



## BORON NITRIDE COATED URANIUM DIOXIDE AND URANIUM DIOXIDE-GADOLINIUM OXIDE FUELS

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### Abstract

Pure urania and urania-gadolinia (5 and 10%) fuels were produced by sol-gel technique. The sintered fuel pellets were then coated with boron nitride (BN). This is achieved through chemical vapor deposition (CVD) using boron trichloride and ammonia. The coated samples were sintered at 1600 K. The analyses under scanning electron microscope (SEM) showed a variety of BN structures, mainly platelike and rodlike structures were observed. Burnup calculations by using WIMSD4 showed that BN coated and gadolinia containing fuels have larger burnups than other fuels. The calculations were repeated at different pitch distances. The change of the radius of the fuel pellet or the moderator/fuel ratio showed that BN coated fuel gives the highest burnups at the present design values of a PWR. Key words: burnable absorber, boron nitride, gadolinia, CVD, nuclear fuel.

### INTRODUCTION

The use of boron compounds and especially boron carbide as burnable absorber in nuclear reactors resulted in some residual poison problems due to the low neutron absorption cross section ( $\sim 760$  b) of boron and in the last decade there has been serious attempts to shift to gadolinium ( $\sim 49000$  b). Gadolinium can be incorporated into urania ( $\text{UO}_2$ ) in the form of gadolinia ( $\text{Gd}_2\text{O}_3$ ) by powder mixing or sol-gel technique. The high amount of gadolinia in the fuel results in significant decrease in thermal conductivity, and some complexities in nuclear design. The full review of information about the use of gadolinia has been given in a recent work [1].

An alternative to gadolinia is the use of zirconium diboride ( $\text{ZrB}_2$ ) coating, so called integral fuel burnable absorber [2-4]. The coating is achieved by sputtering method. However there are technical difficulties in fabrication technique, quality control of the layer, and dissolution of unreacted  $\text{ZrB}_2$ . In addition, the moderator temperature coefficient control is not very satisfactory in a reactor core having  $\text{ZrB}_2$  coated fuel.

The physical and chemical problems associated with  $\text{ZrB}_2$  fuel can be overcome by using boron nitride (BN) coating. It can be coated also on urania-gadolinia fuel so that lower amounts of gadolinia can be used in the fuel, hence a relative improvement is achieved in thermal conductivity. In this research work pure urania and urania-gadolinia fuel pellets were coated by BN. So it unifies the nuclear advantages of both gadolinium and boron.

### BN 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. The process consists of reducing or decomposing a volatile compound at high temperature onto a substrate at relatively low temperature. Low pressure CVD and plasma enhanced CVD processes are also getting important applications. Various chemical substances have been used to deposit BN. The major ones are; (a) reactions of ammonia ( $\text{NH}_3$ ) with boron compounds, such as  $\text{B}_2\text{H}_6$ ,  $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $\text{B}(\text{OCH}_3)_3$ ,  $\text{H}_3\text{BO}_3$ , and

B<sub>10</sub>H<sub>14</sub> [5-23]; (b) thermal decomposition of borazoles such as B<sub>3</sub>Cl<sub>3</sub>N<sub>3</sub>H<sub>3</sub> and B<sub>3</sub>N<sub>3</sub>Cl<sub>6</sub> [24], and borazines such as BH<sub>3</sub>HN(CH<sub>3</sub>)<sub>2</sub>, BHN(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, and B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub> [25-27].

Among those B<sub>2</sub>H<sub>6</sub> and BCl<sub>3</sub> are the most widely used boron compounds, the latter is preferred for its lower price and relatively low handling problems. The addition of boron three chloride (BCl<sub>3</sub>) to NH<sub>3</sub> shows a complex pathway [28] with the overall reaction,



## EXPERIMENTS

In the experiments three different fuels were coated by BN. These fuels are,

- i) pure urania
- ii) urania-gadolinia (5%)
- iii) urania-gadolinia (10%)

Each 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 [29].

The fuel pellets were coated by BN in a tube furnace which is shown in Fig. 1.

BCl<sub>3</sub> vapor introduced through a capillary was purged into the furnace by argon gas. NH<sub>3</sub> gas diluted with H<sub>2</sub> was introduced from a different tube, and mixing and chemical reaction take place in the hot zone of the furnace at a temperature around 875 K. The fuel pellets were located at the exit of the alumina tube where the temperature is between 450 and 500 K. BN powder formed under these conditions can be easily scratched, and rubbed off, but it is sticky. Its surface area determined by BET nitrogen absorption technique was found to be 2.38 m<sup>2</sup>/g.

