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RESEARCH AND DEVELOPMENT PROGRAM

BURNABLE POISON ADDITIONS TO UO_2

For the Period:
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DIVISION

COMBUSTION ENGINEERING, INC.

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TID-4500, 50th Edition

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JOINT UNITED STATES
ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT PROGRAM

BURNABLE POISON ADDITIONS TO UO_2

Prepared by:

G. Zuromsky
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For the Period:

May 1 to September 30, 1967

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BURNABLE POISON ADDITIONS TO UO_2

TABLE OF CONTENTS

	<u>Page No.</u>
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	vi
I. INTRODUCTION	1
II. SURVEY OF PREVIOUS WORK	3
III. EXPERIMENTAL PROCEDURE	5
A. Assessment of Startup Materials	5
B. Milling and Blending Studies	5
C. Sintering Studies	6
IV. RESULTS	9
V. DISCUSSION	14
VI. SUMMARY	18
VII. WORK PLANNED FOR THE NEXT REPORTING PERIOD	19
REFERENCES	20
APPENDIX A	22
APPENDIX B	24

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
1	Properties of Starting Materials	21

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Following Page No.</u>
1	Sinterability Data on UO_2 Pellets in Vacuum Environment	25
2	Sinterability Data on UO_2 and UO_2 -1 w/o B_4C Pellets in Argon Atmosphere	25
3	Microstructure of UO_2 -1 w/o B_4C Pellets Sintered at 1100°C in Argon	25
4	Microstructure of UO_2 -1 w/o B_4C Pellets Sintered at 1250°C in Argon	25
5	Uranium Borides (Arrows A) and Unreacted B_4C (Arrows B) in UO_2 -1 w/o B_4C Pellets Sintered at 1250°C in Argon	25
6	Another View of Uranium Boride (Arrows A) and Unreacted B_4C (Arrows B) in 1250°C Sintered Pellets	25
7	Chemical Analyses of Argon Sintered UO_2 -1 w/o B_4C and UO_2 Pellets	25

BURNABLE POISON ADDITIONS TO UO_2

By

G. Zuromsky and S. S. Christopher

ABSTRACT

Studies have been conducted on UO_2 -1 w/o B_4C pellets sintered at 625°C to 1250°C in argon to investigate the oxidation behavior of B_4C and mode of boron losses. The uranium dioxide powder initially contained 2000 ppm adsorbed moisture and excess oxygen (O/U ratio = 2.16). The data indicated that boron losses involved consecutive reactions by which B_4C was partially oxidized to form intermediate boron oxides at all sintering temperatures. The boron oxides were subsequently removed as volatile products from the pellets. A UO_2 - B_4C reaction was initiated at 1200°C by the formation of uranium boride (UB_4). Changes in the microstructures of pellets sintered over the range of temperatures provided an insight into the manner of B_4C oxidation and the nature of boron losses during the sintering process. It is concluded that a dry, oxygen-free sintering atmosphere is a basic requirement for the preparation of high density UO_2 pellets containing controlled amounts of boron.

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 burnable poisons in UO_2 fuel elements. Prior⁽¹⁾ work on the program had developed vibratory powder 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 ($2500 - 2700^\circ\text{C}/\text{cm}$) without significant axial redistribution of boron. Two 6% enriched 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 specific powers 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 on η_f (ratio of neutrons produced to thermal neutrons adsorbed) and $\Delta\rho$ (difference in reactivity of the core) from the THERMOS program.

It was demonstrated by ex-reactor tests in dynamic and static systems the UO_2 and B_4C react to form UB_4 and CO_2 . 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 fuel elements irradiated in the Saxton reactor.

The present program is concerned with the development of methods for

incorporating B_4C in high density UO_2 pellets by cold pressing and sintering techniques. These studies will include sintering in argon, in argon-hydrogen and in CO/CO_2 atmospheres at temperatures near $1500^\circ C$. The initial study, currently in progress, is investigating the oxidation behavior of B_4C and the mechanisms involved in boron losses during sintering. Results on preliminary tests in this area are included in this report. The major effort will involve the evaluation of powder preparation and sintering atmosphere for UO_2 pellets containing a nominal content of 0.05 w/o B_4C .

