THE PRODUCTION, CHARACTERIZATION, AND NEUTRONIC PERFORMANCE OF BORON NITRIDE COATED URANIUM DIOXIDE FUEL

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ABSTRACT

The fuel pellets produced by sol-gel technique were coated with boron nitride (BN). This was achieved through chemical vapor deposition (CVD) using boron trichloride and ammonia. Mixing and chemical reaction take place at a temperature around 875 K. The coated samples were then sintered at 1600 K.

Thermal reactor physics lattice-cell code WIMS-D/4 was used in the neutronic analysis of CANDU fuel bundle to observe the neutronic performance of the coated fuel. Three types of fuel were considered; fuel made of natural uranium, slightly enriched uranium (SEU, enrichment: 0.82 % U-235), and SEU with various BN coatings. The burnup calculations showed that feasible coating thickness is between 1 to 2 μm.

INTRODUCTION

The technology of burnable absorbers is improving in two branches. One is the use of gadolinia (Gd_2O_3) mixed homogeneously with the fuel, and the other method is to coat the fuel pellets by a thin layer of zirconium diboride (ZrB_2) so-called integral fuel burnable absorber (IFBA). Although gadolinia has recently been extensively used as burnable absorber it has some disadvantages such as low thermal conductivity, very fast depletion, and low moderator temperature coefficient control [1-5]. The fabrication technique of ZrB_2 is quite complicated and dissolution of unburned ZrB_2 during reprocessing create problems [6-7].

The difficulties in sputtering of ZrB_2 can be overcome by the utilization of other deposition methods. A recent technique introduced [8-9] is to coat the fuel with boron nitride [BN], which is deposited on fuel by chemical vapor deposition (CVD). BN has the following advantages; (i) has high thermal stability, (ii) is chemically inert, (iii) is very hard, and withstands high pressures and temperatures, (iv) has excellent corrosion resistance, (v) withstands rapid heating and quenching at 1500 C, (vi) has a thermal conductivity comparable to that of stainless steel.

Boron has a low neutron absorption cross section compared to gadolinium, therefore, it does not rapidly burnout when mixed with fuel and its thickness can easily be adjusted to have negligible residual reactivity at the EOC. It can also be used on gadolinia-containing fuels to have the desired reactivity change during reactor operation.

BORON NITRIDE COATING

BN prepared by CVD has been extensively investigated in the last decade in surface coating, production of synthetic abrasives, and manufacturing integral circuits in solid state electronics [10-15]. BN is easily obtained from boron trichloride (BCl_3) and ammonia (NH_3) through the reaction,

$$BCl_3 + NH_3 \rightarrow BN(s) + 3HCl$$

This is the most well-known technique used in the literature. Besides BN, other undesired intermediate compounds of boron are also formed, and they may deposit on the surface of substrate. The substrate should be sintered at high temperatures (1600-1900 K) to evaporate these undesired compounds. At this stage a considerable weight decrease is expected. The sintering of the substrate yields the formation of hexagonal crystal structures. Hence, the mechanical properties of BN are improved [10]. "$BCl_3 + NH_3$" reaction produces deposits with densities of 1.5 g/cm^3 at 1300 C, but when the deposition temperature is increased to 1600 C the density becomes 2.0 g/cm^3 [12].

EXPERIMENTS

The fuel was produced by sol-gel technique. The method of production and the effects of production parameters on the properties of these fuels were explained elsewhere [15].

The tube furnace used for "$BCl_3 + NH_3$" reaction was given in a former work [9]. Since BCl_3 readily reacts with NH_3 at room temperature and forms a white powder, these gases were introduced separately into the furnace in order to mix them in the vicinity of the substrate and to avoid premature reaction. Argon (Ar) was used as carrier gas for BCl_3. Hydrogen (H_2) was used to improve the purity and thus the properties of the product. In addition it prevents the oxidation of pellets due the possible oxygen leakage. NH_3 was introduced directly into the central zone of the reaction tube through a thin alumina tube, while the mixed gas of BCl_3 and Ar is introduced at a location 20 mm behind the first stream. Mixing and chemical reaction take place in the hot zone of the furnace at a temperature around 875 K. The coated pellets were then sintered at 1600 K. Three pellets partially coated with white BN are shown in Fig.1.

