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JOINT UNITED STATES
ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT PROGRAM

MASTER

BURNABLE POISON ADDITIONS TO UO_2

For the Period:

May 1, 1967 to June 30, 1968

Issued March 1969

NUCLEAR
POWER
DEPARTMENT

COMBUSTION ENGINEERING, INC.

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Summary Report

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For the Period:

May 1, 1967 to June 30, 1968

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BURNABLE POISON ADDITIONS TO UO_2

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ABSTRACT

One of the means by which burnable poisons can be used for reactivity control in power reactors is to add controlled amounts of a poison directly to the fuel material as a homogeneous dispersion. The addition of boron to UO_2 has been limited by the lack of a suitable fabrication technique which would produce the desired properties in the fuel. The objective of this program was to develop the sintering techniques capable of incorporating approximately 400 ppm of natural boron in UO_2 pellets and to attain sintered densities in excess of 90 percent of theoretical. B_4C was added to UO_2 and sintered in argon, hydrogen (argon-10 w/o H_2), vacuum and CO_2 -CO environments at temperatures up to 1600°C . Pellets prepared from essentially stoichiometric UO_2 , containing 120 ppm boron in the form of B_4C , retained 60 to 75 percent of the boron when sintered in argon or in vacuum. Similarly prepared pellets of UO_2 containing 900 ppm boron retained only 10 to 40 percent of the boron under the same sintering conditions. The pellet densities associated with these high boron losses were less than the target 90 percent of theoretical.

The loss of boron during sintering is attributed to the reaction of B_4C with moisture and excess oxygen in the UO_2 to form boron oxides which volatilize at temperatures between 1300°C and 1600°C . The use of a reducing environment to remove oxygen from hyperstoichiometric UO_2 - B_4C pellets during sintering was unsuccessful in improving the retention of boron. Boron which was retained was in the form of UB_4 which formed by reaction of UO_2 and B_4C at temperatures above 1400°C .

I. INTRODUCTION

The present program is a continuation of the program performed under Contract AT(30-1)-3107, as part of the Joint U.S.-Euratom Research and Development Board to develop methods for incorporating boron burnable poisons in UO_2 fuel elements. Prior⁽¹⁾ work on the program had developed vibratory power compaction methods for producing a uniform distribution of B_4C in UO_2 fuel elements. Ex-reactor thermal tests had demonstrated that extensive boron migration did occur in the radial direction under severe thermal gradient conditions ($2500 - 2700^\circ \text{C/cm}$) without significant axial redistribution of boron. Two 6 percent enriched UO_2 fuel rods containing 0.05 w/o B_4C were irradiated in the Saxton Reactor to burnups of 1070 and 6442 Mwd/MTU at peak linear heat ratings of 17.2 and 19.8 kw/ft, respectively. Post-irradiation evaluations⁽²⁾ revealed substantial radial boron redistribution without significant axial movement of boron. The redistribution of boron was attributed to a combination of chemical reactions and in-reactor diffusion controlled mechanisms. Although radial boron redistribution was observed, its effect was minimal η_f (ratio of neutrons produced to thermal neutrons absorbed) and $\Delta\rho$ (difference in reactivity of the core) based on the THERMOS program.

It was also demonstrated, from ex-reactor tests in dynamic and static systems, that UO_2 and B_4C had reacted to form UB_4 and CO_2 at test temperatures of 1150°C and 1850°C . It was also considered possible that oxidation of B_4C by air contamination during vibratory compaction may have taken place to form B_2O_3 and CO_2 . However, the role of oxidants was not established as a means for the observed boron redistribution in ex-reactor experiments and in the fuel elements irradiated in the Saxton reactor.

II. SURVEY OF PREVIOUS WORK

Many attempts ^(3,4,5) have been made to incorporate burnable poisons in sintered UO_2 pellets with reported excessive or erratic losses of boron in hydrogen, helium or hydrogen-nitrogen atmospheres. Some success ⁽⁶⁾ had been reported for high density UO_2 pellets containing up to 120 ppm boron, added as boric oxide (B_2O_3), by sintering at 1325°C in flowing argon followed by reduction in hydrogen at the same temperature and cooling in hydrogen. Work at the Mitsubishi Atomic Power Industries ⁽⁷⁾ had shown that ZrB_2 can be utilized in both vibratory powder compacted rods and in compacted and sintered UO_2 pellets. Another method ⁽⁸⁾ had successfully retained ZrB_2 particles (50-100 μ) in UO_2 pellets by heating to 450°C in hydrogen followed by sintering in vacuum at 1600 - 1650°C for 2 hours. The irradiation performance testing on two vibratorily compacted UO_2 rods containing 50 ppm ZrB_2 ⁽⁹⁾ did not conclusively establish boron redistribution from the limited number of analyses.

None of these investigations have reported experimental data with sufficient detail to provide an adequate insight into the mode of boron loss during sintering. The mechanism of boron removal is speculative and is believed to involve the oxidation of the boron compound (B_4C , B_2O_3 or ZrB_2) with subsequent volatilization of the reaction products. Accordingly, residual amounts of oxygen and moisture under dynamic furnace conditions may completely convert several hundred ppm of boron into volatile products before significant densification of the UO_2 can take place. For these reasons, reactions involving trace amounts of these constituents may occur undetected under normal sintering conditions. Retention of boron in sintered UO_2 pellets requires the removal of oxidants (O_2 , H_2O , CO_2 , reducible oxides) from the powder starting materials, furnace atmosphere and the

furnace system prior to heatup and sintering of $\text{UO}_2\text{-B}_4\text{C}$ pellets.

Boron carbide (B_4C) is a thermally stable compound in inert atmospheres and has a low vapor pressure for all temperatures up to the melting point. It will react readily with oxygen or moistures at temperatures above 500°C to form boron oxide (B_2O_3). The driving force for these reactions was examined from standard free energies of reaction between B_4C (c) and oxygen and moisture for a temperature of 1100°C . These reactions are shown below:

These data show that the high negative free energy of reaction values favor a strong tendency for the oxidation of B_4C to form gaseous B_2O_3 . It is also possible that B_4C may react with moisture to form orthoboric acid (HBO_2) although this possibility is somewhat less than for formation of B_2O_3 . In any case, the mode of boron loss will depend upon the kinetic process of volatilization of B_2O_3 , and cannot be determined solely on the basis of thermodynamic data.

III. PROGRAM OBJECTIVES

The primary objective of this program was the development of cold compaction and sintering methods for incorporating homogeneous dispersions of boron in high density UO_2 pellets.

The program was conducted in three phases:

- 1) The initial study investigated the oxidation behavior of B_4C in UO_2 pellets and the mechanisms involved in boron losses during the sintering process. This series of tests was conducted in vacuum (2×10^{-6} microns) or in purified argon environments at temperatures to 1500°C ;
- 2) An investigation was conducted on pellet densification and boron retention in $\text{UO}_2\text{-B}_4\text{C}$ pellets sintered in the 1400° to 1500°C temperature range in various CO or CO_2 environments. There is evidence^(10,11) that UO_2 densities in excess of 92 percent of theoretical can be attained by sintering under these conditions. Furthermore, the presence of CO_2 , a product of the $\text{UO}_2\text{-B}_4\text{C}$ reaction, may, as a result of its high vapor pressure, inhibit the forward reaction and improve the stability of $\text{UO}_2\text{-B}_4\text{C}$ during the sintering process. A separate series of tests was performed using a reducing atmosphere (argon - 10 percent hydrogen) during the heatup portion of the sintering cycle in an attempt to remove moisture and excess oxygen in the UO_2 prior to sintering in the inert atmosphere;
- 3) An investigation of both axial and radial boron migration was conducted on sintered $\text{UO}_2\text{-B}_4\text{C}$ pellets under simulated reactor thermal conditions.

