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Boron coating on boron nitride coated nuclear fuels by chemical vapor deposition

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Abstract

Uranium dioxide-only and uranium dioxide–gadolinium oxide (5% and 10%) ceramic nuclear fuel pellets which were already coated with boron nitride were coated with thin boron layer by chemical vapor deposition to increase the burn-up efficiency of the fuel during reactor operation. Coating was accomplished from the reaction of boron trichloride with hydrogen at 1250 K in a tube furnace, and then sintering at 1400 and 1525 K. The deposited boron was identified by infrared spectrum. The morphology of the coating was studied by using scanning electron microscope. The plate, grainy and string (fiber)-like boron structures were observed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The materials known as burnable absorbers such as gadolinium oxide (Gd_2O_3) with a high thermal neutron absorption cross-section, and zirconium diboride (ZrB_2) with its relatively lower cross-section are used in the reactor fuels to increase core life and to achieve a better control of the reactor. Due to its high cross-section Gd_2O_3 depletes very fast. Therefore, it is introduced into uranium dioxide (UO_2) as a homogeneous mixing of both uranium and gadolinium. This is done either by powder mixing [1,2] or by sol–gel technique [3–5]. The decrease both in the thermal conductivity and in the melting point of the fuel when the Gd_2O_3 content is greater than 10% are the disadvantages of the use of gadolinia besides its fast depletion rate.

The coating of fuels with ZrB_2 is achieved by using sputtering techniques [6,7]. ZrB_2 has the disadvantages of both complicated fabrication and dissolution difficulty in the reprocessing stage due to the chemical inertness of zirconium. The poor moderator temperature coefficient control of ZrB_2 fuel is another disadvantage. Good fuel reprocessibility and good moderator temperature coefficient control are the advantages of the use of Gd_2O_3. The use of both gadolinium and boron in the same fuel naturally results in a new fuel with improved advantages. To get rid of the adverse effects of ZrB_2, fuels were coated with a thin layer of boron nitride (BN) [8].

Coating of fuels with boron (B) is appealing because boron has higher density than BN. However, boron can make boride with uranium at 1800–2000°C and lower the vitrification temperature of fuels because of its fluxing effect. Therefore, it is not appropriate to coat fuels directly with boron. So, the fuels can be coated first with BN to prevent the interaction of boron with fuel, and then with boron. The main advantages of B coating are as follows:

1. Metallic B has higher density than BN.
2. It resists very high temperatures (melting point = 2300°C).
3. It has high hardness (Vickers hardness = 2800 kg/mm^2).
4. It has high wear and corrosion resistance.

Elementary B exists in two forms: (i) fine crystalline so called amorphous B, which is brown in color, and (ii) crystalline B of dark gray color [9,10].

BN coating can be achieved from the reaction between boron trichloride and ammonia or from the

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decomposition of borane trimethylamine (BTMA) complex [8]. In this work, three different ceramic nuclear fuels coated previously with BN from the precursor of BTMA complex were coated with B by chemical vapor deposition (CVD) method.

The coating films formed by sputtering technique are not smooth, and pinholes appear on the surface. The high cost and the complexity of the process make it unfavorable. Therefore, the method of CVD was preferred here to obtain continuous and smooth coating films.

The deposition process can be assumed to be as follows [11]:

1. H_2 and BCl_3 diffuse to the deposition surface.
2. They react for depositing B and releasing HCl and $HBCl_2$, which are the only intermediate species obtained at equilibrium.
3. HCl and $HBCl_2$ diffuse away from the surface.

The reactions taking place on the surface of the substrate can be mainly summarized by:

$$BCl_3 + 1.5\ H_2 \rightarrow B + 3\ HCl \quad \text{(main reaction)}$$

$$BCl_3 + H_2 \rightarrow HBCl_2 + HCl \quad \text{(side reaction).}$$

2. Experimental procedure

The B deposition on BN coated fuels was accomplished through the reaction taking place between BCl_3 and H_2 in an alumina tube furnace as shown schematically in Fig. 1.

The fuel pellets already coated with BN were located on a U-shaped copper tubing. It was cooled by water to create a temperature gradient between the gas phase and surface of the BN layer. The furnace was purged with an H_2 and argon (Ar) gas mixture, and was heated by a resistive heating element surrounding the alumina tube to the deposition temperature of 1250 K. BCl_3 was carried into the furnace by Ar as a carrier gas. After completion of the coating process the furnace was cooled down to the room temperature under H_2 and Ar atmosphere.