A second phase of the program will investigate the compatibility of sintered UO_2-B_4C pellets with Zircaloy-4 cladding materials. The cladding studies will be performed at $750^\circ F$ ($399^\circ C$) and with fuel centerline temperatures near the melting point in a closed system. UO_2-B_4C compatibility will be evaluated by x-ray diffraction, metallography and electron probe analysis, if it is deemed necessary. Although axial boron migration is unlikely (on the basis of ex-reactor and in-reactor test results which have preceded this portion of the program), a cursory evaluation will be made of axial migration in rods made with UO_2-B_4C pellets.

II. SURVEY OF PREVIOUS WORK

Many attempts ^(3,4,5) have been made to incorporate burnable poisons in UO_2 pellets with reported excessive or erratic losses of boron during sintering in hydrogen, helium or hydrogen-nitrogen atmospheres. Limited success ⁽⁶⁾ has been reported for high density UO_2 pellets containing up to 120 ppm boron, added as boron oxide (B_2O_3), by sintering at 1325°C in argon followed by reduction in hydrogen at the same temperature and cooling in hydrogen. Work at Mitsubishi Atomic Power Industries ⁽⁷⁾ showed that ZrB_2 can be utilized in both vibratory powder compacted rods and in pressed and sintered UO_2 pellets. Another method ⁽⁸⁾ has successfully retained ZrB_2 particles (50 - 100 μ) in UO_2 pellets by heating to 450°C in hydrogen and then sintering in vacuum at $1600 - 1650^\circ\text{C}$ for 2 hours. However, irradiation ⁽⁹⁾ of UO_2 containing ZrB_2 has resulted in gross axial movement of the boron.

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 , B_4C , B_2O_3 , ZrB_2) with subsequent volatilization of the reaction products. Accordingly, residual amounts of oxygen and moisture under dynamic furnace conditions may completely convert a several hundred ppm boron compound into volatile products before significant densification can take place. For this reason, these reactions involving trace amounts of the constituents may occur undetected under normal sintering conditions. Retention of boron in sintered UO_2 pellets must necessarily start with the removal of oxidants (O_2 , H_2O , CO_2 , reducible oxides) from the powder starting materials, furnace atmospheres and the furnace

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

It is reported that boron carbide (B_4C) is thermally stable 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:

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 to react B_4C 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 from thermodynamic data.

III. 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 to determine the requirements for preparing homogeneous mixtures of the two powders for sintering studies. Properties and major impurities reported for the two starting materials are shown in Table I.

Sieve analyses on the 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, irregular shaped, particles. The as-received powder contained 2000 ppm moisture and an 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 serves the dual purpose of reducing the agglomerated powder to a finer particle size and to uniformly blend B_4C additions with the oxide fuel. The operation is performed in U.S. Stoneware,

*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.

rubber lined steel jars of one quart capacity with "Borundum," high density alumina cylinders, 1/2 inch in diameter and 1/2 inch in length, as the grinding media. The initial batch of UO_2 powder was dry milled without additions of organic binders for four hours for the sinterability studies. Results of these studies are discussed in the next section of this report. A batch of 600 grams of UO_2 containing 1 w/o boron carbide was dry milled for 21 hours for use in the preparation of test pellets. One w/o B_4C was used in lieu of 0.05 w/o B_4C to facilitate chemical analyses. Boron analyses on samples of the powder following 1, 3, 7, 15 and 21 hours milling time showed that a minimum of 7 hours is required to provide a homogeneous blend of a mixture of the two powders. A second batch of UO_2 powder without boron carbide was dry milled continuously for 21 hours for use in the preparation of control pellets for the $\text{UO}_2\text{-B}_4\text{C}$ sintering studies.

