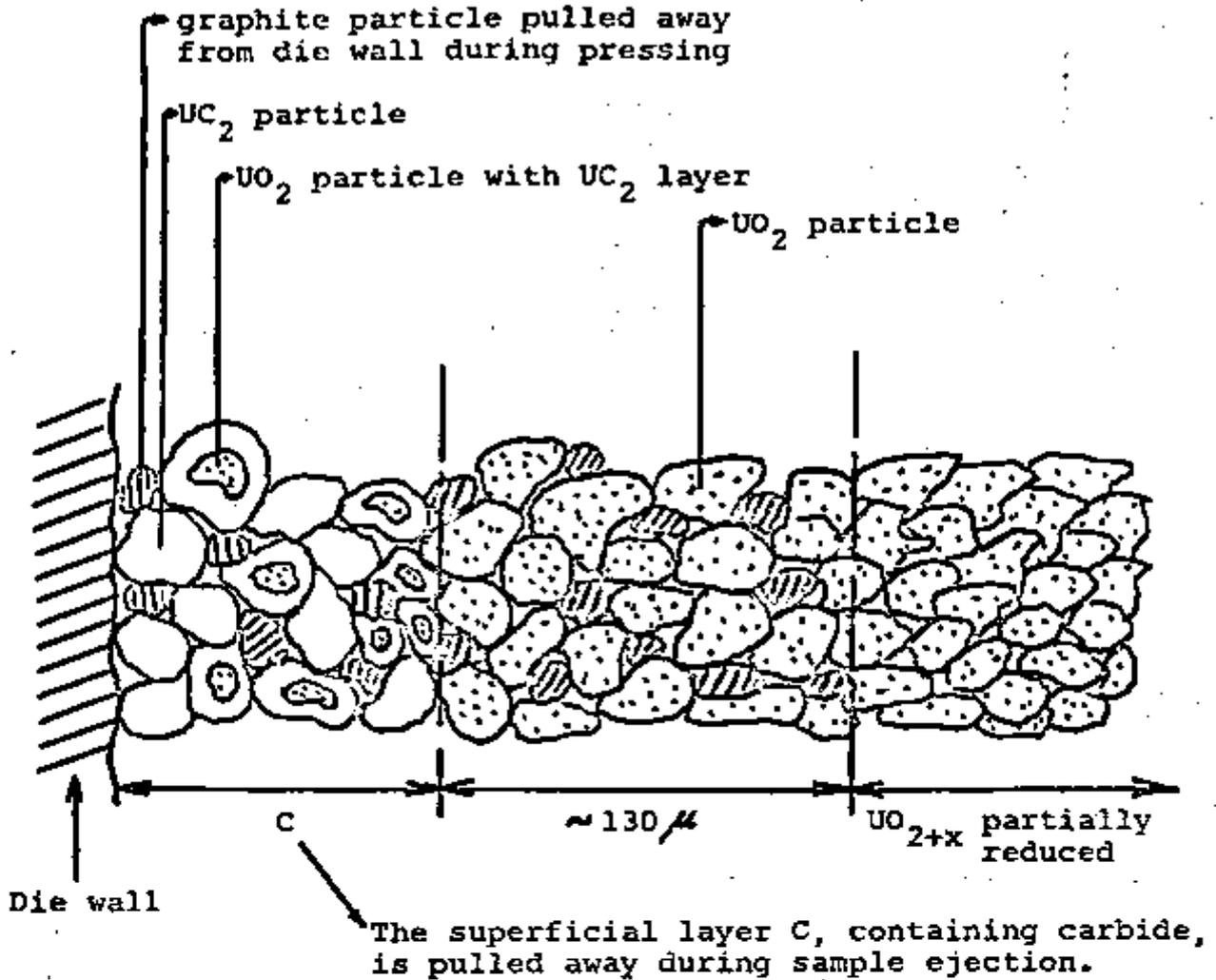
In this phase of the investigation there were strong indications that much carbon was being taken from the die wall by the abrasive uranium oxides, during the course of the pressing. It was also apparent that this effect increased with the die life and consequently was related

to the die wear. This explains why the carbon pickup did not relate simply to the hot pressing temperature, as referred in reference 3.

The formation of a superficial carbon layer on the hot pressed samples is consistent with the observations of Murray et al. (Ref. 53), that indicated the presence of a graphite skin in calcia, alumina and zirconia hot pressed bodies; for these oxides such skin could be removed slowly, by oxidation.

Chemical reaction between graphite and UO_2 was also expected for hot pressing operations developed over $1400^\circ C$. The kinetics for this reaction was studied by Lindemer et al. (Ref. 54). It can be shown from their work (Appendix B) that an appreciable layer of carbide (UC_2) can be formed between graphite powder and UO_2 , when such system is maintained at $1615^\circ C$ for one hour (this temperature and time correspond to the conditions of many of the hot pressing runs developed). Figure 16 gives schematically some aspects of the graphite die wall and UO_2 interaction.

The procedure for loading the die was as follows. The bottom plunger was inserted into the mold leaving a cavity depth of one inch, the material being charged into the cavity over a paper liner. A paper liner and a graphite spacer were inserted after the powder was leveled. Pressure of 300 psi was applied to force the material down to a level so more powder could be charged. This procedure was repeated until sufficient material was available for the desired number of specimens. A final pressure of 450 psi was applied to the assembly before placing it in the hot-press furnace. In some preliminary



Observation:- the mechanism of UO_2 sample - graphite die wall interaction can explain why uranium carbide is not found in the hot pressed samples, either using ceramographic or X-ray techniques.