IV. EXPERIMENTAL PROCEDURE

A. Assessment of Starting Materials

The preparation of high density pellets requires a sinterable powder of suitable physical and chemical properties. The as-received UO_2^* and boron carbide powders were evaluated for chemical composition and particle size distributions to determine the requirements for preparing homogeneous mixtures of the two powders for the sintering studies. Properties and major impurities reported for the two starting materials are shown in table I.

Sieve analyses on the as-received UO_2 powder showed that approximately 80 percent of the powder was less than 200-mesh (74 micron) particle size with the remainder ranging from 200-mesh up to 20-mesh size (840 micron). Microscopic examinations revealed that the initial, finely divided powder had agglomerated into relatively hard, irregularly shaped particles. The as-received powder contained 2000 ppm moisture and a O/U ratio of 2.16. Accordingly, the initial work involved comminution of the agglomerates into a finer particle size to improve the sinterability of the resulting powder. Further conditioning of the powder involved removal of both moisture and excess oxygen to prevent formation of volatile boron compounds (in the UO_2 pellets) during sintering.

B. Milling and Blending Studies

The dry milling operation served the dual purpose of reducing the agglomerated UO_2 powder to a uniformly finer particle size and to homogeneously blend the B_4C additions with the UO_2 powder. This operation was

* Throughout this report, nonstoichiometric uranium dioxide is referred to as UO_2 . For those cases where the O/U ratio is known, the exact stoichiometry of UO_2 is reported.

performed in U. S. Stoneware, rubber-lined steel jars of 1-quart capacity using Burundum high density grinding media, one-half inch in diameter and one-half inch in length.

Table I. Properties of Starting Materials

<u>Uranium Dioxide</u>		<u>High Boron Grade Boron Carbide</u>	
Source: Kerr McGee Corporation		Source: The Norton Company.	
Uranium	87.65%	Boron	77.3%
O/U Ratio	2.16	Carbon	21.8%
Fisher Particle Size	1.05	B ₂ O ₃	0.035%
Porosity	0.65	Fe	0.5 max
Absorbed Moisture	2000 ppm	Al	0.2 max
		Ca	0.1 max
		Mg	0.05 max
Ag	1 ppm max		
Al	24 ppm max		
B	6 ppm max		
Be	1 ppm max		
Bi	2 ppm max		
Cd	0.6 ppm max		
Co	10 ppm max		
Cr	15 ppm max		
C	100 ppm max		
Cu	2 ppm max		
Fe	70 ppm max		
Mg	30 ppm max		
Mn	4 ppm max		
Mo	6 ppm max		
Ni	40 ppm max		
Pb	5 ppm max		
Si	30 ppm max		
Sn	2 ppm max		
Zn	20 ppm max		
Y	5 ppm max		

The initial batches of UO_2 powder, without B_4C additions, were dry milled for various times to study comminuted rates of the agglomerated powder. A milling time of 20 hours was established as the minimum time to attain a uniformly fine particle size.

C. Sintering Studies

1. UO_2 Without B_4C Additions

An assessment of UO_2 sinterability was made by heat treatments in argon or in vacuum at temperatures to 1600°C . Pellets, 1.00 cm in diameter and 1.27 cm in length were compacted at 7 tsi in a hardened steel die to a geometric density of about 5.10 g/cm^3 (47 percent of theoretical). For these studies, the pellets were compacted from milled powder left intentionally in the nonstoichiometric condition with adsorbed moisture in order to compare densification, structure and O/U ratio with subsequent pellets prepared from dried, stoichiometric UO_2 powders.

This series included 3 tests which were conducted on groups of 6 pellets each. The first group of six UO_2 pellets was placed on a tantalum container and heated in purified argon at a rate of $300^\circ\text{C}/\text{hour}$ to 1200°C , held at temperature for 1 hour and cooled overnight in argon. All pellets were irregular in shape with essentially no densification of the lower portion in contact with the tantalum container. The bottom of the container was coated with a white layer, identified as Ta_2O_5 , from reaction with moisture and oxygen released from the heated pellets. No further evaluation was conducted on these pellets.

The second group of six pellets was outgassed initially at 900°C for 1 hour in the same furnace at a pressure of 2×10^{-6} microns and then sintered and cooled in argon as previously. Although, the bottom of the tantalum

container was oxidized, as for the previous sinter, all pellets remained cylindrical in shape. Geometric densities ranged from 8.66 to 8.80 g/cm³ (79 to 80 percent theoretical).

The vacuum outgassing time for the third group of six UO₂ pellets was increased from 1 hour at 900° C to 4 hours at 900° C prior to sintering. Formation of a thin film of the white oxide on the tantalum container was indicative that all moisture as well as a substantial portion of the excess oxygen had been removed from the UO₂ powder compacts during the 4-hour vacuum treatment. Pellets from the second and third sinters were identical in density and in appearance.

A second series of tests was conducted on UO₂ pellets prepared from milled, as-received powder with the objective of obtaining information on stoichiometry (O/U ratio), microstructure and densification behavior. This series was sintered in vacuum at temperatures ranging from 750° C to 1600° C. As per the previous series of UO₂ tests, the pellets were compacted at 7 tsi to a density of 5.10 g/cm³. Each test included 6 pellets placed in an open tantalum container. The furnace temperature was increased at a rate of about 300° C/hour while maintaining a pressure of about 2×10^{-5} microns for continuous removal of moisture and oxygen from the UO₂ pellets. The metallic appearance of the tantalum containers for all test temperatures showed that the low furnace pressures were adequate to remove the moisture and some of the oxygen from the UO₂ at a rate which avoids oxidation of the tantalum. These tests demonstrated the primary requirement of a clean furnace environment such as vacuum or high purity inert gas for the study of UO₂-B₄C reactions.

2. UO_2 With B_4C Additions

Initial sintering tests were conducted using a UO_2 -1 w/o B_4C blend to investigate the effects of adsorbed moisture and hyperstoichiometric UO_2 on the mode of B_4C oxidation and the extent of boron losses by volatilization during sintering over a range of temperatures. One w/o B_4C (7825 ppm boron) was used for these evaluations in lieu of 0.05 w/o (390 ppm boron) to facilitate chemical analyses and interpretation of UO_2 - B_4C reactions by microscopic examinations of sectioned and polished specimens. A subsequent series of sintering tests on UO_2 pellets containing 0.05 w/o B_4C repeated essentially the entire range of sintering temperature in vacuum or in argon environments. Each sintering test included four UO_2 - B_4C pellets and three UO_2 control pellets.

A preliminary sintering test on UO_2 powder containing a 1 w/o B_4C dispersion showed that 20 hours milling time was not adequate to provide a homogeneous dispersion of B_4C particles within the UO_2 pellets. An increase in the milling time from 20 hours to 30 hours developed the desired uniformity of distribution of the B_4C particles. This procedure was used as the basis for preparing all subsequent UO_2 - B_4C powder blends used on the program.