C. Sintering Studies

The sintering behavior of the four-hour milled UO_2 , without boron carbide additions, was investigated by heating in argon and in vacuum at temperature to 1600°C . Pellets, 1.00 cm in diameter by 1.27 cm in length, were compacted at 7 tsi in a hardened steel die to a density of 5.10 g/cm^3 (47 percent of theoretical). For these studies, the milled powders were left intentionally in the non-stoichiometric condition with adsorbed moisture to compare densification, structure and O/U ratio with subsequent pellets that were prepared from dry, stoichiometric UO_2 powder. A group of six pellets was placed in a tantalum container and heated in purified argon in a tantalum resistance furnace at a rate of $300^\circ\text{C}/\text{hour}$ to 1200°C , held at temperature for one hour and then cooled overnight to room temperature. All pellets of the

first sinter were irregular in shape with essentially no densification in 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 pellets. A second group of six pellets was outgassed initially at 900°C for one 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. Densities ranged from 8.66 to 8.80 g/cm^3 (79-80 percent theoretical). Vacuum outgassing of the third group of pellets was increased to four hours at 900°C followed by sintering at 1200°C and cooling in argon. Formation of a thin film of the white oxide on the bottom of the tantalum container was evidence that all moisture as well as a substantial portion of the excess oxygen had been removed from the UO_2 powder during the four-hour vacuum treatment at 900°C . Pellets from the second and third sinters were identical in densities and in appearance.

An additional sintering study was conducted on five groups of pellets compacted from the four-hour milled powder with the objective of obtaining information on stoichiometry (O/U ratio), structure and densification behavior by sintering in vacuum at temperatures between 750°C and 1600°C . As previously, the pellets were compacted at 7 tsi to a density of 5.10 g/cm^3 (47 percent of theoretical). Six pellets were sintered in the tantalum container at each temperature. The furnace temperature was increased at a rate of not greater than $200^\circ\text{C}/\text{hour}$ to maintain a pressure of about 2×10^{-5} microns for continuous outgassing of moisture and oxygen from the pellets during heatup to the sintering

temperature. The low furnace pressure and slow heating rate were effective in the removal of moisture and oxygen, resulting in the complete absence of oxidation of the tantalum container for all sintering temperatures. These data will be useful in establishing the furnace pressure-temperature limits for providing moisture-free and excess oxygen-free pellets of $\text{UO}_2\text{-B}_4\text{C}$ mixtures for sintering experiments in argon or CO/CO_2 atmospheres.

The third sinterability test was conducted on $\text{UO}_2\text{-1 w/o B}_4\text{C}$ pellets to investigate the influence of adsorbed moisture and hyperstoichiometric UO_2 on the mode of B_4C oxidation and the extent of losses by volatilization during sintering over a range of temperatures. A further objective was to determine the maximum temperature at which B_4C would remain stable in a furnace environment of flowing argon. Purified argon was used as the sweep gas, with the intent to initially remove the "freed" moisture and oxygen from the pellets and to provide an inert sintering atmosphere at the elevated temperatures. Since boron losses would occur at an uncontrolled, rapid rate at normal UO_2 sintering temperatures, a range of lower temperatures was selected for this study, at which negligible or partial oxidation and loss of boron would take place.

A silicon carbide resistance furnace was modified to contain an Inconel tube with 1 1/2 inch (3.80 cm) ID for ease of cleaning between each sintering run. Prior to each sintering run, the furnace tube interior was cleaned by stainless steel wire brushing, water rinsing and drying with acetone. A gas purification system including a DeOxo unit and a magnesium perchlorate trap to remove trace impurity gases and moisture was used for the current and subsequent tests. Each sintering run included four $\text{UO}_2\text{-B}_4\text{C}$ pellets and three UO_2 control pellets.

The pellets were positioned on a curved molybdenum sheet to fit the Inconel tube with a UO_2 pellet located at either end and one pellet centered within the row of four $\text{UO}_2\text{-B}_4\text{C}$ pellets. The pellets were located within the midsection of the furnace and argon gas was flowed for about 1/2 hour to displace the air within the furnace tube prior to heatup. The furnace was heated within 2 hours to the sintering temperature, held at temperature for one hour and cooled overnight to room temperature. A constant flow rate of dry argon was maintained within the furnace tube during the entire sintering cycle. The pellets were measured for dimensional and weight changes. The $\text{UO}_2\text{-B}_4\text{C}$ pellets were analyzed for both soluble and total boron contents and the UO_2 pellets for O/U ratio. Selected pellets were also evaluated for microstructure and for crystal structure.