Figure 16. Interaction Between Graphite Die Wall and UO_2 Sample.

experiments the initial pressure in the furnace was slight, but it was increased with time until the maximum temperature was reached. However, in most hot pressing operations the pressure was held constant during all the operation.

The rate of heating was standardized by setting the transformer which controlled the induction generator to give the same energy input each time. At this setting, 1600°C was reached in about 90 minutes. At a temperature 50°C before that required, the voltage was lowered to the appropriate value and the timing for the pressing operation started. It was found that the die temperature increased by about 50°C by the time the transformer had been reset. In this manner it was possible to control the temperature within $\pm 20^{\circ}\text{C}$ at 1600°C .

Argon was used to blanket the die assembly in almost all runs. Without protective atmosphere the die life was reduced to 2 or 3 hot pressing operations.

2. U_3O_8

The same procedure for die filling adopted for UO_{2+x} , X smaller than 0.67, was followed for U_3O_8 . Practically all the reactive hot pressing experiments were developed using the apparatus shown in Figures 10 and 13.

3. ThO_2

Only single specimen hot pressings were investigated, utilizing the system depicted in Figure 14.

4. PuO₂

The hot pressing operations had the same characteristics as those mentioned for ThO₂, in the foregoing section.

5. UO_{2+X} - ThO₂

The same procedure utilized for UO_{2+X}, X smaller than 0.67, was employed in this case. Some runs were also developed in the apparatus shown in Figure 14.

6. UO_{2+X} - PuO₂

The furnace used for this experiment, inside the glove box PF-6 of Argonne National Laboratory Plutonium Facilities, is depicted in Figure 11.

7. PuO₂ - ThO₂

The hot pressing procedure described for UO_{2+X} - PuO₂ was also employed in this case.

F. Density Measurements

Two methods were utilized for measurements of density. For all specimens, a geometrical determination was carried out using a micrometer. A displacement technique, in which the samples were first weighed on an analytical balance and then weighed suspended in a liquid, gave an accuracy of $\pm 0.5\%$ relative density; the liquid employed was bromobenzene.

G. X-ray Analysis

X-ray diffraction techniques were used as one of the means of identification of the eventual presence of UC₂ in the hot pressed samples.

The Straumanis technique was employed to take powder photographs of the -325 mesh crushed samples, using a General Electric X-ray unit and nickel-filtered copper radiation. The times for film exposure varied between 7 and 10 hours at 15 ma and 35 KV settings.

H. Preparation of Samples for Optical and Electron Microscopy

For optical microscopy the bakelite mounted samples were rough ground on wet 400 and 600 grit silicon carbide papers, using a Buehler* Automet; the polishing was developed in three phases with the Automet and diamond paste (14, 6, 1 and $\frac{1}{2}$ micron, respectively), with a final step using 0.1μ γ alumina. The etchant was a solution of H_2SO_4 in H_2O_2 .

For scanning electron microscopy, fractured samples were mounted in aluminum supports and coated in vacuum with a gold-50 v/o palladium alloy.

* Buehler Ltd., Evanston, Ill.

IV. RESULTS AND DISCUSSION

A. Temperature, Time and Pressure Dependence in Hot Pressing

Figure 6 (page 34), 7 (page 35) and 17 (page 63) show typical temperature-time-density (or subsidence) curves for the materials investigated in this paper.

In relation to the influence of pressure, the data obtained for $UO_{2.11} - 15 \text{ w/o } PuO_2$ hot pressed at $1200^\circ C$ for 30 minutes is given in the following Table 9.

TABLE 9
DENSITY VERSUS PRESSURE FOR $UO_{2.11} - 15 \text{ w/o } PuO_2$
HOT PRESSED AT $1200^\circ C$ FOR 30 MINUTES

Pressure (psi)	Density (per cent theoretical)
1280	84.0
2560	87.0
3820	90.5
5100	94.0

Comparison with data presented in figures 1, 2, 3 and 4 reveal that the results obtained in this work are consistent with those reported by other investigators.

The general trends presented by the curves corresponding to PuO_2 , $PuO_2 - ThO_2$ and $UO_2 - PuO_2$, suggest that the same mechanism responsible for the hot pressing densification of UO_2 , operates also in the case of those materials.