In Fig. 2 three pellets partially coated with white BN were shown. X-ray diffraction and infrared spectrum analyses of BN powder were found to be in agreement with the ones given in the literature [30,31].

The pellets were then sintered at 1600 K and 1900 K for 2 hrs. The white BN powder turned into hard glassy material with negligible porosity.

An examination of the surfaces of fuel pellets coated by BN was done by using a scanning electron microscope (SEM) (JSM, Model:6400). Figures 3 and 4 show the coatings on pure UO<sub>2</sub> fuel. A leaflike BN is found to form on UO<sub>2</sub> fuel as seen in Fig. 3. However this is not very common and smooth platelike coating was obtained as in Fig.4. UO<sub>2</sub> grains could be barely seen under the coating.

In Figs. 5 and 6 coatings on UO<sub>2</sub>-Gd<sub>2</sub>O<sub>3</sub> (5%) were shown. In Fig. 5 a completely formed BN plate is seen on the right upper part while the rest of the surface is coated with granular BN. In Fig. 6 the fuel surface is completely covered with BN. The coating in this figure is so thin that electron penetration is sufficient to show also the coated surfaces of UO<sub>2</sub>Gd<sub>2</sub>O<sub>3</sub> (10%) fuel.

In Fig. 7 rodlike BN coating is seen. In Fig. 8 the increased thickness caused cracks on the BN coating. In Figs. 9 and 10 the side views of the coatings were shown in pure UO<sub>2</sub> and UO<sub>2</sub>- Gd<sub>2</sub>O<sub>3</sub> (10%) specimens. The phase on the right hand side is BN which forms only on the surface with no penetration into the fuel in either case.

Rapid heating to 1900 K for sintering usually caused large losses from BN coating. So the proper sintering temperature should not exceed 1600K. Once BN coating is achieved further heating to 1900 K did not change the physical properties of the coating.

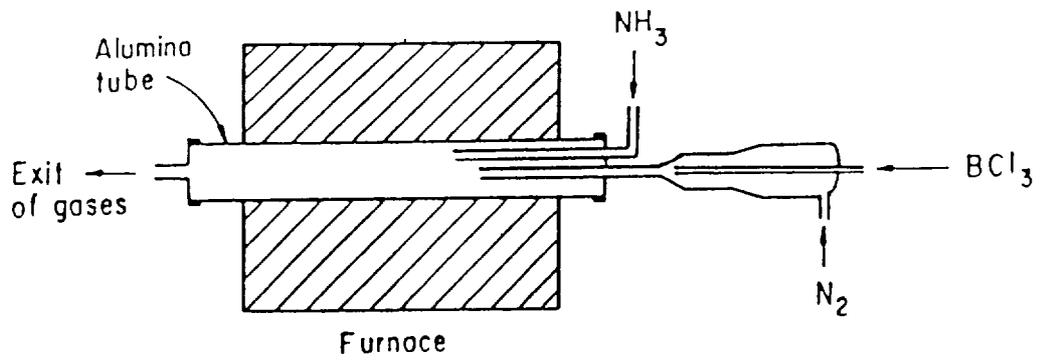


FIG. 1 Furnace for BN Coating

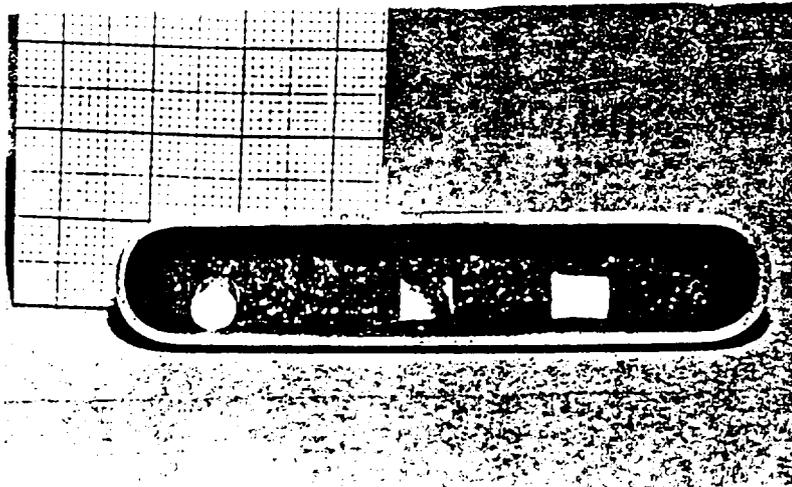


FIG. 2 BN coated fuel pellets (not sintered)



