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BURNABLE POISON ADDITIONS TO UO_2

For the Period:
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POWER
DEPARTMENT

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ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT PROGRAM

BURNABLE POISON ADDITIONS TO UO_2

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For the Period:

October 1 to December 31, 1967

Unclassified
Classification

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BURNABLE POISON ADDITIONS TO UO_2

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ABSTRACT

A series of sintering studies has demonstrated that boron is lost from the UO_2 pellets by consecutive reactions including the oxidation of B_4C to form boron oxides which are subsequently removed as volatile products. UO_2 pellets containing 0.05 w/o and 1 w/o B_4C retained 50 percent ($\pm 10\%$) of the initial boron contents during sintering in the 1400 to 1600°C temperature range. The boron is present as uniformly dispersed particles of uranium borides (UB_4 and UB_2) throughout the sintered UO_2 pellets. The UO_2 -0.05 w/o B_4C pellets were sintered to densities of 90 to 93 percent of theoretical in argon and vacuum environments.

I. INTRODUCTION

The primary objectives of this program is the development of cold pressing and sintering methods for incorporating homogeneous dispersions of boron in high density UO_2 pellets. The second phase of the program will include an investigation of axial and radial boron migrations in the fuel as well as compatibility of Zircaloy-4 cladding with sintered $\text{UO}_2\text{-B}_4\text{C}$ pellets. The tests will simulate reactor thermal conditions of near-melting-centerline temperatures for the fuel at a cladding temperature of $\sim 400^\circ\text{C}$ (750°F).

The initial phase of the experimental work* has investigated the mechanisms for boron losses from UO_2 pellets during sintering. These data and consideration of high negative free energy of reaction values between B_4C and oxygen as elemental oxygen, or moisture, are the bases for the hypothesis that boron losses involve consecutive reactions by which B_4C is oxidized initially to form intermediate boron oxides which are subsequently removed as volatile products from the pellets. The initial work, aimed at confirming these mechanisms, used as-received, hyperstoichiometric uranium dioxide powder (O/U ratio of 2.16) with 2000 ppm adsorbed moisture as the source of oxygen for B_4C oxidation during sintering.

Results from these tests will be utilized in the development of sintering methods for the preparation of high density UO_2 pellets containing controlled amount of boron.

Evaluations on $\text{UO}_2\text{-1 w/o B}_4\text{C}$ pellets sintered in a flowing argon or in a vacuum (2×10^{-6} microns) environment has indicated that B_4C oxidizes to form

*G. Zuromsky and S. S. Christopher, "Burnable Poison Additions to UO_2 ", CEND-3107-324, October, 1967.

boron oxides at temperatures as low as 350°C. The concentration boron oxides within the pellets remains at an essentially constant level with respect to the total boron content for sintering temperatures up to about 1200°C. Losses of boron become significant at temperatures above 1200°C through escape of the highly volatile boron oxides from the porous UO_2 pellets. Physical transport and condensation of B_2O_3 was established from chemical analyses of white deposits found on the cooler surfaces of the furnace tube.

During the current program period, these studies were continued on UO_2 -1 w/o B_4C pellets sintered in the upper temperature range of 1200 to 1600°C in purified flowing argon and in vacuum environments. A similar evaluation was conducted on UO_2 pellets containing 0.05 w/o B_4C to investigate boron retention, UO_2 - B_4C reactions and sinterability over a range of temperatures to 1500°C in flowing argon and in vacuum environments.

Use of inert atmospheres allows a uniform oxidation of B_4C particles to take place within the pellets by reaction with moisture and excess oxygen released from the UO_2 powder during sintering.

II. EXPERIMENTAL PROCEDURE

UO₂-B₄C powder mixtures were dry milled for 30 hours to provide homogeneous blends as well as to reduce the initially agglomerated UO₂ powder* to a uniformly fine particle size. UO₂ powder for control pellets was similarly processed by dry milling for 30 hours without removal of moisture and excess oxygen. All pellets, 1.00 cm in diameter by 1.27 cm in length, were compacted at 7 tsi in a hardened steel die to a geometric density of 5.10 g/cm³ (47% of theoretical). Pellets of UO₂-B₄C composition and UO₂ control pellets were sintered in molybdenum or tantalum containers either in the stabilized zirconia tube furnace with flowing argon at temperatures to 1450°C or in a Brew vacuum furnace for temperatures to 1900°C. The argon gas was purified using a Deoxo unit and sodium perchlorate to remove oxygen and moisture. The vacuum furnace was operated with a chamber pressure of 2×10^{-6} microns during the sintering cycle.

A typical sintering cycle included a two hour heatup to the sintering temperature, one hour at temperature and two hours for cooldown. The cooldown period for the ceramic tube furnace was usually extended to about 16 hours or overnight for the higher temperature sintering tests.

Several groups of UO₂ pellets containing 10 w/o B₄C were sintered at selected temperatures between 1200 and 1900°C for more positive identification of UO₂-B₄C reaction products by x-ray diffraction and metallographic techniques.