Brief descriptions of the analytical methods used on the program are included as Appendix A.

IV. RESULTS

The sinterability data for vacuum sintered UO_2 pellets are shown graphically in Figure 1. Pellet densification as represented by bulk density (Figure 1a) and by diametral shrinkage (Figure 1b), had initiated at about 750°C and progressed at a nearly linear rate with temperature, up to about 1200°C. Further densification continued at a reduced rate as the sintering temperature was increased from 1200°C (9.30 g/cm³-85% of theoretical) to 1600°C (10.10 g/cm³-92% of theoretical). A weight loss of 0.3-0.4 percent for pellets heated at temperatures up to about 1100°C is due chiefly to the removal of adsorbed moisture along with other volatile constituents in the UO_2 powder. The increasingly higher weight losses at temperatures above 1200°C are due

to volatilization of UO_2 at a furnace pressure of 2×10^{-6} microns. Figure 1d shows that significant losses of oxygen begin above 1200°C with the attainment of essentially stoichiometric UO_2 at temperatures between 1300°C and 1400°C in high vacuum.

The sintering behavior of UO_2 pellets with 1 w/o B_4C and without B_4C additions for a range of temperature from 625°C to 1250°C , is described below. 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 UO_2 and UO_2 -1 w/o B_4C pellets sintered at the six temperatures are presented below.

A. 625°C Sinter

All pellets remained unchanged in appearance following the low temperature treatment in flowing argon. Both UO_2 and UO_2 - B_4C pellets had retained the light brown color of the as-compacted powders. Micrometer measurements showed that the UO_2 - B_4C pellets had swelled slightly 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. There was no evidence of oxidation of the molybdenum container from released moisture in the pellets.

B. 800°C Sinter

The 800°C heat treatment also resulted in slight swelling of the UO_2 - B_4C pellets, whereas, the UO_2 pellets showed a consistent density increase from 5.30 to 5.40 g/cm^3 - 48 to 49 percent of theoretical. These small but significant differences in the rate of densification appear to be related, in part, to color changes of the pellets and in the surface appearance of the molybdenum container. The UO_2 - B_4C pellets

were uniformly tan in color both on the surface and throughout the interior, whereas, the UO_2 pellets were dark grey, typical of the sintered oxide. The molybdenum container exhibited a blue oxide discoloration within the immediate region of the UO_2 pellets but remained bright metallic at the locations of the $\text{UO}_2\text{-B}_4\text{C}$ pellets.

C. 1000°C Sinter

The pattern of color changes and rates of densification for pellets of UO_2 , with and without B_4C addition, closely resembles that noted for the 800°C pellets. The $\text{UO}_2\text{-B}_4\text{C}$ pellets were tan colored and sintered to a relatively lower density than the UO_2 pellets (5.94 g/cm^3 54 percent of theoretical vs 7.12 g/cm^3 = 65 percent of theoretical). Weight losses were slightly greater (0.6 percent vs 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 non-volatile boron oxides in the pellets. Similar appearing regions of blue-to-grey surface oxidation was observed on the molybdenum container at location of both UO_2 and $\text{UO}_2\text{-B}_4\text{C}$ pellets.

D. 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 1100-1250°C. The pellets were typically tan or dark grey in color for the two compositions, as noted for the lower temperature sintered pellets. 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 1100-1250°C temperature range. All pellets were of excellent quality without visible evidence of cracks, ruptures or laminations. The molybdenum container showed increasingly

thicker 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.

The furnace Inconel tube limits the maximum operating temperature to about 1250°C . These sintering studies are being extended to 1500°C in flowing argon using a high density, stabilized ZrO_2 tube in the same furnace.

Microstructural examinations of polished sections of argon sintered pellets provided additional information on the nature of B_4C oxidation and on $\text{UO}_2\text{-B}_4\text{C}$ reactions at the elevated temperatures. Figure 3 shows the B_4C constituent in the UO_2 , both as unreacted angular particles and as partly reacted rounded particles (Arrows A). The eroded regions surrounding the reacted particles are believed to have been zones containing boron oxides which had been dissolved during extended polishing of the specimens in the water-abrasive mixtures. The loss of B_4C by oxidation appear to be qualitatively comparable with chemical analyses, of approximately 20 percent conversion into boron oxides.