FIG. 3 Leaflike BN formation



FIG. 4 BN coated uranium fuel



FIG. 5 BN plate formation

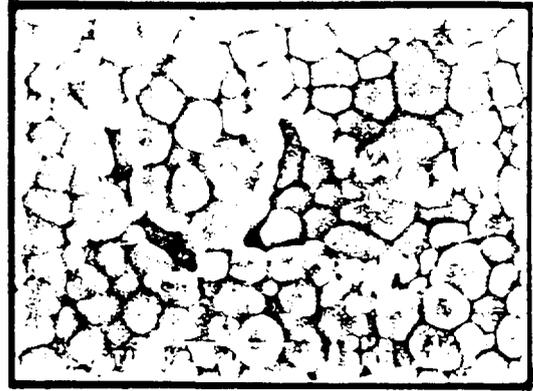


FIG. 6 Thin BN coating



FIG. 7 Rodlike BN coating

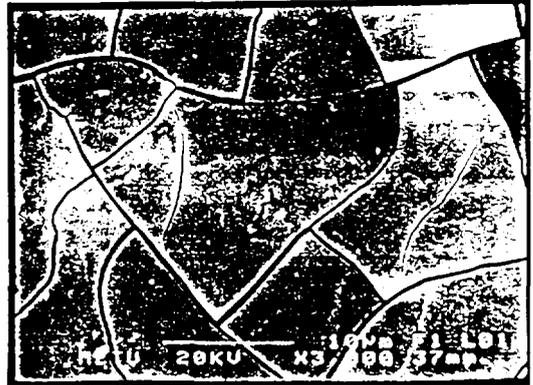


FIG. 8 Cracks on BN coating

## COMPUTER CALCULATIONS

The performance of the fuels in a PWR core were studied by using cluster option of the WIMSD4 code [33]. The calculations were done on about 1/16 th of a KWU assembly where the pitch distance was 1.27 cm. The small matrix used in calculations makes a 5 x 5 assembly. Guide thimbles, instrumentation tube, grids etc. were not considered, and there was no boron in water. The fuel element which contains gadolinia was located at the center, and all fuel elements had their fuel pellets coated with BN. However some calculations were also done with no BN and/or no gadolinia. The enrichment of fuel was 5%, and gadolinia was changed as 0, 5, and 10 %. Two different BN coating thicknesses were considered as 30 $\mu$ m and 70 $\mu$ m. In calculations two different cases were considered. In the first case the fuel diameter was kept constant and the pitch distance was changed by changing the number of fuel elements in an assembly. Hence the ratio of cross sectional area of the total number of rods to the cross sectional area of the moderator changed. In the second case the radius of fuel elements were increased, but the total area of the moderator and the number of fuel rods in an assembly were kept constant so the ratio of the total cross sectional area of the fuel elements to the cross sectional area of the moderator changed.

Figure 11 shows a typical change of  $k_{eff}$  values at different pitch distances. The energy produced when  $k_{eff} = 1$  was shown in Fig. 12 for all the fuels. It is seen that the linearity of the curve is lost at pitch

distances below 1.27 cm. A similar behavior of curves was observed when the change of burnup with respect to the ratio of moderator to fuel area was plotted.

In the second case, when the radius of fuel pellet was increased the difference in burnups disappeared for  $30\mu\text{m}$  and  $70\mu\text{m}$  BN coatings at 1.27 cm pitch distance. The further increase in the pitch distance decreases the closest distance between fuel elements resulting in lower moderation of neutrons. This in turn decreases the burnup in either case as seen from Fig.14. The fuel with  $70\mu\text{m}$  BN coating resulted in lower burnup than  $30\mu\text{m}$  BN coating. In fact as the radius of the fuel pellet increases for a constant BN coating thickness, the fuel with larger diameter contains relatively larger quantities of BN. The pitch distance used in normally operating reactors (e.g. 1.27 cm) seems to be also the best value for BN coated fuels. As the amount of gadolinia and/or the thickness of BN coating increases the burnup also increases as seen from Fig. 14. The dependence of burnup on gadolinia content is not linear.