The boron content in the sintered pellets was chemically determined in two forms:

1. Total boron as B₄C, boron oxides and uranium borides (UB₄ and UB₂)
2. Soluble boron as water soluble boron oxides

*Throughout this report, non-stoichiometric uranium dioxide is referred to as UO₂. Where the O/U ratio is known, the exact stoichiometry is reported.

The chemical procedures for the determination of boron were presented in CEND-3107-324. The sinterability of the pellets was determined from geometric density, diametral shrinkage and weight loss data.

III. RESULTS

A. UO_2 -1 w/o B_4C

The boron content in UO_2 pellets sintered in flowing argon and in vacuum environments is shown graphically in Figure 1. As indicated, two distinct levels of total boron and soluble boron content 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 retention 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 2. The partially oxidized B_4C particles exhibited rounding of the edges with the formation of a surrounding reaction zone containing boron oxides. 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 kerosine-abrasive mixtures to avoid 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 involve complete oxidation and loss of the finer particles and partial oxidation of the larger particles of B_4C . This depletion of B_4C was confirmed by the observed decreasing amount of the finer B_4C particles with increasing sintering temperature. Within this higher temperature range, the UO_2 - B_4C reaction was initiated at 1200 to 1250°C (Arrows in Figure 2) and was essentially completed at 1300 to 1350°C (Figure 3) by formation of uranium tetraboride (UB_4). Finer particles of the UB_4 phase formed in the

FIG. 1 BORON CONTENT (PPM) VS SINTERING TEMPERATURE
 $\text{UO}_2 - 1 \text{ W/O } \text{B}_4\text{C}$

FIG.2 UO_2 -1 W/O B_4C SINTERED AT 1200°C IN ARGON

FIG.3 UO_2 -1 W/O B_4C SINTERED AT 1300°C IN ARGON

lower temperature sintered pellets were not found in pellets sintered above 1400°C, suggesting that boron losses took place by the proposed 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 in the form of a uniform dispersion of the UB_4 phase of very similar particle size, as shown in Figure 4. A high magnification view (Figure 5) shows the globular UB_4 particles containing a fine internal phase which is believed to be unreacted UO_2 .

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 pellets at all sintering temperatures, as shown in Figure 6. Optimum densities of 8.45 g/cm³ and 8.75 g/cm³ were obtained by sintering at 1450°C in vacuum and argon environments, respectively.

UO_2 pellets without boron additions had consistently attained higher densities, reaching 10.0 g/cm³ (91% of theoretical) in the 1400 to 1450°C temperature range in either furnace environment. Diametral shrinkage of both types of pellets increased with increasing sintering temperature in direct relation with pellet densification rate (Figure 7). Sintering in either furnace resulted in similar weight losses for UO_2 pellets containing B_4C (Figure 8). 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.

FIG.4 UO_2 - 1 W/O B_4C SINTERED AT 1450°C IN ARGON

FIG.5 UO_2 - 1 W/O B_4C SINTERED AT 1450°C IN ARGON

FIG. 6 DENSITY (g/cm³) VS SINTERING TEMPERATURE (°C)
UO₂ - 1 W/O B₄C

FIG. 7 DIAMETRAL SHRINKAGE (%) VS SINTERING TEMPERATURE ($^{\circ}\text{C}$)
 UO_2 - 1 W/O B_4C

FIG. 8 WEIGHT LOSS (%) VS SINTERING TEMPERATURE (°C)
 UO_2 - 1 W/O B_4C

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 one hour to twenty hours in the argon furnace. The values for geometric density, diametral shrinkage and weight loss are included as individual data points in Figures 6, 7 and 8. 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), respectively, for UO_2 and UO_2 - B_4C pellets, respectively. Diametral shrinkage and weight loss for the UO_2 pellets were essentially unchanged corresponding to a slight increase in densification. However, both weight loss (1.2 to 1.9%) and diametral shrinkage (15 to 17%) were relatively larger 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 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 4.

UO_2 -1 w/o B_4C reactions were investigated over a range of temperatures by x-ray diffraction methods. The 1200°C sintered UO_2 pellets contained B_4C as a major constituent with trace amounts of the UB_4 phase. Pellets sintered at 1400°C contained only the UB_4 phase. An earlier program (CEND-3107-306) had reported UB_4 formation from UO_2 - B_4C reaction by sintering at 1150°C for 25 hours in flowing helium. The boron compounds in the 1900°C sintered UO_2 pellets included UB_4 as a major phase with minor amounts of the UB_2 phase. Figure 9 shows the duplex structure of the uranium boride particles in the 1900°C sintered pellets. There was no evidence of the UB_{12} phase by x-ray diffraction analysis.

B. UO_2 -0.05 w/o B_4C

Boron retention as a function of sintering temperature in argon and in vacuum environments, is shown graphically in Figure 10. The initial boron content in the blended powder mixture was 380 ppm (0.048 w/o B_4C) with non-detectable soluble boron oxides. Oxidation of B_4C by formation of boron oxides was detected

FIG. 9 $\text{UO}_2 - 1 \text{ W/O } \text{B}_4\text{C}$ DUPLEX STRUCTURE OF URANIUM BORIDES.