$\text{UO}_2\text{-B}_4\text{C}$ pellets sintered at 1200°C in argon were identical in structure to that of Figure 3, except for trace amounts of a metallic-like phase. More extensive formation of the new phase was found in the 1250°C sintered pellets. Figure 4 shows the distribution and general appearance of these particles. The higher magnification views of Figures 5 and 6 show

shiny globular particles (Arrows A), identified as UB_4 by x-ray diffraction, as well as unreacted grey particles of B_4C (Arrow B). Tiny islands of a grey phase within the UB_2 particles may be unreacted B_4C or UO_2 . Approximately 75 percent of the B_4C had been reacted to form the UB_4 phase during the $1250^\circ C$ sinter.

V. DISCUSSION

Sinterability studies conducted on pellets of the four-hour milled UO_2 demonstrated that densities in excess of 9.87 g/cm^3 (90 percent of theoretical) were attained for temperatures above 1400°C in vacuum. An essentially identical sintering behavior was observed in flowing argon for temperatures up to 1250°C . Although adsorbed moisture is readily removed from the pellets at relatively low temperatures, excess O_2 is held interstitially in the face centered cubic crystal structure and requires temperatures of 1300°C to 1400°C for its complete removal. All UO_2 pellets sintered in the two environments exhibited structures free from minor phases, cracks or other defects which could contribute to unusual sintering behavior or to anomalous boron reactions for $\text{UO}_2\text{-B}_4\text{C}$ pellets. Based upon these initial studies, the $\text{UO}_2\text{-B}_4\text{C}$ powder mixture was milled for a longer time of 21 hours in order to ensure a uniformly fine particle size and optimum homogeneity of blend.

The oxidation behavior of B_4C was investigated for temperatures from 625°C to 1250°C in 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 composition of the pellets. It is expected that subsequent pellets with a 0.05 w/o B_4C content will behave in a similar manner without the extensive changes observed at the 1 w/o B_4C level. This study demonstrated that seemingly insignificant amounts of oxidants (oxygen, moisture, CO_2) cause formation of volatile boron compounds at the elevated temperatures.

Moisture released from the compacted powders reacted in a different manner depending upon the composition of the pellets. At the lower

temperatures, the molybdenum containers had "gettered" the moisture released from the UO_2 pellets to cause blue-to-grey oxide film formations. Moisture that had been similarly released from the $\text{UO}_2\text{-B}_4\text{C}$ pellets at the same temperatures had reacted with the B_4C and accordingly was not available to cause any oxidation of the molybdenum. At higher temperatures of 1000°C to 1250°C , the deposits on the molybdenum immediately adjacent to the UO_2 pellets had progressively changed in color from the oxide grey to dark brown of vapor-deposited uranium dioxide. White deposits of B_2O_3 were faintly evident on the molybdenum containers adjacent to $\text{UO}_2\text{-B}_4\text{C}$ pellets sintered at 1000°C in argon and appeared as fairly heavy deposits after the 1250°C sinter. These greater losses of boron resulted in increasingly greater weight losses at temperatures above 1000°C (Figure 2c). The release of excess oxygen within the $\text{UO}_2\text{-B}_4\text{C}$ pellets became a significant factor for continued B_4C oxidation at temperatures above about 800°C . However, essentially stoichiometric UO_2 was not attained until temperatures between 1200°C and 1300°C were reached for the argon sintering cycles used for these tests.

It was noted earlier that white deposits of B_2O_3 had formed on the molybdenum containers for sintering temperatures above 1000°C . The large deposits of B_2O_3 indicate that the $\text{UO}_2\text{-B}_4\text{C}$ pellets were hotter than the molybdenum containers as a result of an exothermic reaction involving oxidation of B_4C in the pellets. Accordingly, condensation of B_2O_3 took place directly onto the cooler molybdenum containers. The magnitude of temperature difference between the $\text{UO}_2\text{-B}_4\text{C}$ pellets and the containers is not known at the present time.