NEUTRONIC ANALYSIS

Thermal reactor physics lattice-cell code WIMS-D/4 was used in the neutronic analysis of CANDU fuel bundle[16]. Standard fuel bundle containing 37 fuel elements was considered for calculations. Three types of fuel were considered; fuel made of natural uranium, slightly enriched uranium (SEU, enrichment: 0.82 % U-235), and SEU with various BN coatings. In all cases fuel pellets are in UO_2 form. The first case, fuel pellets made with natural uranium, represents conventional CANDU reactor fuel bundle. An alternative to the use of natural uranium might be the use of slightly enriched uranium to improve fuel cycle characteristics. Slightly enriched uranium may be taken from reprocessing of LWR spent fuel. Such fuel material contains about 0.82 % U-235 by weight. Fuel pellets in the first two cases are in 0.61 cm in radius. The third type of fuel was considered to analyze the effect of BN coating on the neutronic behavior of the fuel bundle. The thickness of BN coating was considered to be between 1 to 4 μm. This coating is applied to the surface of standard pellets such that the overall radius was increased from 0.61 cm by the thickness of the coating. Density of coating was taken to be 1.8 g/cm^3. In all cases, fuel pellets were assumed to be covered with 0.045 cm thick Zircaloy-4 sheath material.

Computer calculations were performed by using 1 day long time steps such that each time step corresponds to 20 MWD/MTU burnup. The maximum burnup considered in computations is 12,000 MWD/MTU for 600 time steps.

EXPERIMENTAL RESULTS

The originally white BN powder deposited at 875 K on pellets turned into *transparent* film upon sintering at 1600 K. The BN layer is very hard and strongly adherent on the surface of pellets.

The infrared (IR) spectrum of BN powder (Fig.2) were found to be in agreement with the ones given in the literature [10, 17-19], with a strong peak at 1400 cm^{-1} and two weak peaks at about 800 and 880 cm^{-1}. The strong peak is of B-N stretching while the weak ones are of B-N-B stretching [19].

The X-ray diffraction analyses of sintered BN was shown in Fig.3 where the characteristic peak is easily seen at $2\theta=26°$. It is a peak of hexagonal or turbostratic structure [14, 20, 21].

Scanning electron microscope (SEM) pictures of uncoated BN pellet and thin BN coated UO_2 fuel pellet are shown in Fig.s 4 and 5 respectively. In Fig.5 urania grains are barely seen under BN layer. Figure 6 shows the side view of BN coating on urania. The upper layer in the figure is BN coating which forms only on the surface with no penetration into the fuel. It is seen that there is a very good adherence of BN on substrate. The thickness of the coating is uniform and about 10 μm in this figure. Figure 7 was essentially taken by using backscattering technique. The white area shows the heavy atom zone which is the fuel. BN and fuel atoms are not penetrated into each other. BN stays as an inert unpenetrating smooth coating on the fuel.

COMPUTATIONAL RESULTS

Figure 8 shows the variation of k_{eff} as a function of the fuel burnup for natural uranium, and SEU coated with BN with various thicknesses. SEU ("0" μm BN) and SEU(1 μm BN) each has a positive reactivity at the beginning of cycle (BOC) while others have negative reactivity. It seems that SEU (2μm) fuel has a negative reactivity of 0.031 at BOC, and expected to have a good performance in the reactor. The fuels with coating more than 2 μm require additional fissile material to overcome negative reactivity effect. Feasible coating thickness is between 1 to 2 μm such that during the initial stages of burnup it neither requires excessive amount of absorber nor additional fissile material. Criticality will be achieved as in the case of natural uranium loaded core without making any change in the configuration of core.

It was found from the calculations that the number density histories for fissile isotopes U-235 and Pu-239 and absorber material boron showed a slight variation as a function of the thickness of BN coating. In Figure 9, the variations of the number densities of fuel constituents are given as a function of burnup for 3μm BN coated fuel case. Boron depletes out exponentially by four orders of magnitude in 10,000 MWD/MTU. Pu-239 concentration increases with a decreasing rate and reaches to 5.793×10^{19} atoms/cm^3 at 12,000 MWD/MTU burnup. The initial U-235 concentration is 1.849×10^{20} atoms/cm^3 whereas the final concentration is 3.407×10^{19} atoms/cm^3.