FIG. 10 BORON CONTENT (PPM) VS SINTERING TEMPERATURE (°C)
 $\text{UO}_2 - 0.05 \text{ W/O } \text{B}_4\text{C}$

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 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. Similarly, approximately 50 percent of the boron was retained in pellets sintered for one hour at 1400 to 1500°C.

The presence of 0.05 w/o B_4C appears to slightly enhance the normal sinterability of UO_2 , as shown in Figure 11. The boron-containing pellets attained geometric densities of 9.85 to 10.30 g/cm³ (90 to 93% of theoretical for UO_2) for the temperature range of 1200 to 1500°C in the argon and vacuum environments. Diametral shrinkage of all pellets exhibited a similar behavior as the rate of densification with increasing temperature of sintering (Figure 12). 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 furnace (Figure 13). The increasingly higher weight losses with sintering temperature were followed by changes in the appearance of the interior surfaces of the tantalum pellet 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

FIG. 11 DENSITY (g/cm³) VS SINTERING TEMPERATURE (°C)
UO₂ - 0.05 W/O B₄C

FIG. 12 DIAMETRAL SHRINKAGE (%) VS SINTERING TEMPERATURE (°C)
 UO₂ - 0.05 W/O B₄C

FIG. 13. WEIGHT LOSS (%) VS SINTERING TEMPERATURE (°C)
 $\text{UO}_2 - 0.05 \text{ W/O B}_4\text{C}$

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 14). 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 sintered at the highest temperatures to investigate the uniformity of the boron dispersion.

FIG. 14 $\text{UO}_2 - 0.05 \text{ W/O B}_4\text{C}$ SINTERED AT 1300°C IN ARGON. ARROWS LOCATE UB_4 PHASE

IV. DISCUSSION OF RESULTS

The boron data in Figures 9 and 10 show similar oxidation behavior for UO_2 pellets with 0.05 w/o and 1 w/o B_4C additions over a range of sintering temperatures extending up to 1200°C . 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 the gradual disappearance of finer particles of B_4C with increasing temperature for UO_2 -1 w/o B_4C pellets. 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 .

The UO_2 - B_4C reaction appeared to have been completed after one hour at 1300°C with 4500 ppm boron in the form of the UB_4 phase in UO_2 containing 1 w/o B_4C . Sintering at 1300°C for 20 hours further reduced 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 oxidation 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. In the case of UO_2 containing 0.05 w/o B_4C , 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 3 and 5).

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. 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 MoB₂ reactions of boron oxide vapors with the molybdenum containers and also from condensed B₂O₃ on the cooler surfaces of the furnace tube.

These data form the basis for the proposed mechanism for boron losses in UO₂ pellets during sintering in environments containing oxygen or moisture. The following reactions are involved.

1. Water soluble boron oxides are formed by oxidation of B₄C by adsorbed moisture and excess oxygen in the UO₂. Significant volatilization of boron oxides does not take place until temperature of 1200°C is reached, resulting in essentially constant levels of boron oxide formation.
2. Increasingly higher boron losses occur at temperatures above 1200°C from volatilization of boron oxides from the UO₂ pellets. Further oxidation of B₄C and UB₄ continues by reaction with oxygen released from the UO₂ at the elevated temperatures.
3. A residual boron level is reached in UO₂ pellets sintered for one hour at temperatures of 1400 to 1600°C under conditions of essentially stoichiometric UO₂ (O/U ratio of 2.01 to 2.02) in an inert environment.

V. SUMMARY

1. Pellets containing 0.05 w/o and 1 w/o B_4C exhibit similar oxidation behavior over the range of sintering temperatures in argon and vacuum environments. Boron oxides formed from B_4C oxidation remain stable at temperatures up to $1200^\circ C$ to form essentially constant levels of soluble and total boron contents. At the higher sintering temperatures of 1300 to $1600^\circ C$, rapid volatilization of boron oxides in both types of pellets reduces the total boron levels to about 50 percent of the initial values.
2. 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. The 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 $1300^\circ C$.
3. Retention of boron, chiefly as UB_4 , is attributed to the non-oxidizing conditions of essentially stoichiometric UO_2 in an inert environment existing at temperatures above about $1400^\circ C$.
4. The UB_4 phase is formed by a UO_2 - B_4C reaction at temperatures between 1200 and $1350^\circ C$. A further reaction involves the formation of the UB_2 phase at temperatures above about $1500^\circ C$. The uranium borides appear as uniform dispersions in the sintered UO_2 pellets.

VI. WORK PLANNED DURING THE NEXT REPORTING PERIOD

1. Boron retention in UO_2 pellets will be optimized: a) by initially removing adsorbed moisture in the UO_2 by means of a low temperature vacuum drying operation, and, b) by hydrogen reduction of UO_2 to stoichiometric composition prior to sintering in the selected furnace environments, including argon, vacuum and CO/CO_2 mixtures.
2. Construction of the "hot rod" apparatus will be completed for thermal gradient tests to investigate boron migration in sintered UO_2 pellets. Cored pellets containing nominal 0.05 w/o B_4C will be prepared for these tests.