The oxidation behavior of B_4C appears to involve consecutive reactions

by which B_4C is initially oxidized to boron oxides which are then lost from the pellets as volatile products. An explanation of these reactions is included in Appendix B. It is shown in Figure 7a that 1500 to 2100 ppm boron, as boron oxides, are formed at 625°C and 800°C with insignificant losses by volatilization at these temperatures. This reaction was also observed in the microstructure by a rounding of the B_4C particles with a surrounding zone of water soluble reaction products. At temperatures above 1000°C, boron losses increased rapidly, as noted by higher weight losses (Figure 2c) of UO_2-B_4C pellets and by condensation of relatively heavy deposits 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 7a indicate that, over the 625°C 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. Final losses of boron take place by the volatilization of these reaction products. These changes above 1250°C are indicated in Figure 7a as decreasing total boron, by oxidation of B_4C , to the 1500 to 2100 ppm boron level, with subsequent loss of boron oxides by volatilization. It is expected that data from the 1300°C to 1500°C sintering tests will provide additional confirmatory information on the proposed mechanism of boron loss in UO_2-B_4C pellets.

At the present time, the preliminary data are insufficient to determine the oxidation behavior of uranium boride at temperatures

above 1200°C. Chemical analyses (Figure 7a) indicate that boron oxides may be formed from uranium boride by consecutive reactions similar to those noted for B_4C . On this basis, the mechanism for boron loss is the same regardless whether B_4C or UB_4 is the source material for oxidation to boron oxides.

The data in Figure 7 show the dependency of boron loss to sintering conditions of temperature and oxygen availability. Initially, B_4C reacts with moisture released from the UO_2 at the lower temperatures to form an essentially constant level of boron oxides in the pellets. At temperatures above 1000°C, at which significant volatilization of boron oxides takes place, the oxidation reaction of B_4C is maintained by a continual supply of oxygen released from hyperstoichiometric UO_2 (Figure 7a). Thus, the net boron content is maintained by replacement of lost boron oxides by further oxidation of B_4C . On this basis, the remaining B_4C (or uranium borides) will be converted completely to volatile boron oxides at a temperature of 1500-1600°C.

VI. SUMMARY

1. Powder mixtures containing homogeneous dispersions of B_4C in UO_2 were prepared by dry milling for 21 hours. The milling operation also comminuted the agglomerated UO_2 powder to a fine particle size of improved sinterability.

2. Pressed pellets of milled UO_2 powder had sintered to densities in excess of 9.87 g/cm^3 (90% of theoretical) at temperatures above 1400°C in vacuum or in argon. These data were used for comparison with the sinterability of UO_2 pellets containing B_4C additions.

3. Boron behavior in UO_2 -1 w/o B_4C pellets with 2000 ppm adsorbed moisture and excess oxygen (O/U ratio of 2.16) in the UO_2 powder has been investigated over the temperature range of 625°C to 1250°C in flowing argon. Boron oxides were formed at all sintering temperatures by partial oxidation of B_4C with moisture or oxygen released in the pellets. Losses of boron oxides above 1000°C were replenished by continued oxidation of B_4C (and possible UB_4 above 1200°C) to maintain an equilibrium level of 1500 to 2100 ppm boron as boron oxides in the pellets.

4. 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.

5. These data indicate a necessary requirement for a completely dry, oxygen-free atmosphere for the retention of boron in UO_2 pellets sintered to high densities.

VII. WORK PLANNED FOR THE NEXT QUARTERLY PERIOD

1. Complete sintering studies on UO_2 -1 w/o B_4C pellets from 1300°C to 1500°C in flowing argon to extend the knowledge on oxidation behavior of B_4C , mode of boron losses, UO_2 - B_4C reactions and process of pellet densification. These data will be used to establish the conditions of the furnace environments which will be used for the sintering of UO_2 -0.05 w/o B_4C pellets.