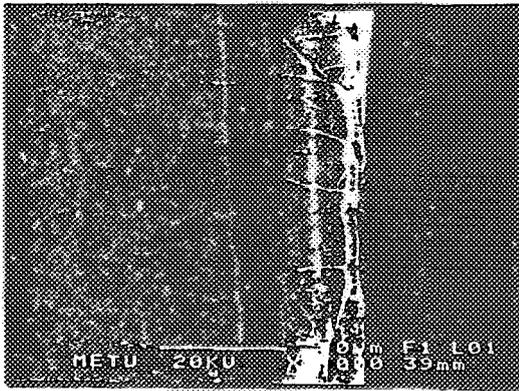


FIG. 9 Side view of BN coating

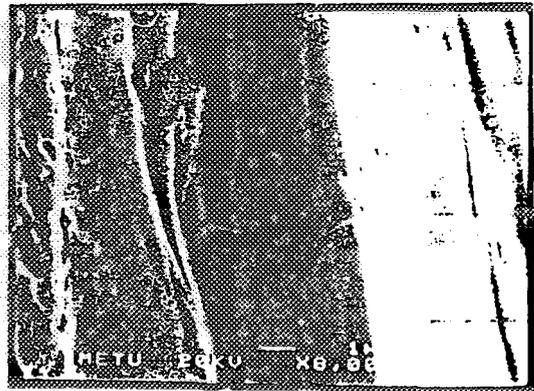


FIG. 10 Another side view

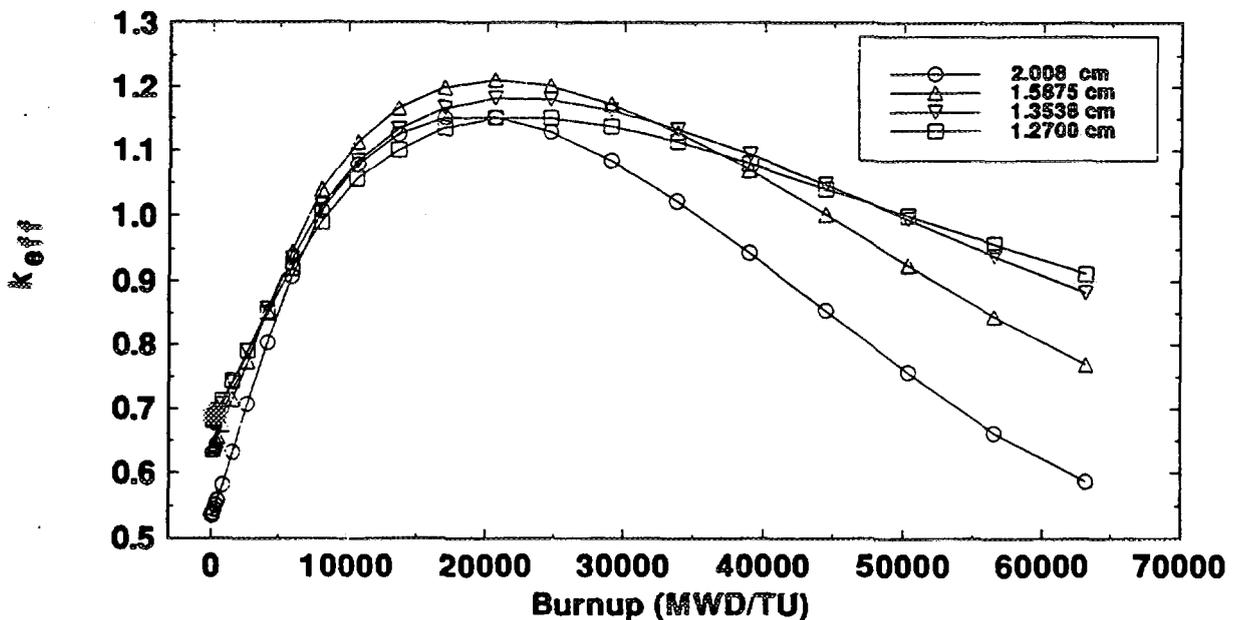


FIG. 11  $k_{eff}$  values at different burnups (enr: 5%, BN:  $70\mu\text{m}$ )