The B formed on BN was identified by its infrared (IR) spectrum. The coating morphologies of B were obtained by using a scanning electron microscope (SEM).

3. Results and discussion

3.1. Color

The color of B was reported to vary from brown for the fine crystalline so-called amorphous state to dark gray for the crystalline form [10]. The same variation was observed also in this study.

3.2. IR Spectrum

The IR spectrum of B produced from BCl_3 is given in Fig. 2. It was reported that B has three absorption peaks at 1080, 800, and 750 cm^{-1} [10]. All peaks are due to B–B vibrations. The first two peaks can be clearly seen from Fig. 2, the third one also exists but it is very weak.

3.3. Microstructure of B coated on BN

The SEM pictures of B coatings on the previously BN coated pellets are shown in the figures below, where I, II and III denote the BN coated fuels UO_2-only, UO_2–Gd_2O_3 (5%) and UO_2–Gd_2O_3 (10%), respectively.

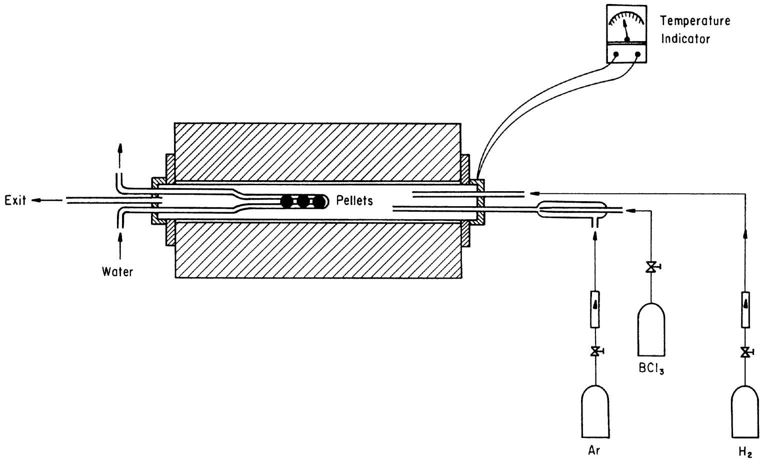

Fig. 1. CVD apparatus.

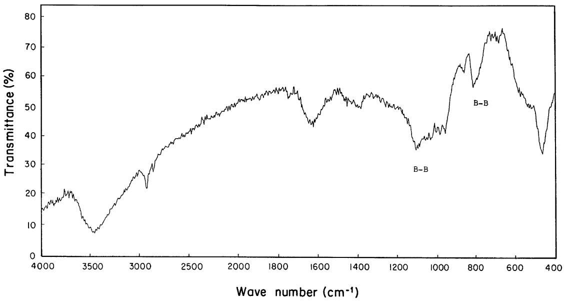

Fig. 2. IR of boron.

The grain sizes of uncoated fuels were found as 4, 6 and 12 μm for I, II and III fuels, and the grain sizes of BN coated on I, II and III were found to be 4.75, 2.2 and 2 μm, respectively [8]. The grains of B coating is seen in Fig. 3. Its average grain size is 1.04 μm.

The appearance of the BN grains looks like uncoated fuel grains not like BN grains. This is probably due to the cubic crystal structure of urania and the rhombic structure of B. The crystal structure of BN is hexagonal.

Boron also forms a continuous structure in the form of long thin fiber as seen from Fig. 4.

The average size of B grains on II is 0.84 μm, which is smaller than the grains on I. The grains formed on II are relatively irregular in shape as seen from Fig. 5. The fiber-like B structure was also observed on II as seen in Fig. 6. It is wider and longer than the one in Fig. 4.

The B grains on III are seen in Fig. 7. The average grain size is 0.63 μm, which is smaller than the sizes of grains on II. The grains look hemispherical in appearance. The relatively sharp corners seen in Fig. 3 were distorted in Fig. 5 and completely disappeared in Fig. 7. This must be due to the increased amount of gadolinia in fuel, because the increase in gadolinia changes the surface potential of the fuel and, thus, the fractal dimensions of grains [12,13]. This in turn may even result in different epitaxial growths [14].