Another series of sintering tests involved the use of a hydrogen treatment of the UO_2 - B_4C in attempt to optimize the boron retention in the sintered pellets. The first method employed a hydrogen reduction step to remove moisture and excess oxygen from as-received UO_2 powder prior to the preparation of UO_2 - B_4C blends. The second method included the use of hydrogen during the heatup portion of the sintering cycle to remove moisture and excess oxygen from pellets prepared from as-received UO_2 and B_4C blends. Both of these methods were aimed at the prevention of B_4C oxidation and loss of boron during sintering.

Tables II and III include all sintering conditions involving the use of

Table II. Experimental Procedure for Sintering Blends C_R and D_R

Blend*	Initial Loading		Sintering Environment	Sintering Temperature, ° C	Total Retained Boron ppm
	w/o B ₄ C	ppm B			
C _R	0.015	120	Argon	1300	101
C _R	0.015	120	Argon	1350	87
C _R	0.015	120	Argon	1400	89
C _R	0.015	120	Argon Heatup to sintering	1000	101
C _R	0.015	120	temperature & cool in argon	1300	115
C _R	0.015	120	- 10 w/o hydrogen	1325	100
C _R	0.015	120	Vacuum	1400	75
C _R	0.015	120	Vacuum	1500	40
C _R	0.015	120	Vacuum	1600	90
D _R	0.115	900	Argon	1300	290
D _R	0.115	900	Argon	1350	260
D _R	0.115	900	Argon	1400	173
D _R	0.115	900		1200	450
D _R	0.115	900	Argon Heatup to sintering	1300	159
D _R	0.115	900	temperature & cool in argon	1350	170
D _R	0.115	900	- 10 w/o hydrogen	1400	150
D _R	0.115	900		1425	50
D _R	0.115	900	Vacuum	1425	340
D _R	0.115	900	Vacuum 1600	262	

* The subscript "R" indicates that these blends were prepared from hydrogen-treated UO₂ powder.

NOTE: The pellets for each sintering test were initially vacuum-furnace dried at less than one micron pressure at 250° C prior to the sintering cycle.

Table III. Experimental Procedure for Sintering Blends A and E

Blend	Initial		Vacuum	Furnace Environments for Indicated Temp. Range		
	Loading			Argon -		Argon -
	w/o B ₄ C, ppm B			10 v/o Hydrogen	Argon	10 v/o Hydrogen
A	1.0	7825	RT→250	250→500	500→1300	1300→RT
A	1.0	7825	RT→250	250→900	900→1300	1300→RT
A	1.0	7825	RT→250	250→1000	900→1300	1300→RT
A	1.0	7825	RT→250	250→1200	1200→1300	1300→RT
A	1.0	7825	RT→250	250→1000	1000→1400	1400→RT
A	1.0	7825	RT→250	250→1200	1200→1400	1400→RT
E	0.023	180	RT→250	250→500	510→1300	1300→RT
E	0.023	180	RT→250	250→900	500→1300	1300→RT
E	0.023	180	RT→250	250→1000	500→1300	1300→RT
E	0.023	180	RT→250	250→1200	1200→1300	1300→RT
E	0.023	180	RT→250	250→1300	1300	1300→RT
E	0.023	180	RT→250	--	250→1300→RT	--
E	0.023	180	RT→250	--	250→1350→RT	--
E	0.023	180	RT→250	250→1300→RT	--	--
E	0.023	180	RT→250	250→1300→RT	--	--

hydrogen. Four powder blends of $\text{UO}_2\text{-B}_4\text{C}$ used in this series of tests, have the designation, "A", "E", " C_R " and " D_R ", with 7825, 180, 120 and 900 ppm boron as B_4C , respectively. The subscript "R" indicates that the as-received UO_2 powder was preconditioned by heating in a flowing reducing atmosphere (argon - 10 v/o hydrogen) for 1 hour at 1000°C to reduce the O/U ratio from 2.16 to 2.06. These two powder blends were milled and stored under dry argon to minimize moisture and oxygen pickup. The Blend "C" boron content was considered a possible lower limit of interest for nuclear applications in light water reactors. Sintering tests using 0.05 w/o B showed about 50 percent boron losses and prompted the use of Blend " D_R " with double the boron content. The sintering temperatures and furnace environments used for Blends C_R and D_R are included in table II.

A production process which would avoid the pretreatment of UO_2 powder and accomplish the reduction and drying of the fuel powder during the sintering cycle would have economic advantages. An evaluation of such sintering procedures was conducted with Blends "A" and "E". Sintering studies were conducted in several CO-CO_2 environments to investigate boron retention and sinterability of pellets prepared from Blend C (120 ppm boron), Blend E (180 ppm boron) and a new powder mixture containing 650 ppm boron, as B_4C . The premixed CO-CO_2 gases included 10, 30 and 50 v/o CO in CO_2 and 100 percent CO, respectively. The sintering cycle involved vacuum outgassing at 250°C , heating 1400°C in flowing CO-CO_2 atmosphere with a sintering time of 1 hour and cooling overnight to room temperature. Duplicate sintering tests indicated good reproducibility of boron content and density for each powder blend.

3. Furnace Descriptions

The series of $\text{UO}_2\text{-B}_4\text{C}$ pellets were sintered in two types of furnaces with the following capabilities:

- a) The Brew Vacuum Furnace provided temperatures up to about 2000°C at low chamber pressures to about 2×10^{-6} microns. The furnace chamber could be evacuated and backfilled with purified argon for sintering tests requiring an inert gas in lieu of an evacuated environment. A typical sintering cycle included a 2-hour heatup to the sintering temperature, 1 hour at temperature, and cooldown in approximately 2 hours;
- b) The silicon carbide resistance furnace allowed a greater variety of gaseous atmospheres which included purified argon, argon-10 v/o hydrogen and preblended mixtures of CO and CO_2 gases. The initial sintering tests were conducted at temperatures up to 1200°C in Inconel tubes, with a 3.80-cm (1 1/2 inches) inside diameter, for ease of cleaning between sintering tests. For sintering at temperatures above 1200°C , tubes of impervious stabilized zirconia were used for sintering the maximum furnace temperature of 1500°C . The pellet containers were fabricated from 0.005-inch thick tantalum or molybdenum sheet. The gas purification system developed for this furnace included a DeOxo unit, a magnesium perchlorate trap and a zirconium chip gettering furnace, connected in series to remove moisture and trace impurities from the incoming gases. This gas purification line employed a stainless steel valve system for convenient change of gas type (inert or reducing) for duplex sintering cycles. The purified, incoming gases were monitored for

dew point periodically, using an Alnor Dewpoint instrument. All components of the gas purification system were connected by stainless steel tubing to reduce the possibility of oxidation and gas contamination. Periodically, the ceramic furnace tubes were replaced when inspection showed internal deposits or deterioration of the tube material. Due to the use of the ceramic tube, the furnace heatup time ranged from 2 to 4 hours. A 1-hour time at temperature was used with an overnight cooldown in the flowing gaseous environment.

4. Sinterability

The sinterability of the pellets was determined from geometric density, diametral shrinkage and weight loss data. The $\text{UO}_2\text{-B}_4\text{C}$ pellets were analyzed for both water-soluble boron oxides and total boron (included as B_4C , boron oxides and uranium borides - UB_4 and UB_2). The pellet stoichiometry was checked in representative cases. Representative sintered pellets were examined for microstructure and crystal structure using standard metallographic and x-ray diffraction procedures. Brief descriptions of the analytical procedures used on the program are included as part of Appendix A.