CONCLUSIONS

1. The IR spectrum analyses of BN powder was found to be in agreement with the reported values in the literature. A strong absorption peak was found at 1400 cm^{-1} and the weaker ones appeared at about 800 and 880 cm^{-1}.
2. X-ray diffraction analyses of powder and sintered BN were found to be in agreement with the reported values in the literature.
3. The side views of the coating showed that BN coating forms only on the surface and has no penetration into the fuel. Furthermore, there is a very good adherence of BN on the substrate. BN and fuel atoms are not penetrated into each other. BN stays as an inert unpenetrating smooth coating on the fuel.
4. SEU fuel coated with 2 μm BN gives a negative reactivity of 0.031 at BOC. Feasible coating thickness is in between 1 to 2 μm.
5. The number density of boron decreases exponentially by four orders of magnitude in *10,000* MWD/MTU.
6. Pu-239 production and U-235 depletion at extended time are almost identical in all coated fuels.

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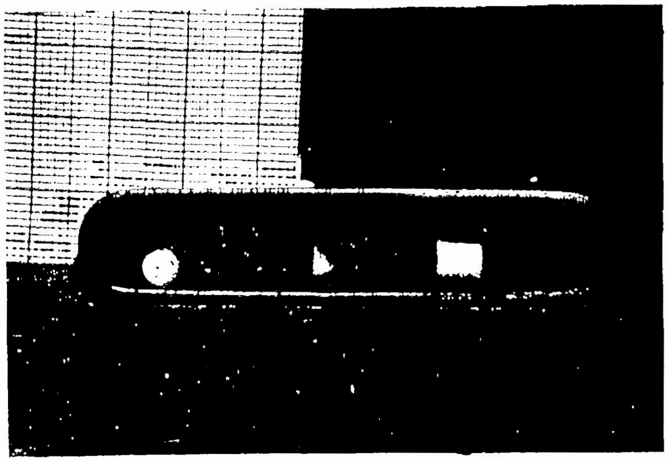