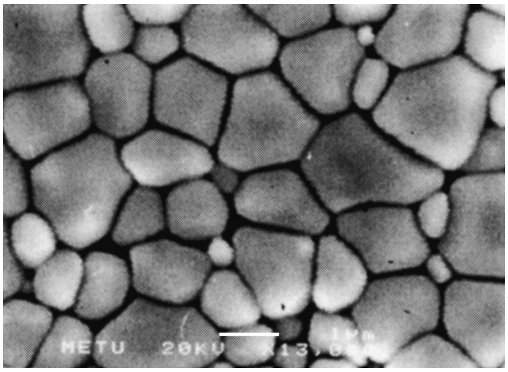

Fig. 3. B on I (13000×).

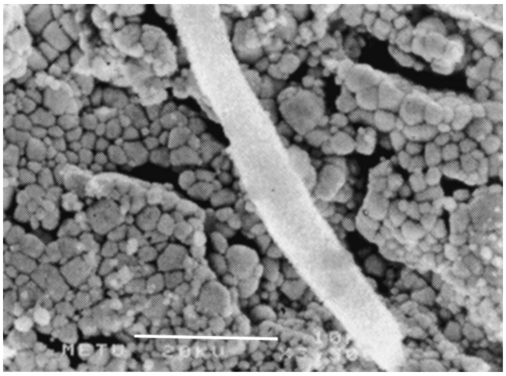

Fig. 4. B on I (3300×).

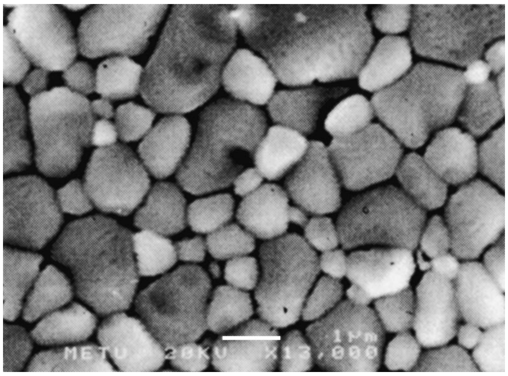

Fig. 5. B on II (13000×).

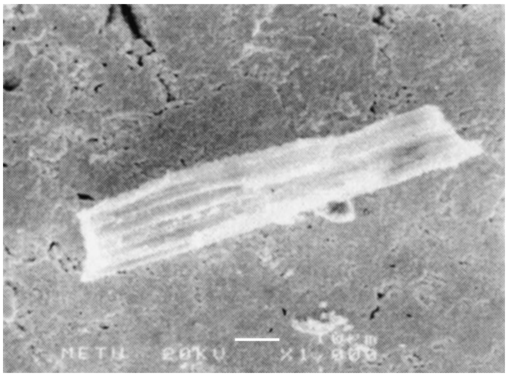

Fig. 6. B on II (1000×).

The crowded and small size rod shaped B structures are seen on the surface of the much smaller grains in Fig. 8.

Two different grains are seen in Fig. 9. The B grains with relatively large sizes were deposited on very small grains. The magnified view of the small and gravel shaped grains are seen in Fig. 10. In contrast to large grains above them, they have very sharp corners.

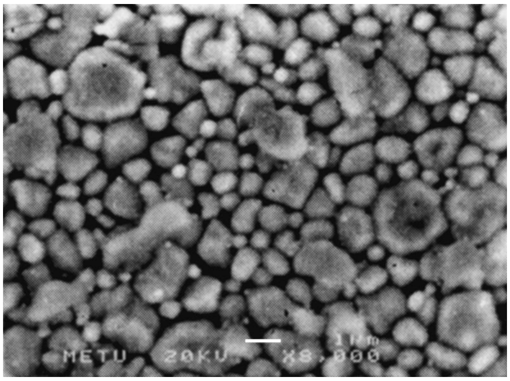

Fig. 7. B on III (8000×).