D. Boron Migration Studies

The principle of the thermal gradient apparatus for boron migration studies was based upon the design of equipment constructed on another Atomic Energy Commission (AEC) contract and had been described in CEND-186⁽¹²⁾. The test method utilized an axially positioned tungsten heater rod within a column of sintered UO_2 pellets containing the boron burnable poison. High radial temperature gradients were developed within the pellets by passage of an electric current through the heater rod while maintaining the externally

water-cooled Zircaloy-4 cladding to temperatures near 300° C.

The principal components of the apparatus are described below:

- a) The test element and cooling jacket are contained within a rectangular brass chamber 30.48 cm (12 inches) long by 15.24 cm (6 inches) wide by 12.70 cm (5 inches) deep. The chamber cover, containing the viewing window, is removable for insertion and removal of the test element. The system can be evacuated to a pressure of about 10^{-5} microns and then backfilled with argon.
- b) The cylindrical water-cooled brass jacket is flanged at both ends for ease of insertion and removal of the test element. Both ends of the cladding test element are sealed with O-rings to the flanged ends of the cooling jacket. The annular space between the test element and the cooling jacket contains flowing de-ionized water for heat removal.
- c) The power terminals at both ends of the chamber use water-cooled copper bellows with split copper clamps to allow easy coupling to the tungsten heater rod. This arrangement provides high electric current capacity while accommodating axial thermal expansion of the heater rod during the tests. The terminals are sealed by O-rings and electrically insulated from the chamber by Plexiglass plates.

E. Preparation of Annular $\text{UO}_2\text{-B}_4\text{C}$ Pellets

Fifty UO_2 pellets containing 330 ± 20 ppm boron were prepared for the migration tests by argon sintering at 1350° C to a geometric density of 10.2 g/cm³ (93 percent theoretical density). The OD and ID of the pellets were finish ground to 0.1413 ± 0.0002 cm (0.3590 ± 0.0010 inch) and 0.00300 ± 0.0001 cm (0.0765 ± 0.0005 inch), respectively. All pellets were end faced to a length

of 0.197 cm (0.500 inch). The diameter of the tungsten heater rods was centerless ground to provide intimate pellet-to-heater rod contact. Two test elements, each containing 16 1/2-inch-long pellets, were assembled over the heater rods and contained within the Zircaloy-4 cladding. The elements were radiographed to confirm the stacking and then vacuum dried overnight at 200° C prior to testing.

The operating temperature of the heater rod was determined from an electrical resistivity-temperature curve for tungsten. The electrical resistivity was calculated from the input current and the voltage across the element.

V. RESULTS

A. UO₂ Without B₄C Additions

The sinterability data for vacuum sintered UO₂ powder compacts are shown graphically in figure 1. Pellet densification, as represented by geometric density (figure 1a) and by diametral shrinkage (figure 1b), started at approximately 750° C and progressed at a linear rate with sintering temperature up to about 1200° C. Further densification continued at a reduced rate from 1200° C (9.30 g/cm³, 85 percent of theoretical) to 1600° C (10.10 g/cm³, 92 percent of theoretical). Weight losses of 0.3 to 0.4 percent for pellets heated to 1200° C are due chiefly to the removal of adsorbed moisture and volatile constituents in the UO₂ powder. The increasingly higher weight losses for temperatures above 1200° C are due to volatilization of UO₂ at a furnace pressure of 2×10^{-6} microns. Figure 1d shows that significant losses of oxygen begin about 1200° C with the attainment of essentially stoichiometric UO₂ at temperatures between 1300° C and 1400° C in high vacuum.

B. UO₂ With B₄C Additions

The sintering behavior of UO₂ pellets with 1 w/o B₄C and control pellets of UO₂ for a range of temperature from 625° C to 1250° C, is described in paragraphs B1, B2, B3 and B4. This series of tests was conducted in the Inconel tube furnace with a continuous flow of dry argon during the entire sintering cycle. Density, shrinkage and weight loss data are included graphically in figure 2. General descriptions of UO₂ and UO₂-1 w/o B₄C pellets sintered at the six temperatures are included along with the results of the sintering tests.

Figure 1a

Figure 1c

Figure 1b

Figure 1d

Figure 1. Sinterability Data on UO_2 Pellets

Figure 2a

Figure 2c

Figure 2b

Figure 2. Sinterability Data on UO₂ and UO₂ - 1 w/o B₄C Pellets

1. 625° C Sinter

All pellets remained unchanged in appearance following the low temperature treatment in flowing argon. Both UO_2 and $\text{UO}_2\text{-B}_4\text{C}$ pellets had retained the light brown color of the as-compacted powders. Micrometer measurements showed that the $\text{UO}_2\text{-B}_4\text{C}$ pellets had increased in diameter by approximately 0.001 inch (0.0025 cm) on the 1/2-inch (1.27 cm) pellet length. The UO_2 pellets were unchanged in dimensions.

2. 800° C Sinter

The 800° C heat treatment also resulted in slight swelling of the $\text{UO}_2\text{-B}_4\text{C}$ pellets, whereas, the UO_2 pellets showed a consistent density increase from 5.30 to 5.40 g/cm³ - 48 to 49 percent of theoretical. These small but significant differences in the rate of densification appear to be related, in part, to the stoichiometry of the pellets.

3. 1000° C Sinter

The rates of densification for pellets of UO_2 , with and without B_4C addition, closely resembles that described for the 800° C sintered pellets. The $\text{UO}_2\text{-B}_4\text{C}$ pellets sintered to a relatively lower density than the UO_2 pellets (5.94 g/cm³ - 54 percent of theoretical *versus* 7.12 g/cm³ - 65 percent of theoretical). Weight losses were slightly greater (0.6 percent *versus* 0.4 percent) for the UO_2 pellets than for the $\text{UO}_2\text{-B}_4\text{C}$ pellets indicating probable retention of some of the released moisture and oxygen in the form of nonvolatile boron oxides in the pellets.

4. 1100, 1200 and 1250° C Sinters

The rate of densification of the UO_2 pellets continued to be about 15 percent greater than that for the $\text{UO}_2\text{-B}_4\text{C}$ pellets within the temperature range of 1100° to 1250° C. Weight losses for the $\text{UO}_2\text{-B}_4\text{C}$ pellets increased

sharply from 0.6 to 1.1 percent, as compared to a 0.7 to 0.8 percent increase for UO_2 pellets within the 1100° to 1250° C temperature range. All pellets were of excellent quality without visible evidence of cracks, ruptures or laminations. The molybdenum container showed deposits of a white glassy material at the location of the $\text{UO}_2\text{-B}_4\text{C}$ pellets and a dark brown discoloration adjacent to the UO_2 pellets. The white deposit was identified as B_2O_3 by x-ray diffraction. The dark brown deposit consists of two face-centered cubic structures of uranium dioxide of very nearly equal lattice parameters. The remainder of the pellet container, after each sintering test, remained bright metallic in appearance.

Twelve sintering tests were conducted on UO_2 pellets containing 1 w/o B_4C additions to investigate the mode of boron loss during sintering. The temperatures for sintering ranged from 350° to 1600° C. The boron contents in UO_2 pellets sintered in flowing argon and in vacuum environments are shown graphically in figure 3. As indicated, two distinct levels of total boron and soluble* boron contents were established at relatively low sintering temperatures (near 600° C) and remained essentially unchanged with temperature up to about 1200° C. Both sintering environments appeared to promote similar B_4C reactions and boron retentions within this range of temperatures. Evidence of oxidation of B_4C to form water soluble boron oxides in pellets sintered at 1200° C, in argon, is shown in figure 4. The partially oxidized angular particles of B_4C exhibited rounding of the edges with the formation of a surrounding reaction zone containing boron oxides.