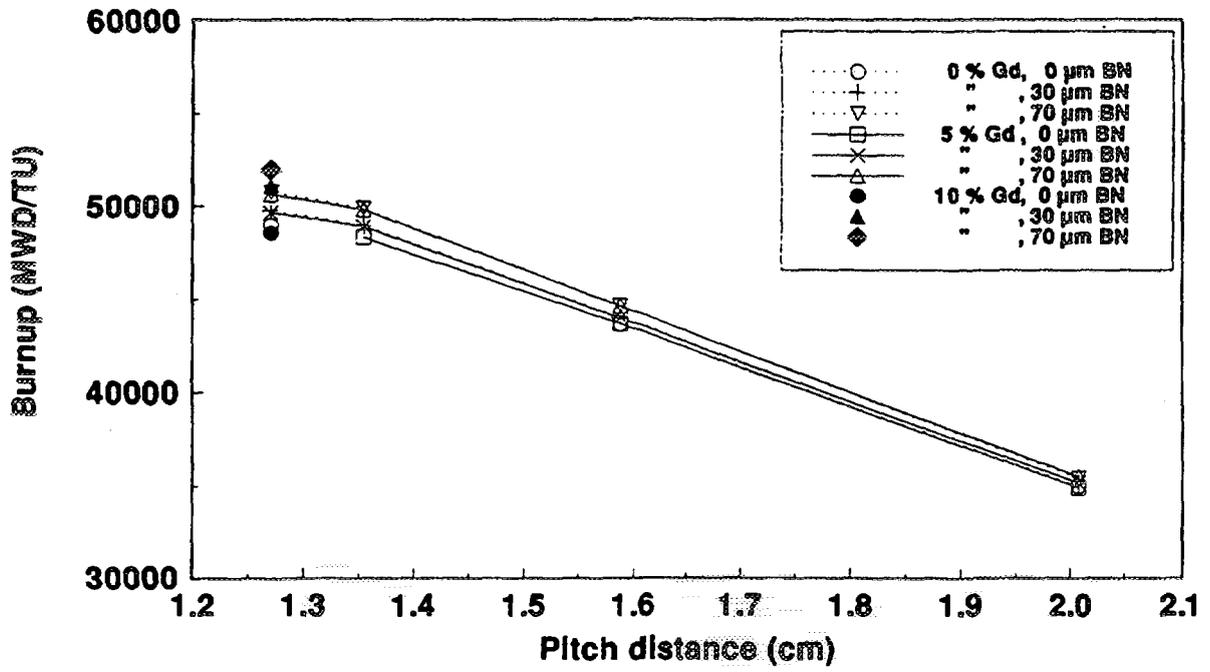


FIG. 12 Change of burnup

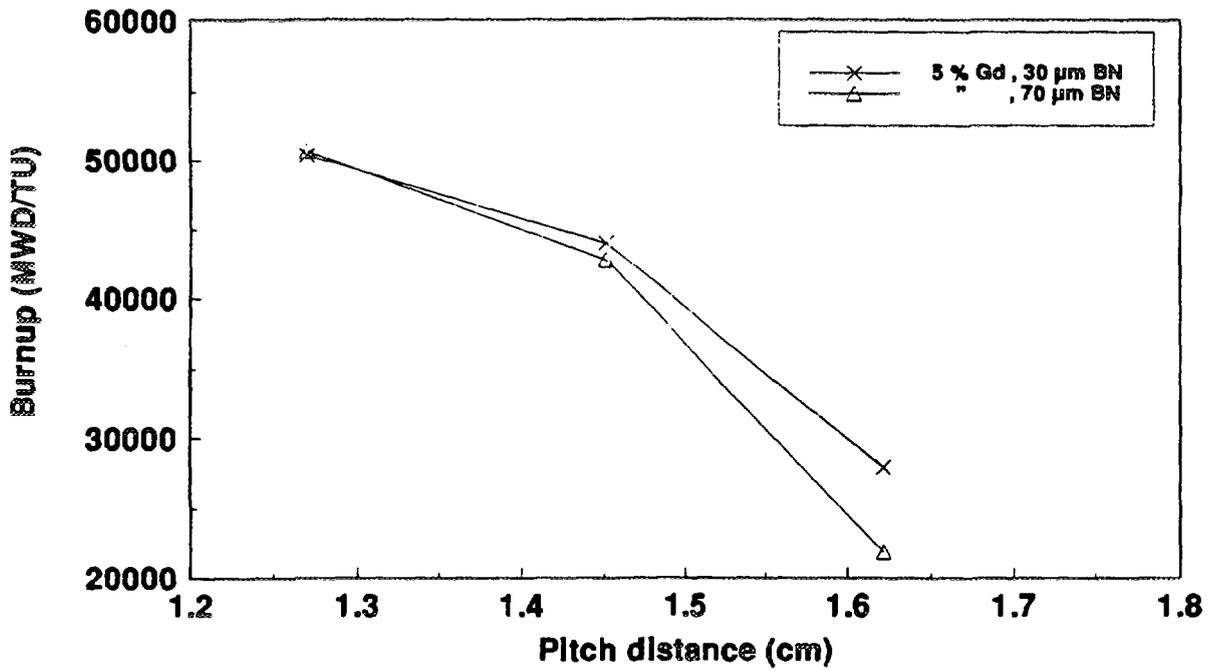


FIG. 13 Change of burnup

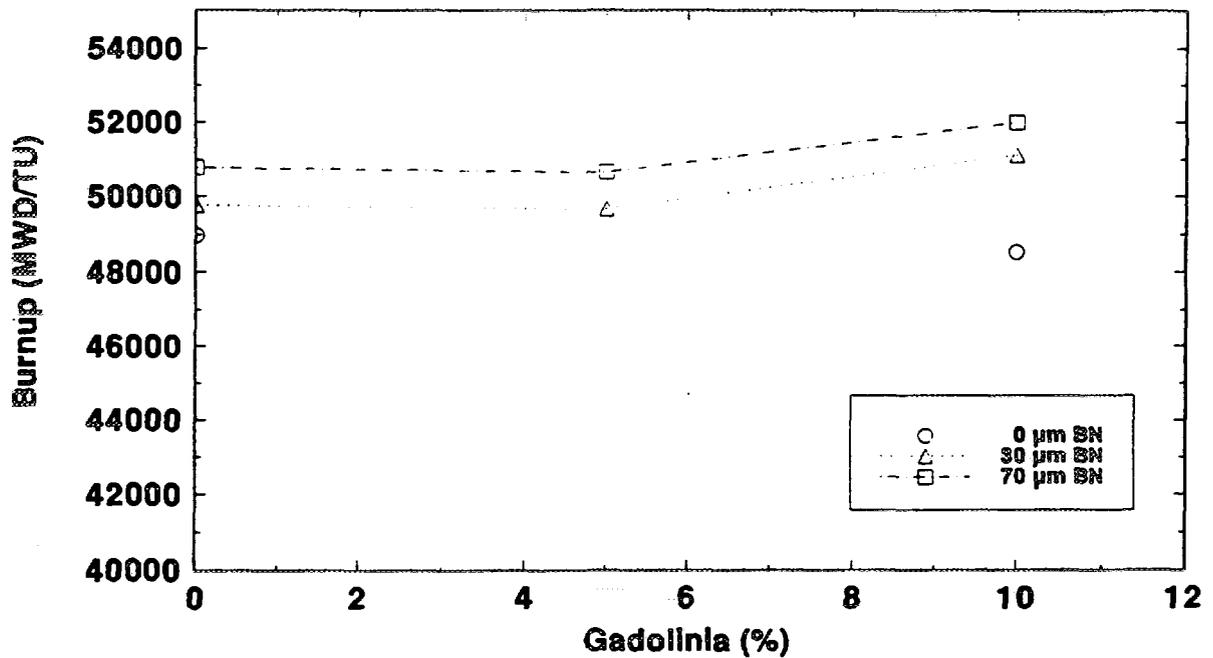


FIG. 14 Change of burnup with gadolinia

## CONCLUSIONS

1. BN coating of nuclear fuels by CVD was accomplished.
2. Platelike and rodlike BN layers formed on fuel pellets.
3. Computer calculations showed that BN coating improved the fuel burnup of uraniagadolinia fuel.
4. The highest burnup was achieved at the present design specifications of a PWR

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## REFERENCES

- [1] INTERNATIONAL ATOMIC ENERGY AGENCY: Burnable Absorber Fuel, Final Report on the Co-ordinated Research Programme on Burnable Absorber Fuel, IAEA-TECDOC, 1993.
- [2] SIMMONS, R.L. et.al., Nucl. Tec. 80 (1988).
- [3] PRITCHETT, J.E. et.al, Operating Experience with ZrB<sub>2</sub> Integral Fuel Burnable Absorbers, ANS 1987 Winter Meeting Proc., 117-118 (1987).
- [4] SRINILTA, S. et.al., A Comparison of Gd and ZrB<sub>2</sub> as Integral Fuel Burnable Absorbers in PWRs, ANS 1987 Winter Meeting Proc (1987)., 124-126.