FIGURE 1. BN DEPOSITED FUEL PELLETS

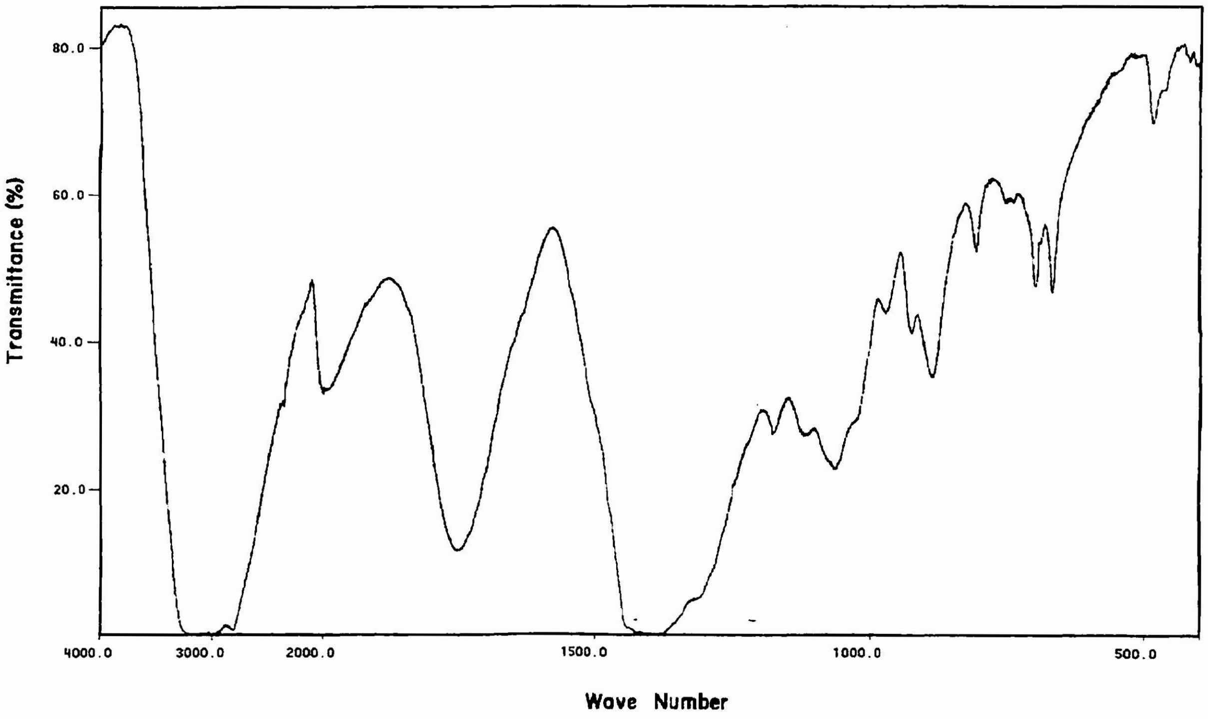

FIGURE 2. IR SPECTRUM OF BN POWDER

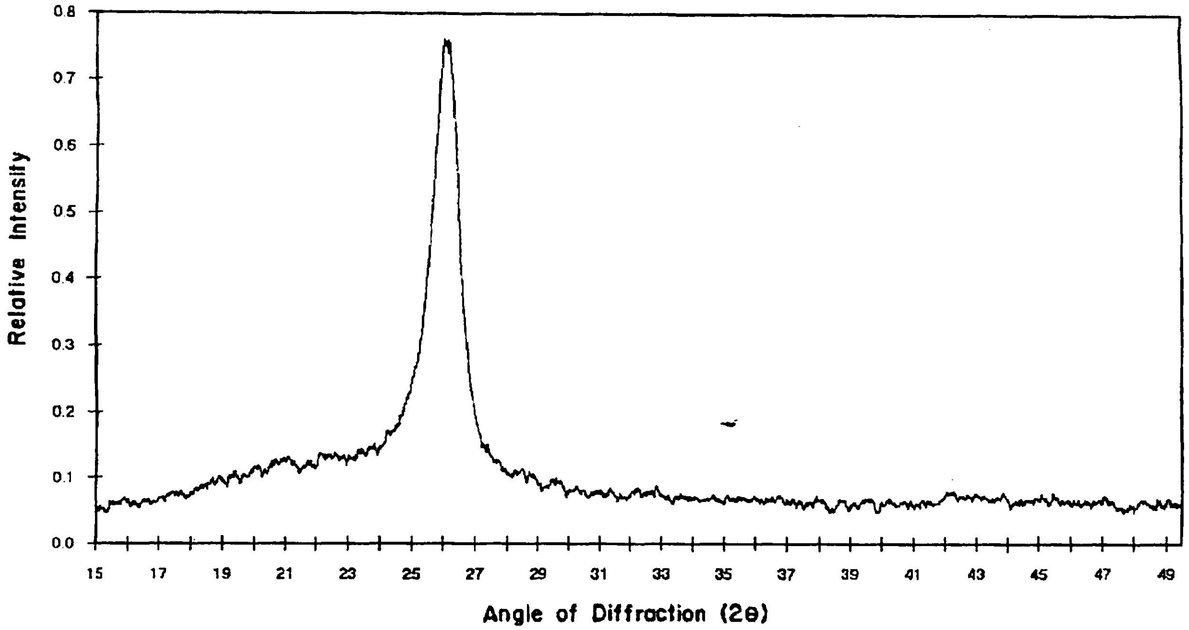

FIGURE 3. XRD PATTERN OF BN POWDER

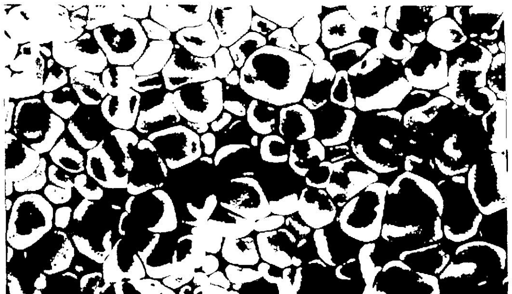

FIGURE 4. UNCOTED PICTURE OF UO_2

FIGURE 5. BN COATING ON UO_2