* Those compounds which are water soluble have been identified as "soluble borons" for the purposes of this study and are included in the determination of total boron.

Figure 3. Boron Content (ppm) vs Sintering Temperature
 $\text{UO}_2 - 1 \text{ w/o } \text{B}_4\text{C}$

Specimen preparation which included extended polishing in water-abrasive mixtures had delineated the zone by dissolution of boron oxides and erosion of the highly porous UO_2 surrounding the B_4C particles. Additional specimens were prepared by polishing in kerosene-abrasive mixtures to avoid aqueous dissolution of boron oxides. No new information was obtained since the porous reaction zone appeared to be extremely friable and eroded rapidly during the preliminary polishing operations.

Losses of total boron and soluble boron increased rapidly as the sintering temperatures were extended above 1200°C with both furnace environments. Depletion of boron appeared to initially involve complete oxidation and loss of finer B_4C particles as well as partial oxidation of the larger particles of B_4C . This depletion of B_4C was confirmed by microscopic examinations which showed a decreasing amount of the finer B_4C particles with increasing sintering temperatures. Within this higher temperature range, the UO_2 - B_4C reaction started at 1200° to 1250°C (arrows in figure 4) and was complete at 1300° to 1350°C (figure 5) by formation of uranium tetraboride (UB_4). Finer particles of the UB_4 phase were found in the pellets sintered at lower temperature but were not found in pellets sintered above 1400°C , suggesting that boron losses took place by an oxidation and volatilization mechanism.

Sintering of UO_2 -1 w/o B_4C pellets for one hour in the 1400° to 1600°C temperature range resulted in approximately 50 percent retention of boron as a uniform dispersion of UB_4 with very similar particle size as that shown in figure 6. A view at higher magnification (figure 7) shows the detailed features of globular UB_4 particles containing a fine internal phase which is believed to be unreacted UO_2 .

6017

MAG 1000X

Figure 4. $\text{UO}_2\text{-I}$ w/o B_4C - 1200°C in Argon

6016

MAG 1000X

Figure 5. $\text{UO}_2\text{-I}$ w/o B_4C - 1300°C in Argon

6020

MAG 150X

Figure 6. $\text{UO}_2\text{-I}$ w/o B_4C - 1450°C in Argon

6018

MAG 1000X

Figure 7. $\text{UO}_2\text{-I}$ w/o B_4C - 1450°C in Argon
Higher Magnification View

Sinterability data on UO_2 , with and without B_4C additions, were evaluated to provide additional information on the mechanism of boron losses during sintering. The addition of 1 w/o B_4C retarded the densification of UO_2 at all sintering temperatures, as shown in figure 8. Optimum geometric densities of 8.45 g/cm^3 in vacuum and 8.75 g/cm^3 in argon were obtained by sintering at 1450°C .

UO_2 pellets, without boron additions, had consistently attained higher densities, reaching 10.0 g/cm^3 (91 percent of theoretical) in the 1400° to 1450°C temperature range in argon or vacuum. Diametral shrinkage of both types of pellets increased with increasing sintering temperature in direct relation to the pellet density (figure 9). Sintering in either furnace resulted in similar weight losses for UO_2 pellets containing B_4C (figure 10). UO_2 pellets without B_4C additions showed 0.9 and 5.5 percent weight losses, respectively, in argon and vacuum environments, as compared with the 1.9 percent weight loss for UO_2 -1 w/o B_4C pellets sintered under identical conditions in the two furnaces.

A single sintering test was conducted on UO_2 and UO_2 -1 w/o B_4C pellets by extending the time at 1300°C from 1 hour to 20 hours in the argon environment. The values for geometric density, diametral shrinkage and weight loss are included as individual data points in figures 8, 9 and 10. Density increases were approximately 4 percent (9.75 to 10.15 gm/cm^3) and 7 percent (8.35 to 8.90 gm/cm^3) for UO_2 and UO_2 - B_4C pellets, respectively. The diametral shrinkage and weight loss for the UO_2 pellets were unchanged or corresponded with a slight increase in densification. However, both weight loss (1.2 to 1.9 percent) and diametral shrinkage 15 to 17 percent) were higher for the UO_2 - B_4C pellets than for UO_2 pellets without B_4C additions. Boron analyses show 2500 ppm total boron and the complete absence

Figure 8. Density (g/cm³) vs Sintering Temperature (°C)
UO₂ - 1 w/o B₄C

Figure 9. Diametral Shrinkage (%) vs Sintering Temperature (°C)
 $\text{UO}_2 - 1 \text{ w/o } \text{B}_4\text{C}$

Figure 10. Weight Loss (%) vs Sintering Temperature ($^{\circ}$ C)
 UO_2 - w/o B_4C

of soluble boron. The retained boron was present as a uniform dispersion of the UB_4 phase in the relatively dense UO_2 matrix. The structure is similar to that shown in figure 6.

UO_2 - 1 w/o B_4C reactions were investigated over a range of temperatures by x-ray diffraction methods. There was no x-ray evidence of UO_2 - B_4C reaction for sintering temperatures up to about $1200^\circ C$. The pellets sintered at $1200^\circ C$ contained B_4C as a major constituent with trace amounts of the UB_4 phase. Pellets sintered at $1400^\circ C$ contained only UB_4 as the second phase. An earlier program (CEND-3107-306)⁽²⁾ had reported UB_4 formation from UO_2 - B_4C reaction by sintering at $1150^\circ C$ for a longer time of 25 hours in flowing helium. An increase in the sintering temperature to $1900^\circ C$ in argon showed UB_4 as a major reaction phase with minor amounts of the UB_2 phase. Figure 11 shows the duplex structure of the uranium boride particles in the $1900^\circ C$ sintered pellets. There was no evidence of the UB_2 phase by x-ray diffraction in the high-temperature sintered structure.

6186

MAG 1000X

Figure 11. Duplex Structure of Uranium Borides Formed at $1900^\circ C$ in Argon - UO_2 -1 w/o B_4C

Figure 12. Boron Content (ppm) vs Sintering Temperature ($^{\circ}$ C)
 UO_2 - 0.05 w/o B_4C

Figure 13. Density (g/cm^3) vs Sintering Temperature ($^{\circ}\text{C}$)
 $\text{UO}_2 - 0.05 \text{ w/o B}_4\text{C}$

5. UO_2 - 0.05 w/o B_4C

Boron retention as a function of sintering temperature in UO_2 pellets containing a nominal 0.05 w/o B_4C addition is shown graphically in figure 12. The initial boron content in the blended powder mixture was measured at 380 ppm (0.048 w/o B_4C) with nondetectable soluble boron oxides. Oxidation of B_4C by formation of boron oxides was detected chemically in pellets sintered at 600° C in argon, the lowest temperature for this series of tests. Undoubtedly significant oxidation would have occurred at still lower temperatures as had been demonstrated in the case of UO_2 pellets containing 1 w/o B_4C .

The total boron and soluble boron contents remained at essentially constant levels for sintering temperatures up to about 1200° C. Essentially identical B_4C reactions and boron losses as volatile compounds were observed in pellets sintered in either a vacuum or an argon furnace environment. The rapid decrease in boron contents for temperatures above 1200° C closely resembles the boron behavior in UO_2 - 1 w/o B_4C pellets sintered within the same temperature range. Here, again, approximately 50 percent of the boron was retained in pellets sintered for 1 hour in the 1400° to 1500° C region.