- [5] RAND, M. J. and ROBERTS, M. J., *Electrochem. Soc.*, 115, 23 (1968).
- [6] MURARKA, M. J., CHANG, C.C., WANG, D.N.K., and SMITH, T.E., *J. Electrochem. Soc.*, 126, 1951 (1979).
- [7] HIRAYAMA, M. and K. SHOHNO, *J. Electrochem. Soc.*, 122, 1671 (1975).
- [8] STEELE, S.R., FEIST, W. and GETTY, W. "Research On Thin Film Tunnel Cathodes, Recombination Cathodes and Similar Cold Cathodes", Final Rep., (Contract DA 28-043-AMC-0035(E)), (September, 1966).
- [9] STEELE, S.R., PAPPIS, J., SCHILLING, H. and SIMPSON, J. "Chemical Vapor Deposited Materials For Electron Tubes". Ist. Triannu. Rep., (Contract DAA 1307-68C-0156) (June 1986).
- [10] BARONIAN, W., *Mater. Res. Bull.*, 7, 119 (1972).
- [11] SANO, M. and AOKI, M., *Thin Solid Films*, 83, 247 (1981).
- [12] MOTOJIMA, S., TAMURA, Y., *Thin Solid Films*, 88, 269 (1982).
- [13] TAKAHASHI, T., ITOH, H., TAKEUCHI, A., *J. Cryst. Growth*, 47, 245 (1979).
- [14] TAKAHASHI, T., ITOH, H., KURDODA, M., *J. Cryst. Growth*, 53, 418 (1981).
- [15] GEBHARDT, J.J., *Proc. 4th. Int. Conf. on "Chemical Vapor Deposition"*, Boston, MA, Electrochemical Society, Princeton, NJ, 460 (1973).
- [16] CLERC, G., GERLACH, P., *Proc. 5th. Int. Conf. on "Chemical Vapor Deposition"*, Slough, Electrochemical Society, Princeton, NJ., 777 (1975).
- [17] ZUNGER, A., KATZIR, A., HALPERIN, A., *Phys. Rev. B*, 13, 5560 (1976).
- [18] POWELL, C.F., OXYLEY, J.H., BLOCHER, J.M., "Vapor Deposition", Wiley, New York, 663, (1966).
- [19] HANIGOFSKY, J.A., et al., *J. Am. Ceram. Soc.* 74[2], 301-305 (1991).
- [20] LEE, W.Y., et al., *J. Am. Ceram. Soc.*, 74[9], 2136-40 (1991).
- [21] MATSUDA, T., et al., *J. Mater. Sci.*, 21, 649-658 (1986).
- [22] PIERSON, H.O., *J. Compos. Mater.*, 9, 228 (1975).
- [23] NASLAIN, R., et al., *J. Am. Ceram. Soc.*, 74 [10], 2482-88 (1991).
- [24] CONSTANT, G., FEURER, R., *J. Less-Common Met.*, 82, 113 (1981).
- [25] SCHMOLLA, W., and HARTNAGEL, H.L., *Solid State Electronics*, 26, 10, 931-939 (1983).
- [26] PACIOREK, K.J.L., et al., *Inorg. Chem.* 27, 2432-2436 (1988).
- [27] MAYA, L., and RICHARDS, H.L., *J. Am. Ceram. Soc.*, 74, [2] 406-409 (1991).
- [28] GAFRI, O., GRILL, A., and ITZHAK, D., *Thin Solid Films*, 72, 523-527 (1980).
- [29] GUNDUZ, G., *Uranium-Gadolinium Oxide Fuel Production Sol-Gel Technique*, Final Report, IAEA Vienna (1992).
- [30] TAINE R.T and NARULA C.K., *Chem. Review* 90, 73 (1990).
- [31] LEE W.Y., LACKEY W.J., *J. Am. Ceram. Soc.*, 74, 2642 (1991).
- [32] ROTH M.J., MACDOUGALL J.D., KEMSHELL P.B., *The Preparation of Input Data for WIMS*, AEW-R 538, (1967).