2. Initiate sintering studies on UO_2 -0.05 w/o B_4C pellets in several furnace environments including vacuum, argon, hydrogen and CO-CO_2 mixtures. Methods will be investigated for the removal of adsorbed moisture and excess oxygen from the UO_2 powder, either as a separate step or during the heatup cycle prior to sintering. Control pellets of UO_2 and UO_2 -1 w/o B_4C will be included in selected sintering tests as an aid in the evaluation of processes involving boron reactions and the densification of the pellets.

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TABLE I

Properties of Starting Materials

<u>Uranium Dioxide</u>		<u>High Boron Grade Boron Carbide</u>	
Source: Kerr McGee Corporation		Source: 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
Ag	1 ppm max	Ca	0.1 max
Al	24 ppm max	Mg	0.05 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		
V	5 ppm max		

APPENDIX A

ANALYTICAL METHODS

1. 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.

a. 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 two hours. The filtrate from this solution is diluted to 500 ml in a volumetric flask. Aliquotes of this volume are transferred to a 50 ml flask containing 5 ml quinalizarin and the volume increased to 50 ml with concentrated H_2SO_4 , and 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.

b. 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 ml in a volumetric flask and aliquotes containing quinalizarin are analyzed spectrophotometrically by the method described for soluble boron analysis.

c. 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 three hours at 1000°C in air furnace.

2. 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 four hours using a water slurry containing 0.3 micron α - Al_2O_3 abrasive and for 16 hours with 0.05 micron γ - 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.

3. 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

W. C. Taylor

The preliminary data shown in Figure 7a 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.
 $B_{xO_y}(c)$ represents water soluble boron oxides.
 $B_2O_3(g)$ represents the boron lost from the pellets.

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

$$[B_4C]_f = [B_4C]_{i-X}$$

$$B_{xO_y}(c) = X - Y$$

$$B_2O_3(g) = Y$$

where: $(B_4C)_i$ = initial concentration

$(B_4C)_f$ = final concentration

The rate laws for these products are given by:

$$\begin{aligned} -\frac{d}{dt} B_4C &= K^1 [(B_4C)_{i-X}] && \text{disappearance of } B_4C \\ +\frac{d}{dt} B_{xO_y}(c) &= K^1 [(B_4C)_{i-X}] - K^2 [B_2O_3(g)] && \text{production of } B_{xO_y}(c) \\ +\frac{d}{dt} B_2O_3(g) &= K^2 [B_{xO_y}(c)] && \text{boron loss} \end{aligned}$$

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

$$B_{xO_y}(c) = [(B_4C)_i] \left[\frac{K^2 (1 - e^{-K^1 t})}{K^2 - K^1} - \frac{K^1 (1 - e^{-K^2 t})}{K^2 - K^1} \right]$$

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 the figure below.

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.

Figure 1a

Figure 1c

Figure 1b

Figure 1d

Figure 1 Sinterability Data On UO₂ Pellets In Vacuum Environment

Figure 2a

Figure 2c

Figure 2b

Figure 2 Sinterability Data On UO₂ And UO₂ - 1 W/O B₄C Pellets In Argon Atmosphere

Photo No.
5888

Unetched

Mag. 500X

Figure 3 Microstructure Of $\text{UO}_2 - 1 \text{ W/O } \text{B}_4\text{C}$ Pellets
Sintered At 1100°C In Argon

Photo No.
5890

Unetched

Mag. 250X

Figure 4 Microstructure Of $\text{UO}_2 - 1 \text{ W/O } \text{B}_4\text{C}$ Pellets
Sintered At 1250°C In Argon

Photo No.
5886

Unetched

Mag. 500X

Figure 5 Uranium Borides (Arrows A) And Unreacted B_4C (Arrows B)
In $UO_2 - 1 W/O B_4C$ Pellets Sintered At $1250^\circ C$ In Argon

Photo No.
5887

Unetched

Mag. 500X

Figure 6 Another View Of Uranium Borides (Arrows A)
And Unreacted B_4C (Arrows B) In $1250^\circ C$ Sintered Pellets

Figure 7a

Figure 7b

Figure 7 Chemical Analyses Of Argon Sintered UO_2 - 1 W/O B_4C And UO_2 Pellets