Those pellets sintered in the 1200° to 1500° C range using the 0.05 w/o B_4C addition densified as well as companion pellets not containing B_4C (figure 13). Pellets of UO_2 with and without B_4C additions showed very high losses in weight during sintering at temperatures above about 1200° C in the vacuum environment (figure 14). The increasingly higher weight losses with sintering temperature were followed by changes in the appearance of the interior surfaces of the tantalum containers. These surfaces remained

bright metallic for temperatures up to 1200° C and then were coated with increasingly thicker formations of reddish brown deposits at the higher temperatures. These deposits were identified as UO_2 by x-ray diffraction analysis. The exterior surfaces of the containers remained unchanged in appearance for all sintering tests. Sintering in argon resulted in low weight losses with a maximum value of 0.75 percent at 1400° C. The pellet containers retained their original metallic luster except for local deposition of UO_2 adjacent to the pellets.

The UB_4 phase appears as fine particles within the UO_2 matrix (figure 15). Because of the low boron concentration, the boron content in sintered pellets was based on chemical analysis. Metallographic examination was, therefore, limited to selected pellets to compare the uniformity of boron distribution.

6311

MAG 1000X

Figure 15. Structure Formed By Sintering at 1300° C
in Argon - UO_2 -0.05 w/o B_4C

C. Hydrogen Sintering

The influence of various furnace environments and sintering temperatures on hydrogen pretreated UO_2 containing 0.015 w/o B_4C (Blend C_R), is shown in figure 16. Boron retentions of 60 to 75 percent were achieved in argon and in vacuum. Sintering at temperatures above 1400°C resulted in a pellet density of 10.0 g/cm^3 (91 percent T.D.). Use of a duplex sintering environment involving heatup in argon to 1325°C and cooling in argon - 10 v/o hydrogen did not improve the boron retention. The O/U ratios of both argon sintered and argon sintered plus argon - 10 hydrogen cooled pellets ranged from 2.01 to 2.03. Sintering in vacuum at 1425°C and at 1600°C resulted in 75 ppm and 90 ppm boron retentions (62 and 75 percent). The reason for the high losses of boron (67 percent) in pellets sintered at 1300°C is not known.

The soluble boron content, in the form of boron oxides, for six sintered pellets from Blend C was less than 10 ppm. Microscopic examinations confirmed that the relative amount of the B_4C and UB_4 in the pellets were in agreement with the chemical analyses. Fine particles of the UB_4 phase were uniformly dispersed in the UO_2 matrix. All pellets were free of fissures, cracks, chips or significant distortion which may have resulted from the sintering process.

Sintering data on pellets of Blend D_R prepared in an identical manner as Blend C_R except for the higher boron content (900 ppm *versus* 120 ppm) are shown in figure 17. Excessive boron losses occurred for all combinations of sintering temperature and environment tested. The boron analyses are included in table II and plotted in figure 17. Sintering in the 1300° to 1400°C temperature range resulted in total boron retentions of 20 to 30 percent in

Figure 16. Sintering Data for Blend C_R

Figure 17. Sintering Data For Blend D_R

argon, 5 to 20 percent in the duplex environment and 40 percent in vacuum. The large losses of boron were substantiated by microscopic examination which showed trace amounts of the UB_4 phase and numerous voids resulting from B_4C oxidation and subsequent volatilization of boron oxides. These voids are responsible for the low pellet densities which ranged from 8.75 g/cm^3 to 9.60 gm/cm^3 (79.4 to 87.5 percent T.D.) for sintering temperatures of 1300° to 1400° C . The high boron losses for all sintering conditions were unexpected and cannot be explained on the basis of the available information.

The effect of the reducing environment during the heatup portion of the sintering cycle for Blend E pellets is shown in figure 18. Boron content and sinterability data are plotted against the maximum temperatures to which the pellets were heated in the reducing (argon - 10 hydrogen) environment. This temperature is identified as the "maximum reducing temperature" to distinguish it from other sintering temperatures involving argon or vacuum environment.

Some interesting trends were observed on the extent of boron retention as a result of the use of hydrogen for temperatures where B_4C can oxidize readily and form volatile reaction products. Approximately 15 percent of the total boron was lost for "maximum reducing temperature" of 500° , 900° and 1000° C . Use of hydrogen at the upper temperature range of 1200° and 1300° C resulted in higher losses of boron. Pellet densities decreased from 10.10 gm/cm^3 (92.3 percent T.D.) to 9.80 gm/cm^3 (89.3 percent T.D.) as the "maximum reducing temperature" was increased from 500° to 1200° C . Use of hydrogen at 1300° C resulted in a sharp decrease in pellet density to 8.50 g/cm^3 (77.5 percent T.D.) in direct relationship with the large loss of boron for this test. The constant weight loss, shown in figure 18, is due to similar losses of adsorbed moisture, excessive oxygen and other volatile constituents in the Blend E

* Data Points for Cases Where Hydrogen Was Not Used During Heatup (○ , □) Are Plotted At the Sintering Temperature

Figure 18. Sintering Data for Blend E

powder for the same sintering temperature of 1300° C.

The high boron losses for "maximum reducing temperature" above 1000° C may involve the formation of other volatile reaction products, possibly boranes (B_xH_y) as well as boron oxides. The identity of these additional species was considered beyond the scope of this program.

Pellets prepared from the original blend of as-received UO_2 and 1 w/o B_4C were sintered with some of the batch E pellets to compare current data with those previously reported on boron retention and sinterability. The current results, shown in figure 19, include "maximum reducing temperature" of 500° to 1200° C and a sintering temperature of 1300° C in argon, as well as two additional tests at "maximum reducing temperature" of 1000° and 1200° C and argon sintering at 1400° C. These data indicate that boron losses under the present sintering conditions are comparable to boron losses in earlier tests reported in CEND-3107-328. These results indicate that the presence of hydrogen during heatup to temperatures up to 1200° C did not significantly affect the amount of boron retention. Soluble boron phases constituted approximately 25 percent of the total boron, in agreement with data from argon or vacuum sintering. The constancy of pellet density, shrinkage and weight loss over the range of "maximum reducing temperature" is due to the dependency on sintering temperature.

The high B_4C content in pellets of Blend A made it convenient to study the behavior of B_4C with "maximum reducing temperature". Pellets heated in argon - 10 percent hydrogen at temperatures of 500° to 1200° C and sintered at 1300° C in argon showed essentially identical UO_2 microstructures containing about 80 percent UB_4 and 20 percent unreacted B_4C particles. The B_4C particles were angular to rounded in appearance and were surrounded by

Figure 19. Sintering Data for Blend A

a porous zone. Figure 20 shows two angular B_4C particles surrounded by highly porous regions and an incompletely formed UB_4 phase from the UO_2-B_4C reaction. Those pellets which were preheated in hydrogen and sintered in argon at $1400^\circ C$ contained only the UB_4 phase in the UO_2 . Similar observations for pellets of the same powder blend and sintered at 1300° and $1400^\circ C$ in argon or in vacuum were reported previously.