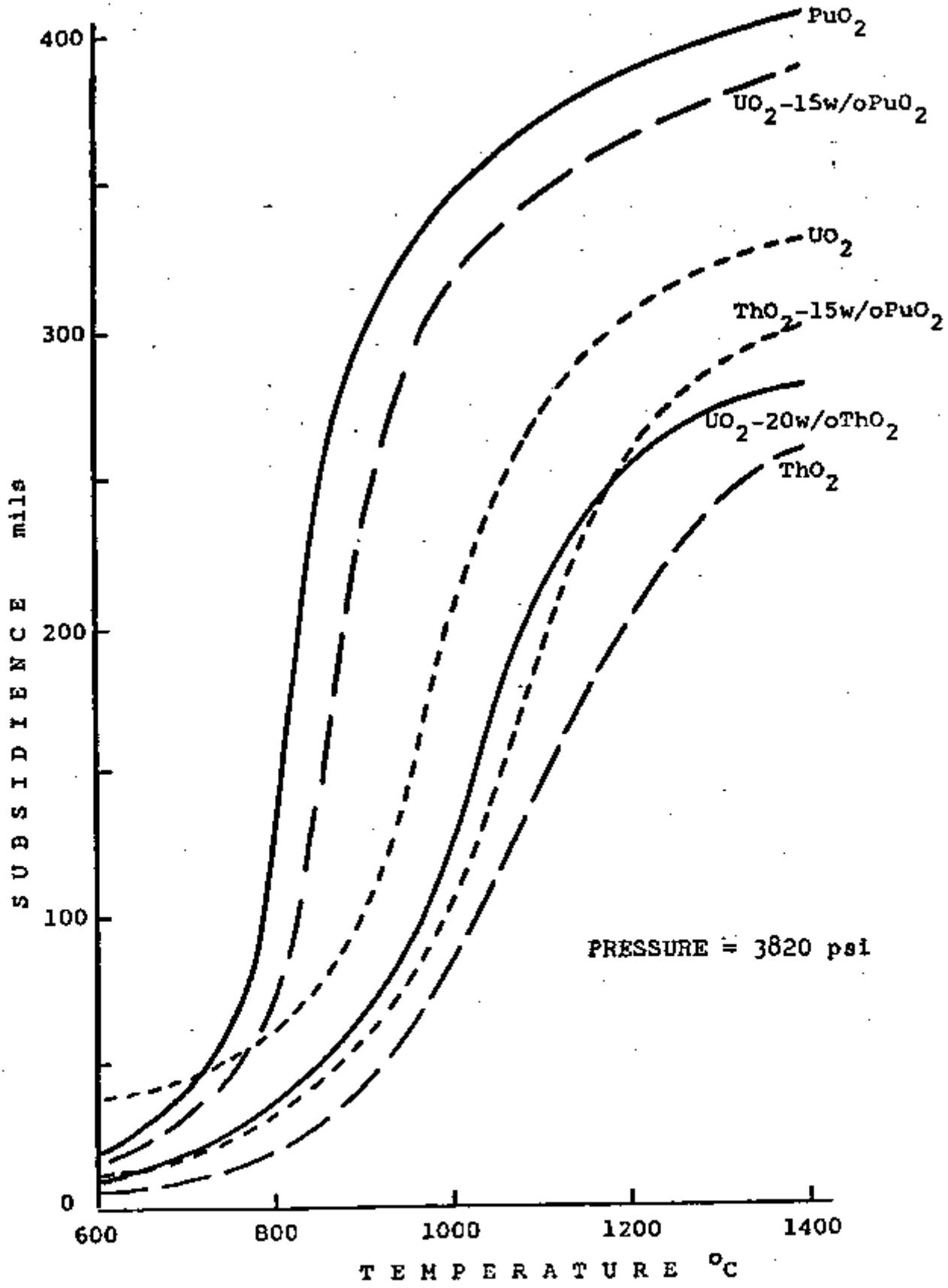


Figure 17. Densification of Actinide Oxides Compositions During Hot Pressing.

B. Effect of Particle Size

The results of experiments developed with UO_2 code TF-1 and UO_2 code TF-4, confirm the observation of Murray et al. (Ref. 23) that particle size has much influence on hot pressed bodies final densities.

The densities for TF-1 and TF-4, pressured sintered at $1400^{\circ}C$ and 2560 psi for 30 minutes were respectively 85.9 and 87.6% of the theoretical value (the TF-1 and TF-4 powders particle sizes are given in table 8). Compositions of $UO_2 - 15$ w/o PuO_2 utilizing TF-1 and TF-4, hot pressed at $1200^{\circ}C$ and 2560 psi for 30 minutes, reached densities of 84.9% and 87.7%, demonstrating again that the coarser powder densifies with more difficulty.

C. Microstructure Analysis

Some results of the optical microscopy study are depicted in figures 18-27.

Scanning electron fractographs, obtained with a "Cambridge Stereo Scan" microscope, are shown in figures 28-36; most of them were taken at 20 kV, with aperture #2 (approximately 50 micron opening).

D. Experimental Results and the Current Hot Pressing Theories

On a qualitative basis, the curves obtained in this investigation are very similar to those given by Amato, in reference 45. It seems reasonable to admit that the plastic flow model developed by Mackenzie and Shuttleworth and modified by Murray and McClelland

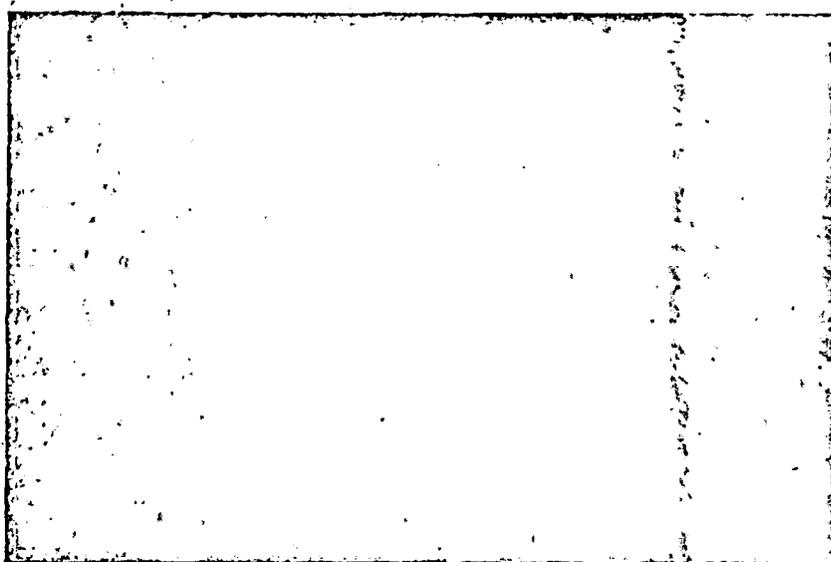


Figure 18. External Dark Layer in Hot Pressed UO_2 -20w/o ThO_2 (1625°C). It is approximately 130 Microns Thick, and the Dark Color is probably due to Particles from the Graphite Die Wall. 76x