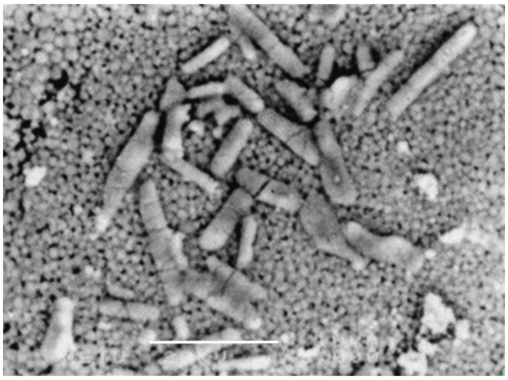

Fig. 8. B on III (3000×).

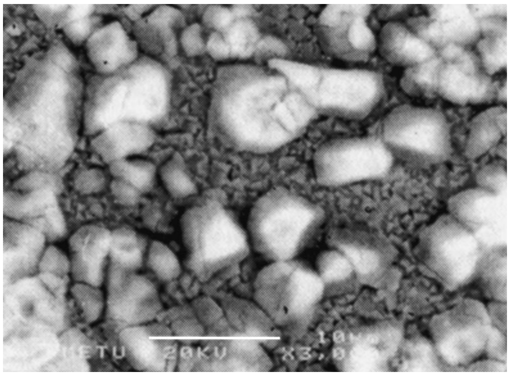

Fig. 9. B on III (3000×).

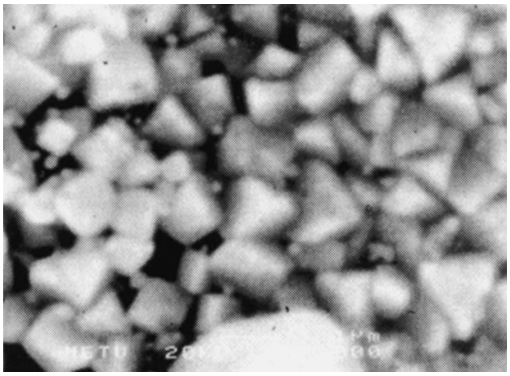

Fig. 10. B on III (13 000×).

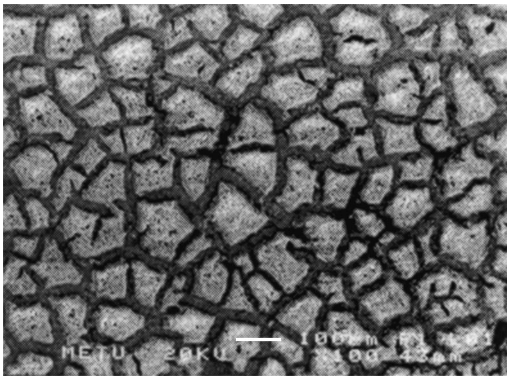

Fig. 11. Repeated B coating on III (100×).

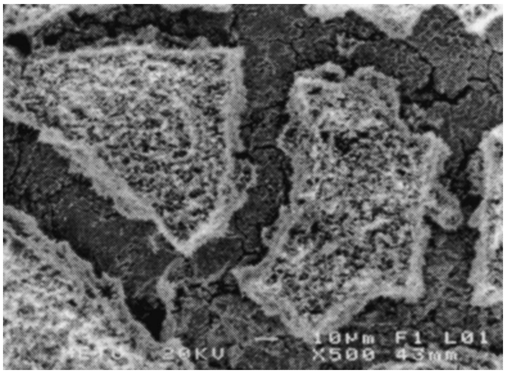

Fig. 12. Repeated B coating on III (500×).

To study the effect of repeated coating, the specimens were coated for a second time under the same conditions. The appearance of the coating varied from previously grainy structure to a very different structure resembling cracked soil. In Figs. 11 and 12, B islands are seen at (100×) and (500×) magnifications, respectively. The highly magnified (8000×) view of an island is seen in Fig. 13. It shows high irregularity in shape.

The repeated B coating on II is seen in Fig. 14. Here, the borderlines between B islands are very thin than the lines seen in Fig. 11. Thin B fibres and leaf-like B structures were also observed as seen from Fig. 15. Lamellar structures are seen especially on the boundaries as seen from Fig. 16.