6187

MAG 500X

Figure 20. B_4C Particles and UB_4 Reaction Phase

D. CO - CO₂ Sintering Studies

All CO - CO₂ tests were conducted under identical conditions of pellet heatup, cooldown and time at temperature to study boron retention *versus* CO - CO₂ composition. The results of these tests are included in figure 21 for

Figure 21. Sintering Data for Runs Using CO - CO₂

UO₂ pellets containing 120, 180 and 650 ppm boron. Pellets starting with 120 ppm boron, as B₄C, retained approximately 50 percent of the initial boron for all CO - CO₂ sintering atmospheres. Pellets with 180 ppm and 650 ppm boron showed similar patterns of decreasing boron retentions with increasing percentage of CO. Pellets with the higher boron loading retained approximately 50 percent boron for both the 10 CO - 90 CO₂ and 30 CO - 70 CO₂ atmospheres and decreased to 20 to 30 percent boron retentions for the 50 CO - 50 CO₂ and the 100 percent CO atmospheres. The rate of boron loss was the greatest for the 650 ppm boron pellets as shown in figure 21. The increasing rates of boron loss with increasing CO content for the 650 ppm boron pellets were verified by the presence of angularly shaped voids which are believed to be prior sites of B₄C particles removed by oxidation and volatilization during sintering.

A comparison of the data for sintered pellets of Blend C and Blend E compositions shows that removal of moisture and excess oxygen from the UO₂ powder in Blend C by hydrogen treatment was not effective in improvement in boron retention for this range of B₄C additions. The higher weight losses for Blend E pellets are due to removal of moisture from the as-received UO₂ powder used in the preparation of this UO₂-B₄C blend. Due to sintering at the same temperature of 1400° C, pellets of the three boron contents showed essentially identical sinterability for the range of CO - CO₂ atmospheres. All pellets were similar in appearance with no evidence of cracks or fissures due to the sintering process.

VI. DISCUSSION OF RESULTS

The oxidation behavior of B_4C was investigated for temperatures ranging from 325° to 1600° C on UO_2 - 1 w/o B_4C pellets containing intentional amounts of moisture and oxygen. Oxidation reactions involving B_4C were observed at all test temperatures and had significant effects on sinterability and on the final composition of the pellets. It is shown in figure 3 that 1500 and 2100 ppm boron, as boron oxides, are formed at 625° and 1000° C with insignificant losses by volatilization at these temperatures. This reaction was also observed in the microstructures by a rounding of the B_4C particles with a surrounding zone of water soluble reaction products. At temperatures above 1000° C total boron losses increased rapidly. This conclusion is based on chemical analysis, higher weight losses in sintering and condensation of B_2O_3 on the molybdenum containers. However, pellets sintered at the higher temperatures also contained 1500 to 2100 ppm boron as boron oxides. The data in figure 3 indicated that over the 625° to 1250° C temperature range the concentration of the intermediate reaction product, boron oxides, can remain essentially constant for a long time while the initial B_4C content and boron losses vary considerably. Accordingly, boron losses are reflected by decreasing amounts of total boron (included as B_4C) with increasing temperature or by extended time at a specific temperature until all B_4C is converted into boron oxides.

The UO_2 - B_4C reaction appeared to have been completed after 1 hour at 1300° C with 4500 ppm boron in the form of the UB_4 phase. Sintering at 1300° C for 20 hours further reduced the amount of the UB_4 phase, by about 50 percent, to 2500 ppm boron. Chemical analyses showed a complete absence of boron oxides, indicating that the rate of boron losses exceeded the oxida-

tion rate of UB_4 . Sintering at the upper temperature range of 1400° to 1600° C resulted in apparent equilibrium levels of 3000 to 4000 ppm boron, as UB_4 , and 500 ppm boron, as boron oxides.

The boron data in figure 12 show similar oxidation behavior for UO_2 pellets with 0.05 w/o over a range of sintering temperatures. The relatively higher rate of oxidation for the 0.05 w/o B_4C pellets was attributed to a more complete reaction of very finely comminuted B_4C particles in the milled powder mixture. This observation was based on metallographic examinations which showed a gradual disappearance of finer particles of B_4C with increasing temperature. On this basis, a UB_4 phase of very nearly equal particle size was formed by UO_2 reaction with the unoxidized portions of the largest B_4C particles at temperatures above 1200° C. Approximately 50 percent of the total boron remained as the UB_4 phase in pellets sintered at 1300° to 1500° C.

There was no metallographic evidence relating to the possible oxidation of UB_4 . This observation was based on the appearance of the sharply delineated particles without any indication of reaction zones present within the porous UO_2 matrix (figures 7 and 9).

The boron oxides did not appear to volatilize at a significant rate for temperatures up to 1200° C, as indicated by the constant levels noted for soluble boron and total boron contents in figures 3 and 12. The highly volatile nature of these oxides at elevated temperatures rapidly reduces the total boron within the pellets. Evidence of boron transport was confirmed by x-ray diffraction identification of MoB and MoB_2 reactions of boron oxide vapors with the molybdenum containers and also from condensed B_2O_3 on the cooler surfaces of the furnace tube.

The experimental work conducted under this program has been unsuccessful in retaining usable boron levels by sintering B_4C with UO_2 . High losses make it necessary to start with excess B_4C to retain the desired 200 to 500 ppm. When these excess quantities oxidize and volatilize they make it difficult to achieve usable densities (greater than 90 percent theoretical density). Even if the retention and density levels could be improved, reproducibility of the process has not yet been established. Changes in composition, sintering temperature, furnace environment, powder treatment and other sintering parameters were not sufficient to provide a reproducible process.

These data form the basis for the proposed mechanism for boron losses in UO_2 pellets during sintering in environments containing oxygen or moisture. The following reactions are involved:

- a) Water-soluble boron oxides are formed by oxidation of B_4C by adsorbed moisture and excess oxygen in the UO_2 . Significant volatilization of boron oxides does not take place until a temperature of $1200^\circ C$ is reached, resulting in essentially constant levels of boron oxide formation.
- b) Increasingly higher boron losses occur at temperatures above $1250^\circ C$ from volatilization of boron oxides from the UO_2 pellets. Further oxidation of B_4C and UB_4 continues by reaction with oxygen released from the UO_2 at the elevated temperatures. A residual boron level is reached in UO_2 pellets sintered for 1 hour at temperatures of 1400° to $1600^\circ C$ utilizing essentially stoichiometric UO_2 (O/U ratio of 2.01 to 2.02) in an inert environment.

The use of vacuum-outgassing accompanied by the several hydrogen reduction schemes or by the use of $CO - CO_2$ atmospheres was not successful in im-

proving boron retention in sintered UO_2 pellets. It is speculated that high purity furnace environments and a clean furnace system may be inadequate to avoid B_4C oxidation due to the unavoidable accumulation of oxidants from several different sources. These sources may include the following:

- 1) Formation of CO_2 and/or CO from UO_2 - B_4C reaction with release of oxygen from the UO_2 at temperatures above 1250°C . Large losses of boron were observed at the temperature for UO_2 - B_4C reaction;
- 2) Residual trace amounts of moisture, oxygen and CO_2 in the purified gases;
- 3) Reduction of oxides or release of adsorbed oxygen on the interior surfaces of the furnace system at elevated temperatures.

The combined quantities of oxygen from all sources at the elevated temperatures may be adequate to reduce the boron content to less than one-half of the initial amount prior to formation of the more oxidation resistant UB_4 phase in the densely sintered UO_2 structure. Some of these sources of oxygen appear to be a part of the sintering cycle and are peculiar to the chemical properties of UO_2 and B_4C . On this basis, prevention of oxidation of B_4C in UO_2 is impractical using the methods studied and, accordingly, more novel sintering methods for incorporating B_4C in UO_2 must be investigated.