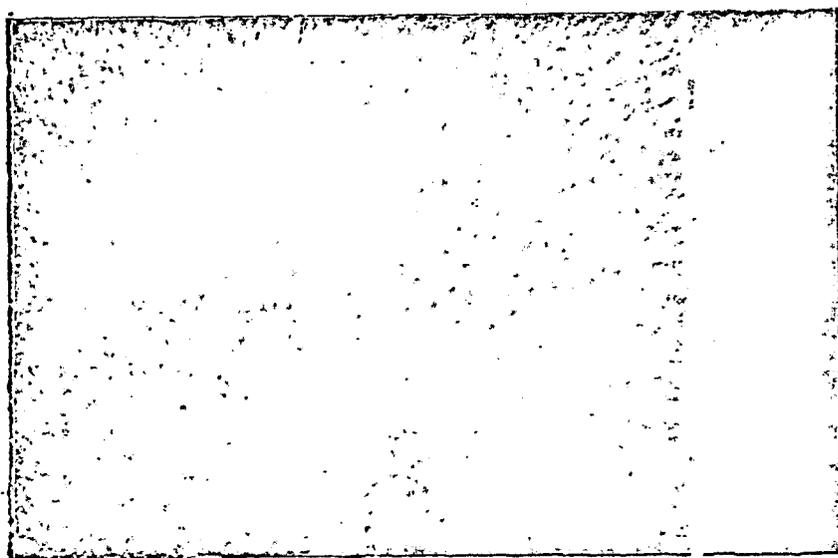


Figure 19. External Layer in Cold Pressed and Sintered UO_2 -20w/o ThO_2 . 76x

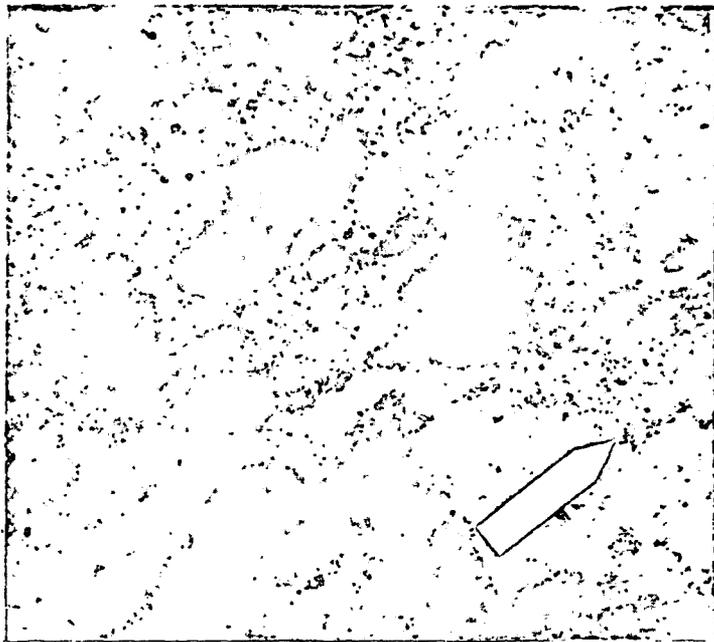


Figure 20. UO_2 -15w/o PuO_2 Hot Pressed at 1200°C and 3820 psi. The Agglomerations are oriented in a Direction Perpendicular to the Applied Force (see arrow). As Polished, 535x.

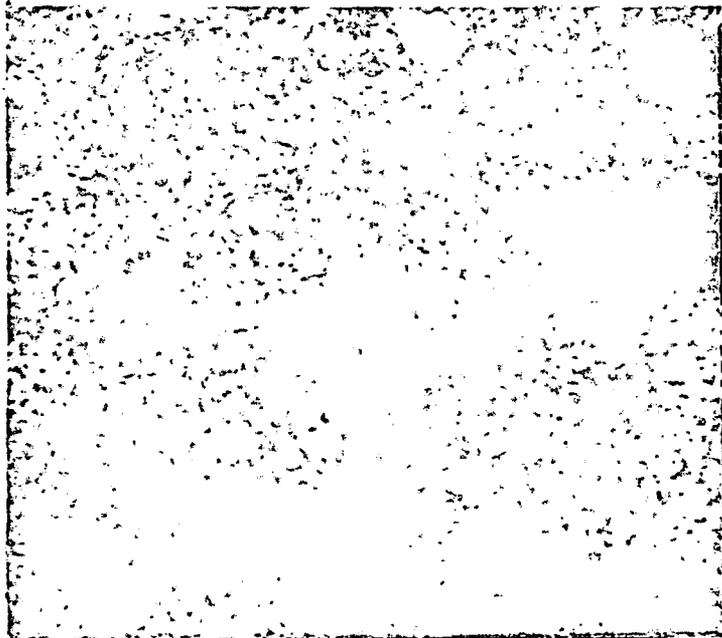


Figure 21. Typical Agglomerations in Wet-Milled UO_2 -20w/o ThO_2 , Hot Pressed at 1625°C . The Average Agglomeration Size is 15 Microns. As Polished, 1430x.



Figure 22. Agglomerations in Hot Pressed UO_2 . As Polished, 322x.



Figure 23. Grain Boundaries in Agglomeration. UO_2 Hot Pressed, Etched, 798x.



Figure 24. Grain Boundaries in Agglomerations. UO_2 Hot Pressed at $1625^{\circ}C$. Etched with H_2SO_4 - 10 v/o H_2O_2 , 798x.