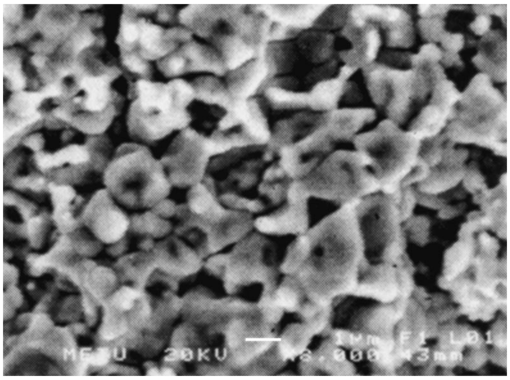

Fig. 13. Irregular B structures (100×).

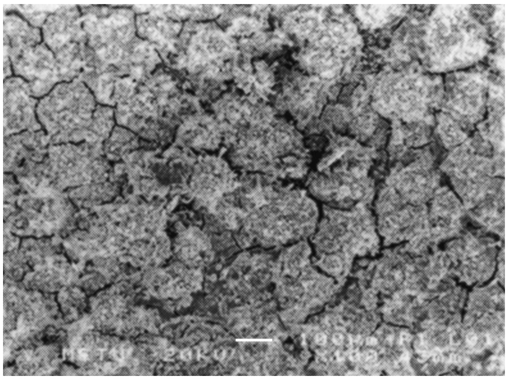

Fig. 14. Repeated B coating on II (500×).

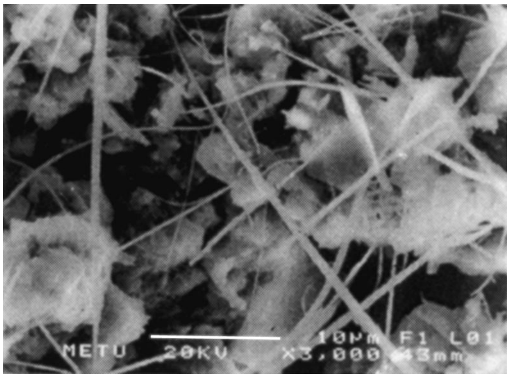

Fig. 15. B fibers on II (3000×).

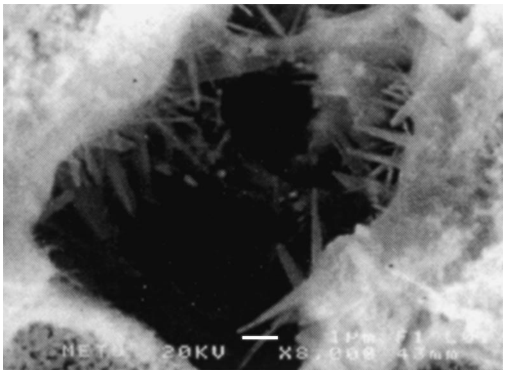

Fig. 16. Lamellar B (3000×).

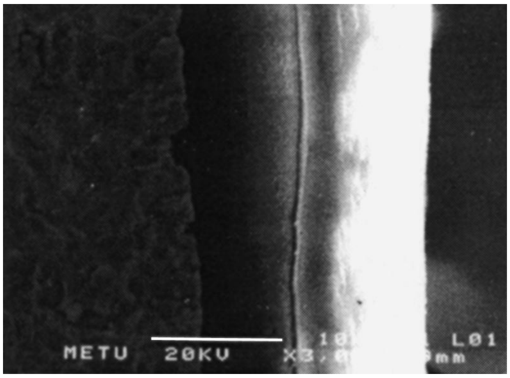

Fig. 17. Interfaces of fuel/BN/B (3000×).

The cross-sectional views of BN and B layers are seen in Fig. 17. This picture was taken from the cross-section of a specimen broken mechanically.

The excellent adherence of B onto BN layer is seen from the boundary layer between BN and B layers. This is of primary importance for fuel stability when burning inside the reactor. BN adheres on the fuel and B adheres on the BN firmly providing a good mechanical rigidity and stability.

4. Conclusions

1. B can be deposited from BCl_3 by CVD on BN, which was already deposited on fuels.
2. The IR spectrum of B powder produced by CVD method is in agrement with the literature.
3. B deposited onto BN layer shows grainy structure in all fuels. Also some B fibres on II, and short rod shaped and gravel type B structures on III were observed.
4. The sizes of grains decrease with increase in Gd_2O_3 content in the fuels.
5. By repeated coating, the grainy structure turns into cracked soil structure.
6. The excellent adherence of B onto BN layer, and BN onto fuel was observed from the SEM picture of fuel/BN/B interfaces.

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