VII. SUMMARY

A. Pellets containing 0.05 w/o and 1 w/o B_4C exhibited similar oxidation behavior over the range of sintering temperatures (1300° to 1600° C) in argon and vacuum environments. Boron oxides formed from B_4C oxidation by adsorbed moisture and excess oxygen in the UO_2 remained stable at temperatures up to 1200° C to form essentially constant levels of soluble and total boron contents. At the higher sintering temperatures of 1300° C and 1600° C, rapid volatilization of boron oxides in both compositions of pellets reduces the total boron levels to about 50 percent of the initial values.

B. The poor sinterability of UO_2 -1 w/o B_4C pellets is attributed to the presence of boron oxides as liquid or vapor phases at all sintering temperatures. However, low concentrations of boron oxides in the UO_2 -0.05 w/o B_4C pellets did not adversely affect sinterability, resulting in pellet densities of 90 to 93 percent of theoretical for temperatures above 1300° C.

C. Retention of boron, chiefly as UB_4 , is attributed to the nonoxidizing conditions of essentially stoichiometric UO_2 in an inert environment existing at temperatures above about 1400° C.

D. The UB_4 phase is formed by a UO_2 - B_4C reaction at temperatures between 1250° and 1300° C. A further reaction involves the formation of the UB_2 phase at temperatures above 1500° C. The uranium borides appear as uniform dispersions in the sintered UO_2 pellets.

E. It is hypothesized that boron losses involve consecutive reactions by which B_4C is oxidized initially to form boron oxides which are then lost as volatile products from the pellets.

F. Use of hydrogen as part of the powder mixture preparation or sintering process resulted in the following:

- 1) Pellets prepared from hydrogen reduced UO_2 and containing 120 ppm boron, as B_4C , retained 60 to 75 percent of the initial boron content in high density UO_2 pellets. Sintering conditions included argon or vacuum environments for temperatures up to 1600°C ;
- 2) Pellets prepared from hydrogen reduced UO_2 but containing a higher boron content of 650 ppm boron, as B_4C , exhibited high losses of boron for all sintering temperatures and all furnace environments (argon, vacuum or hydrogen);
- 3) Pellets prepared from as-received UO_2 and 180 ppm boron, as B_4C , showed high losses of boron during sintering cycles involving heatup in hydrogen, sintering at 1300°C in argon, and cooling in hydrogen. Boron losses in excess of 50 percent may have involved the formation of volatile hydrogen-boron species (boranes or oxyboranes as well as boron oxides);
- 4) Sintering at 1400°C in several $\text{CO} - \text{CO}_2$ atmospheres resulted in boron losses greater than 50 percent.

G. A reproducible process for retaining B_4C during sintering of $\text{B}_4\text{C}-\text{UO}_2$ pellets was not demonstrated. Boron losses were not predictable; therefore, adequate makeup in the initial compositions could not be provided.

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APPENDIX A

ANALYTICAL METHODS

A. CHEMICAL ANALYSES

Soluble boron and total boron contents in $\text{UO}_2\text{-B}_4\text{C}$ pellets are determined spectrophotometrically using the colored quinalizarin complex.

1. Soluble Boron Procedure

The sintered pellet is crushed with a steel mortar and pestle to minus 325-mesh particle size. The powdered sample is reacted in a 0.1 N sodium hydroxide solution for 2 hours. The filtrate from this solution is diluted to 500 milliliters in a volumetric flask. Aliquots of this volume are transferred to a 50-milliliter flask containing 5 milliliters of quinalizarin and the volume increased to 50 milliliters with concentrated H_2SO_4 ; the color is allowed to develop over a 1/2-hour period. Boron content is determined in a spectrophotometer by comparing absorbance with that of standard boron solutions.

2. Total Boron Procedure

The powdered $\text{UO}_2\text{-B}_4\text{C}$ pellet is fused with potassium persulfate in a quartz flask at 300°C and dissolved in water. The solution is made up to 500 milliliters in a volumetric flask and aliquots containing quinalizarin are analyzed spectrophotometrically by the method described for soluble boron analysis.

3. O/U Ratio

The oxygen-to-uranium ratio is determined by the pyrogravimetric method. The uranium dioxide pellet is ignited to U_3O_8 by heating for 3 hours at 1000°C in air furnace.

B. MICROSTRUCTURE

The pellets are contained in epoxy resin mounts and sectioned diametrically for surface preparation. Following rough polishing with a series of silicon carbide papers (80-, 240-, 400-, and 600-grit), the pellet surface is vibratory polished for 4 hours using a water slurry containing 0.3 micron γ - Al_2O_3 abrasive and for 16 hours with 0.05 micron α - Al_2O_3 abrasive. Examinations are conducted at magnifications to 1000X on the unetched specimens for B_4C or boron reaction products. Photomicrographs of selected microstructures are usually taken at 250X or 500X.

C. X-RAY DIFFRACTION

A small fragment representative of the surface or interior of the pellet is finely ground and mounted on a glass fiber for exposure of Debye-Scherrer patterns. The d-spacings are compared with those on ASTM cards for identification of the constituents in the pellets. The method is insensitive to constituents of less than about 5 w/o, requiring concentration of boron compounds by dissolution of the uranium dioxide in nitric acid. Variations in the stoichiometry of the uranium dioxide pellets are determined from changes in the lattice parameters.

APPENDIX B

The data shown in figures 3 and 12 can be explained on the basis of consecutive reactions in which B_4C is oxidized to water-soluble boron oxides. These intermediate reaction products are subsequently lost by volatilization from the UO_2-B_4C pellets. Consider the following consecutive reactions:

where:

K^1 and K^2 are rate constants for the reactions;

$B_{x/y}O(c)$ represents water-soluble boron oxides;

$B_2O_3(g)$ represents the boron lost from the pellets.

After time "t" during which "X" moles of $B_{x/y}O(c)$ have been formed and "Y" moles of $B_{x/y}O(c)$ have volatilized, the concentrations of the various compounds are:

$$[B_4C]_f = [B_4C]_i - X$$

$$B_{x/y}O(c) = X - Y$$

$$B_2O_3(g) = Y$$

where: $(B_4C)_i$ = initial concentration

$(B_4C)_f$ = final concentration

The rate laws for these products are given by:

$$-\frac{d}{dt} B_4C = K^1 [(B_4C)_i - X] \quad \text{disappearance of } B_4C$$

$$+\frac{d}{dt} B_{x/y}O(c) = K^1 [(B_4C)_i - X] - K^2 [B_2O_3(g)] \quad \text{production of } B_{x/y}O(c)$$

$$+\frac{d}{dt} B_2O_3(g) = K^2 [B_{x/y}O(c)] \quad \text{boron loss}$$

These differential equations can be solved to give the boron loss at any time "t" as follows:

$$B_{x/y}O(c) = [(B_4C)_i] \left[K^2 (1 - e^{-K^1 t}) \right] - K^1 (1 - e^{-K^2 t}) / K^2 - K^1$$

A plot showing the concentrations of these species with time when the rate constants are in the ratio $\frac{K^1}{K^2} = 2$ is shown in figure B-1.

While this development assumes constant time or temperature as the independent variable, a similar plot results if the time is held constant and the rate constant is considered as a function of temperature. The figure below shows a relatively constant level of soluble boron in the UO_2 pellets over a fairly wide range of sintering temperatures. Therefore, ...

Figure B-1. Time or Temperature