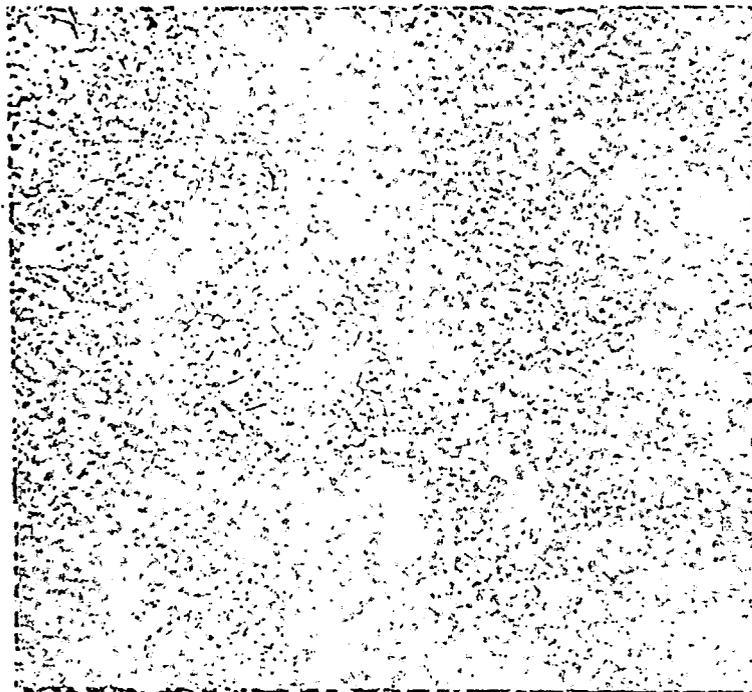


Figure 25. Grain Growth in Agglomerations.
Dry-Milled UO_2 -20w/o ThO_2 , Hot
Pressed at 1625°C . Etched, 798x.

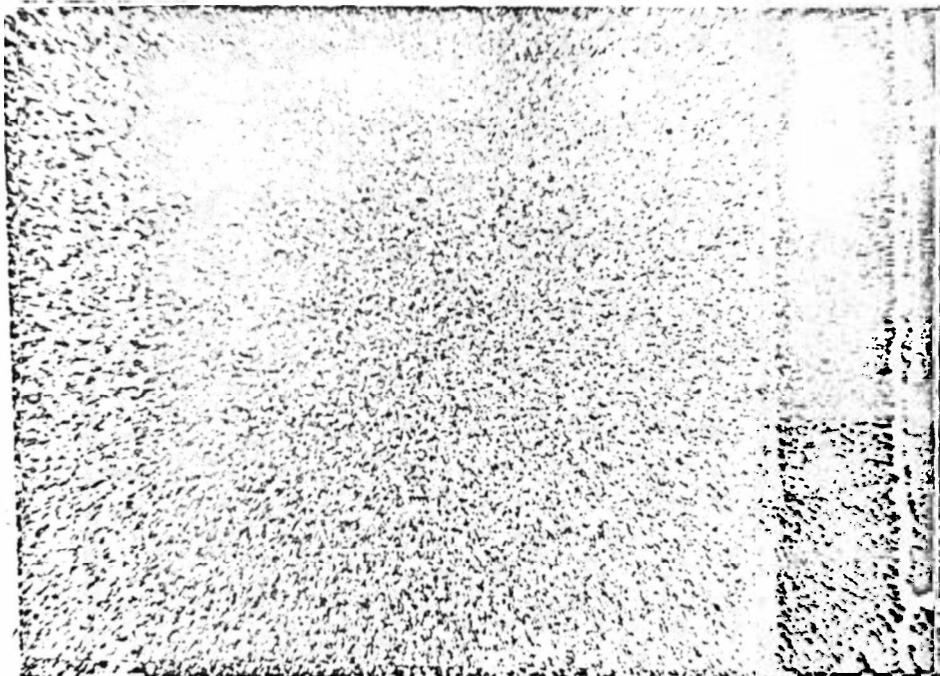


Figure 26. Composition Gradient in Reactive Hot Pressing of Uranium Oxide. U_3O_8 was the starting Material and $UO_{2.08}$ the resulting Composition. As Polished, 51x.



Figure 27. Central Part of the Sample shown in Figure 26. The Crack is about 19 Microns Wide. As Polished, 306x.

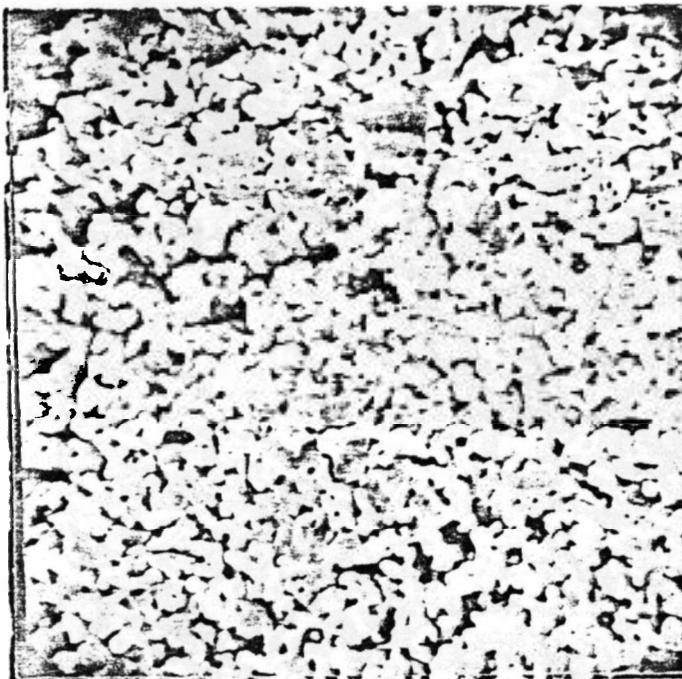


Figure 28. Scanning Electron Microscope (SEM) Fractograph of 76.2% Dense UO₂ Sample, Hot Pressed at 1400 °C. 4370x.