FIGURE 6. SIDE VIEW OF BN COATING ON UO_2

FIGURE 7. SIDE VIEW OF BN COATING WITH BACKSCATTERING TECHNIQUE

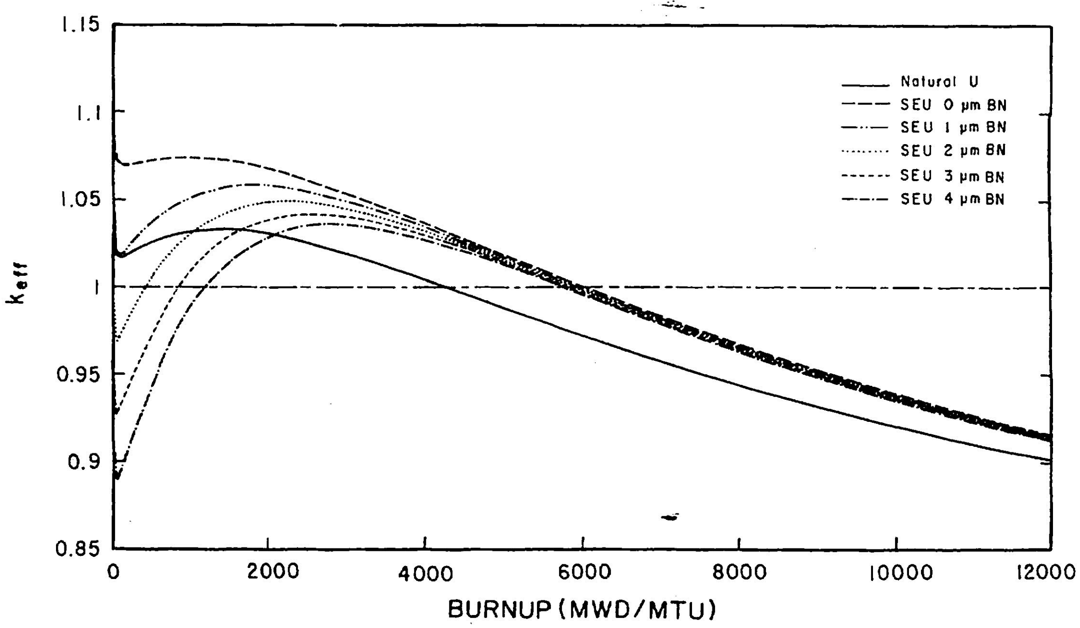

FIGURE 8. KEFF VALUES FOR UO_2 COATED BY BN

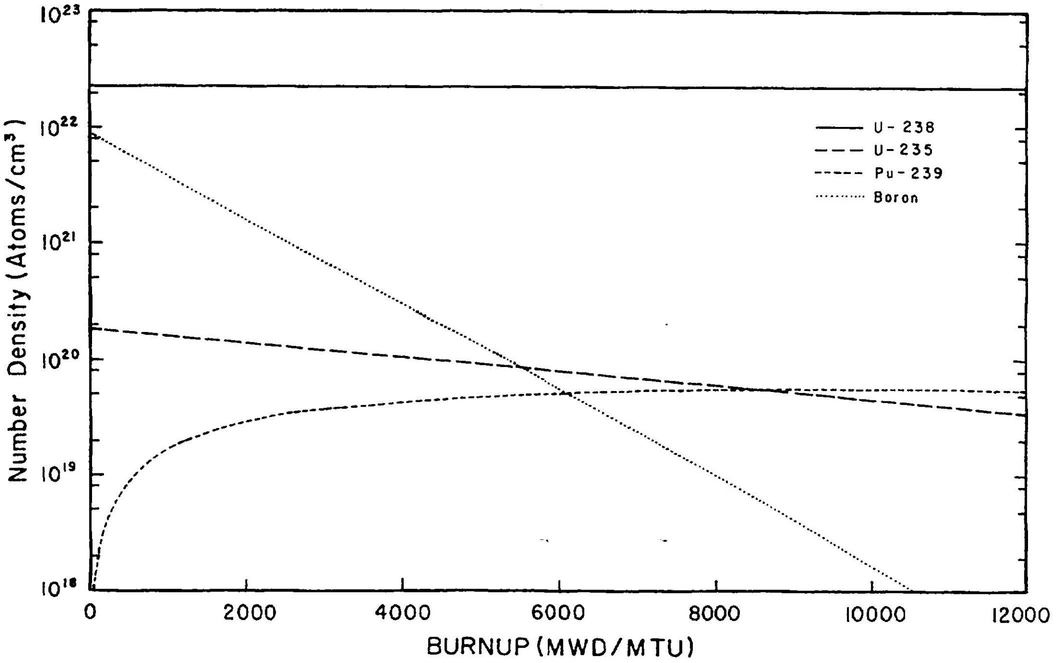

FIGURE 9. VARIATIONS OF THE NUMBER DENSITIES OF FUEL CONSTITUENTS AS A FUNCTION OF BURNUP