Figure 29. SEM Fractograph of the same Sample shown in Figure 28. 11620x.

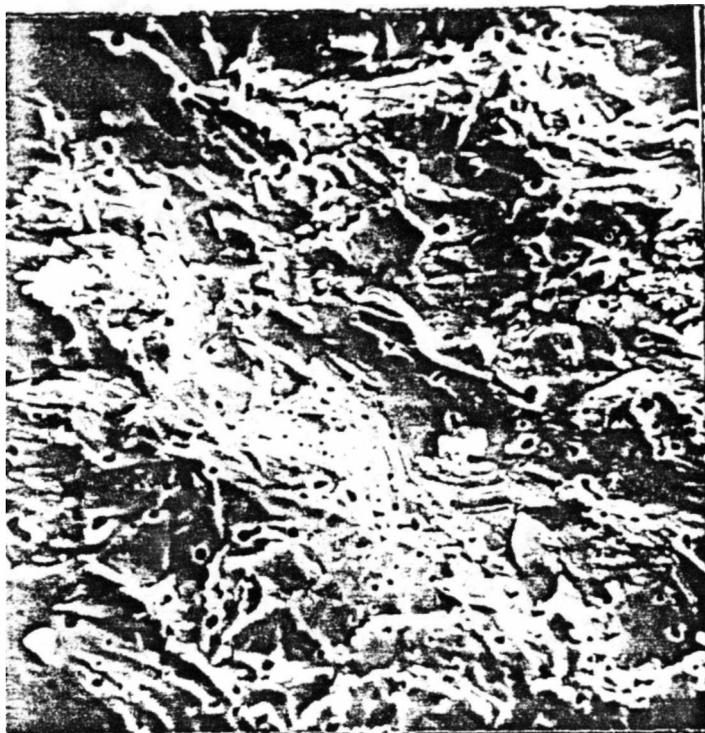


Figure 30. SEM Fractograph of Wet-Milled UO_2 -20w/o ThO_2 Hot Pressed at 1625 °C and 88% Dense. There is Evidence of Flow Orientation and Creep Deformation. 2250x.

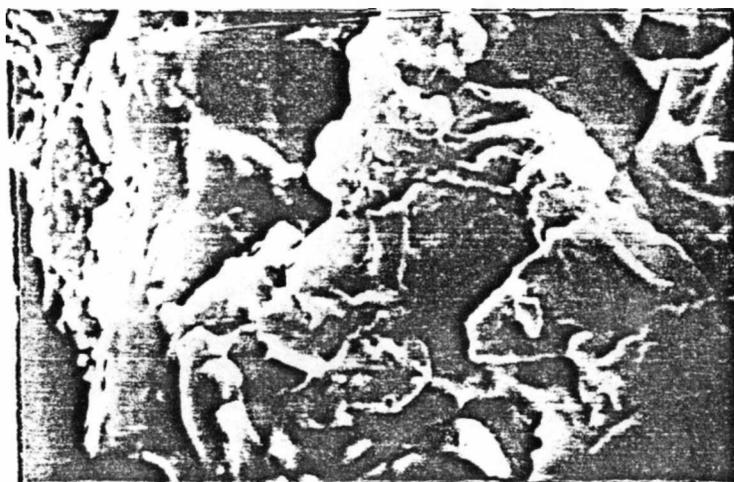


Figure 31. SEM Fractograph of the same Sample shown in Figure 30. It depicts the Zone of the External Layer, showing Platy Morphology; Large Voids due to Reduction by Carbon. 6120x.

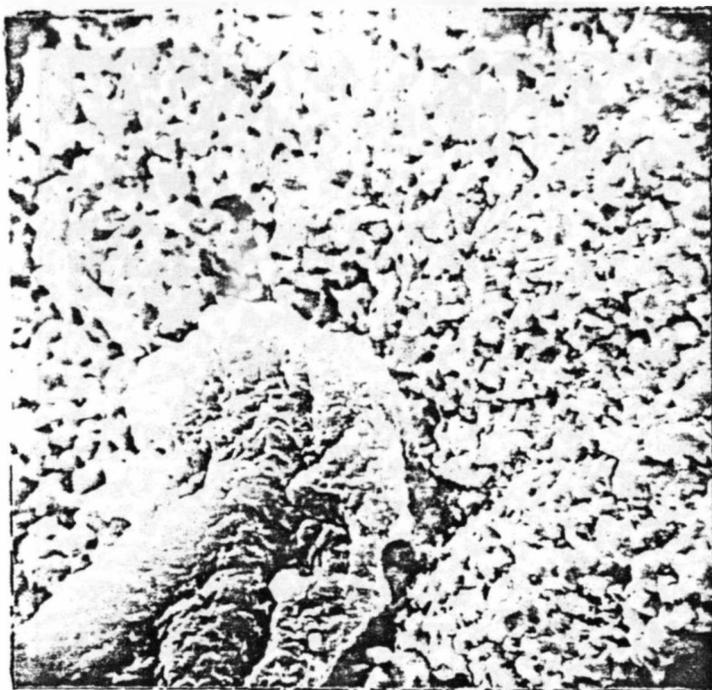


Figure 32. SEM Fractograph of Dry-Milled UO_2 -20w/o ThO_2 , Hot Pressed at 1625°C , showing Large Agglomerate. 2330x.

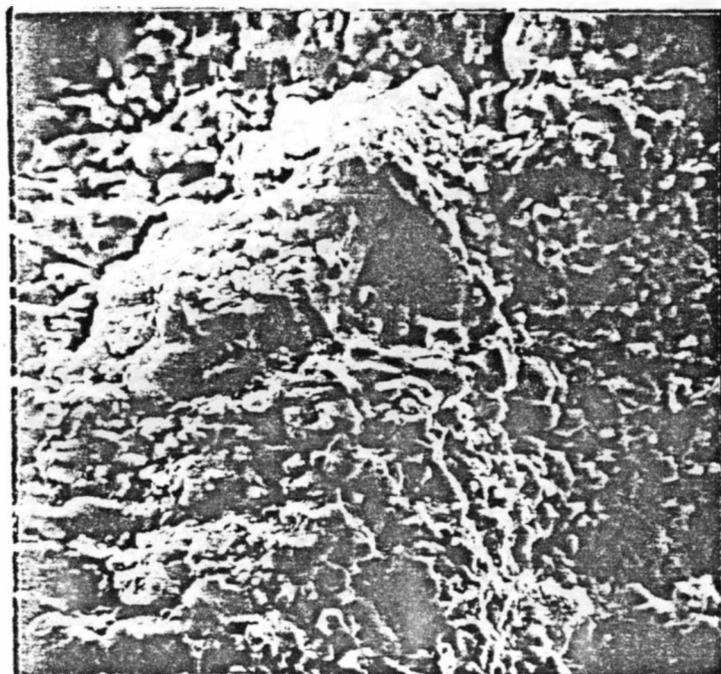


Figure 33. SEM Fractograph of the same Sample shown in Figure 32, depicting another Large Agglomerate. 2540x.

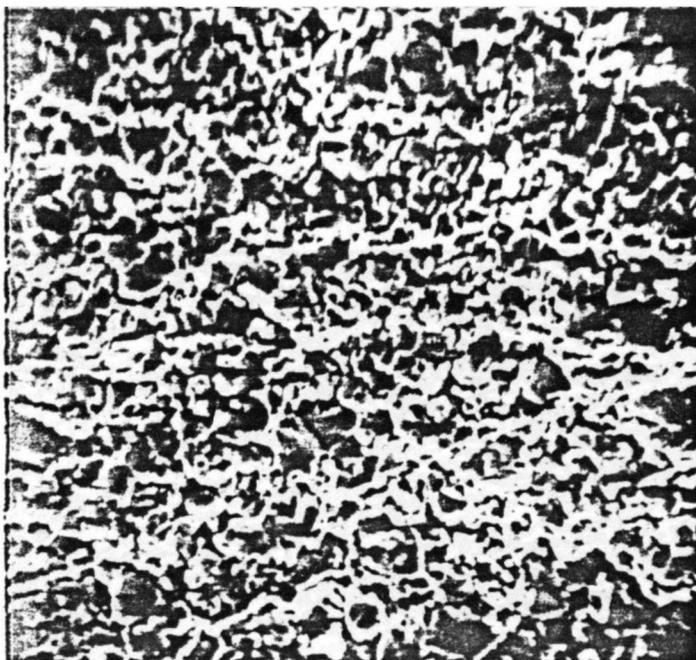


Figure 34. SEM Fractograph of 86% Dense Wet-Milled Cold Pressed and Sintered (1625 °C) UO_2 -20w/o ThO_2 Samples. 1020x.



Figure 35. Agglomeration in the same Sample shown in Figure 34. SEM Fractograph, 2250x.

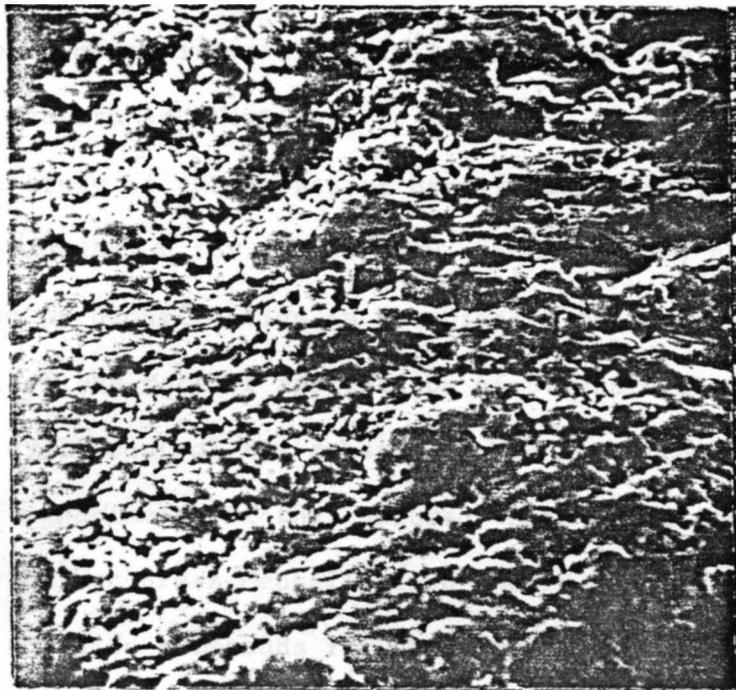


Figure 36. SEM Fractograph of Dry-Milled isostatically Pressed UO_2 -20w/o ThO_2 , 87% Dense, showing Areas of Large Densification, probably corresponding to Agglomerates; This Characteristic Microstructure is similar to those found in the Hot Pressed Materials previously described, Ball-Milled by the same Procedure. 2290x.

can be applicable in the densification of all the actinide oxide compositions studied here. Again referring to the work of Amato, the previously mentioned model is more likely to hold than the creep model adopted by Nabarro and Herring.

A detailed study of the stages of densification during hot pressing is a natural recommendation for future work. Such a study could elucidate the mechanism of densification in relation to microstructural changes. Control of the rate of application of pressure correlative with temperature cycle control and subsidence may be a requirement for refinement of experiments of this nature. More specifically relating powder morphology to hot press densification should lead to improved specification of actinide compounds for fuel fabrication.

V. CONCLUSIONS

1. $\text{UO}_{2+x} - \text{ThO}_2 - \text{PuO}_2$ mixtures can be successfully hot pressed in the temperature range 1000 - 1400°C, at pressures of 4000 psi in 5 to 30 minutes. If wet-milling or a "Spex Mixer/Grinder" is adopted for the mixing of the powders, the pressure sintered samples present agglomerations smaller than 44 μ and they can be considered for nuclear reactor fuel applications.
2. Reactive hot pressing of U_3O_8 can produce high density $\text{UO}_{2.08}$ samples, but internal cracks may develop if the cooling conditions are not proper.
3. Densities as high as 91% of theoretical can be attained at 1200°C, 3820 psi and 30 minutes.
4. It is possible to hot-press multiple layers of $\text{UO}_{2+x} - \text{ThO}_2 - \text{PuO}_2$ mixtures, yielding samples of thickness variation within $\pm 0.5\%$.
5. The maximum rates of densification of actinide oxides mixtures occurs at temperatures under 1100°C, for pressures of about 4000 psi. This suggests that the hot pressing of the actinide oxides and its mixtures can be successfully developed at temperatures lower than 1200°C.
6. Particle size and powder morphology influence the final density of hot pressed actinide oxides and their mixtures. Finer powders can reach higher densities than the coarse ones.
7. There is strong influence of the applied pressure on the final density, at temperatures of 1200°C.

8. When ATJ or CS grade graphites are used, the carbide layer formed during hot pressing is probably destroyed during the sample ejection from the die, or remains partially on the die walls. This effect, combined with abrasion by the powders during pressing, causes heavy die wear.
9. Refractory metals such as W, Mo and Ta interact strongly with actinide oxides mixtures, when used as separators of samples, during multispecimen hot pressing. Less interaction was observed for separators made with "glassy carbons" or Poco graphite; this suggests their utilization as die inserts to avoid contamination.
10. The development of continuous hot pressing apparatuses operating in the 1200-1400^oC range opened a new perspective for the application of the pressure sintering technique, competitive with classical ceramic forming processes. This is particularly true for the actinide oxide mixtures containing plutonium, that must be handled inside a glove box. Small, highly automated, continuous hot press equipment would facilitate fabrication of actinide materials in the limited space of protective enclosures.

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APPENDIX A
NOMENCLATURE

With the introduction of a variety of techniques for sintering, several terms are now in common usage. Definitions of sintering and related terms are suggested here.

Sintering - Mechanism by which solid bodies are bonded by atomic forces through the application of pressure and/or heat (Ref. 1).

Powder Molding - Sintering of powders with the application of pressure alone (Ref. 55).

Thermal Sintering - Sintering with the application of heat alone (Ref. 55).

Molding Without Pressure - Equivalent to thermal sintering (Ref. 55).

Hot Pressing - Sintering by simultaneous application of pressure and heat (Ref. 55). Jones (Ref. 56) defines this term as pressing at temperatures above that at which the material is capable of retaining work hardening.

Cold Pressing - Pressing at room temperature (Ref. 56).

Warm Pressing - Pressing at temperatures over the atmospheric and below those corresponding to hot pressing, as defined by Jones (Ref. 56).

Chill Pressing - Pressing at temperatures below atmospheric (Ref. 56).

Pressure Sintering - Equivalent to hot pressing (Ref. 57). Goetzl (Ref. 58) suggests hot pressing may be distinguished from pressure sintering. In the later operation, a furnace treatment is implied, whereby the powder or compact, passing through the heating cycle, is subjected to

static pressure, usually of moderate degree and generally exerted by dead weights.

Activated Sintering - Thermal sintering in which the process rate is modified by means of powder physical or chemical treatments, alteration of atmosphere, or deliberate small additions, with improvement of the sintered compact properties (Ref. 59).

Calcintering - Simultaneous calcination (driving off a gas) and thermal sintering of a decomposing powder (Ref. 31).

Pressure calcintering - Calcintering with application of pressure.

Decomposition Pressure Sintering - Equivalent to pressure calcintering (Ref. 27).

Reactive Hot Pressing - Hot pressing of a powder with enhanced reactivity associated with dislocation and decomposition reactions (without gas evolution), as well as phase inversions (Ref. 60).

APPENDIX B

KINETICS OF THE GRAPHITE-URANIUM
DIOXIDE REACTION AT 1615°C

T. B. Lindemer et al. (Ref. 54) studied the kinetics of the graphite- UO_2 reactions from 1400° to 1756°C, for the case of 95% dense UO_2 microspheres with a diameter of about 200 micron.

If r_0 is the total radius of the microsphere at time $t = 0$ and r its radius at a time t ($r_0 - r$ being the thickness of a UC_2 layer), the following relation (Ref. 9, equation 1) is valid:

$$\frac{1}{3} - \left(\frac{r}{r_0}\right)^2 \left(1 - \frac{2r}{3r_0}\right) = k_D \frac{t}{r_0^2}$$

At 1615 °C and $t = 60$ minutes, $k_D t/r_0^2 = 0.02$ (Ref. 54, Figure 3). For these values, from the above equation it was calculated that $\frac{r}{r_0} = 0.85$, indicating the formation of a relatively thick layer of uranium carbide.

In their investigation, Lindemer et al. showed also that around the UO_2 microsphere core only UC_2 was formed, the diffusion of oxygen through the UC_2 layer being the rate controlling mechanism.