In this study, pure urania (UO$_2$) and urania-gadolinia (UO$_2$-Gd$_2$O$_3$), 5 and 10% Gd$_2$O$_3$ fuels were first produced by sol-gel (solution-gelation) ceramic fuel preparation technique. The sol-gel micro sphere pelletization technique is a recent and advanced concept of fabrication of fuel pellets that is because it ensures excellent micro homogeneity in the prepared pellets. The sintered fuel pellets were then coated with boron carbide (B$_4$C). This coating is performed through chemical vapor deposition (CVD). The chemical vapor deposition consists of essentially of reducing or decomposing a volatile compound of coating material upon a heat surface on the size of micron dimensions.

In this work, boron carbide was deposited in a silica glass. Afterwards, the XRD spectra of B$_4$C coatings were taken by using B$_4$C on the surface of the silica glass. The spectra results were in agreement with the ones in the literature. The experiments showed that the composition of the coating changed with deposition temperature. There was boron rich coating in the low experimental temperatures while the coating in the high temperatures was found to be rich in the carbon content. The morphology and the thickness of the coating have been investigated by using Scanning Electron Microscopy (SEM). The investigation under the SEM revealed a fine grained and some rod like layered boron carbide coatings.

**Key words :** Uranium dioxide, gadolinium oxide, boron carbide, CVD, nuclear fuel.

**INTRODUCTION**

Boron carbide, B$_4$C is a neutron absorbing material used to control the reactivity of nuclear reactors by the control rods with a neutron capture reaction of $^{10}\text{B(n,}\alpha)^7\text{Li}$. In addition to neutron absorbers, boron carbide is used as many functional materials, such as the anticorrosion and refractory material at high temperature with high hardness, wear resistant components, lapping and polishing powders, armor tiles, radiation protection and shielding, light weight cermets, boron raw materials, solid fuel for ducted rockets, boronizing agent and welding electrodes.

Recently, B$_4$C and its composite are highly attractive in using for a thermo generator (thermoelectric energy converter) that has been used for decades to provide electric power to spacecraft. The thermoelectric material can be used for the direct conversion of thermal into electric energy. The high-energy conversion efficiency of B$_4$C is due to a high thermo power (see beck coefficient) and high electrical and low thermal conductivity.$^{1}$
The improvement of physical and neutronic properties of a nuclear fuel plays a very important role to develop advanced fuel. There are a large number of material used as burnable absorbers, such as natural B ($\sigma_a=760$ barns) and enriched B-10, gadolinia ($\sigma_a=49000$ barns), ZrB$_2$ and BN, which are in the form of coating on the fuel pellets$^{(2,3)}$. The advantages using burnable absorbers are to provide smooth reactor control, to improve reactor performance through longer cycle lengths, and to load the core with relatively enriched fuel. Gadolinia is mixed into urania either by dry or by wet sol-gel techniques and coprecipitation methods$^{(4,5)}$.

Meanwhile, the CVD technique is used to coat a thin layer of advanced materials. CVD application areas may be explained as integrated circuits, optoelectronic devices and sensors, micro machines, and fine metal and ceramic powders.

The sol-gel processes have been applied to produce oxides or carbides of fissile or fertile materials or a homogeneous mixture of both. Generation and handling of high radio toxicity of Pu, U-233 and Th is eliminated by sol-gel.

It is well known that the properties of materials show a huge change when particle size is reduced to sub micrometric or nanometric scale. The magnetic and transport properties of materials were widely affected by the particle size reduction studies. In this method, urea was used as jellifying agent due to its low decomposition temperature (200-250 °C) compared with other jellifying agents (such as: citric acid, polyvinyl alcohol, etc.).

Recently, the sol-gel derived products have many application areas. Powder and thin films can be used for electronic, optical, and optoelectronic components and devices, capacitors, memory devices, IR detectors, and wave guides, optic sensors, thermal insulation, and antireflection coatings. In addition, lenses, mirror substrates, graded index optics, optical filters, sensors, passive and nonlinear active wave guides, lasers, membranes for separation and filtration are under development.

In this paper, the microstructure and XRD spectra of B$_4$C coated fuel is examined under scanning electron microscope (SEM), as well as XRD spectra of coated B$_4$C compound. Three different fuels are coated with B$_4$C by the CVD technique$^{(6)}$.

**EXPERIMENTAL**

In this experiment, three different nuclear fuel pellets were used as the substrates. One was pure urania ($\text{UO}_2$), and the second one and third one 5% and 10% gadolinia containing fuels ($\text{UO}_2$-Gd$_2$O$_3$ 5% and $\text{UO}_2$-Gd$_2$O$_3$ 10%). The pure urania and urania-gadolinia fuels used in this study were prepared by sol-gel technique, and Gündüz et al investigated their physical and chemical properties$^{(3)}$.
The boron carbide coating is generally carried out by the CVD reaction of boron halides with methane, Cl2, CCl4, C3H6, C2H4, carborane (C3B1H1) etc., under excess H2 atmosphere using thermal CVD, plasma enhanced CVD and pyrolysis techniques, about 1000-1600 °C.

In this study, BCl3-CCl4-H2 reactants were used by thermal CVD with three reactive gas mixtures at three different coating temperatures (1000 °C, 1100 °C and 1175 °C). Details of the experimental results including FTIR analysis were explained in another paper (6). In this paper, boron carbide coated fuel pellets were examined under scanning electron microscope. Also, the x-ray diffraction spectra of rhombohedral boron carbide coating were investigated in a range of 15°<20<60°.

RESULTS AND DISCUSSIONS

In literatures, the color of boron carbide deposits was reported to vary from red brown to black. These colors were also noted in this study. However, the color of stable B4C was reported light black. This color was also noted at the experiment of 1175 °C case.

The optical microscope pictures of boron carbide coated at three different temperatures have color of light brown in boron rich boron carbide at low temperatures and however light black at carbon rich boron carbide at high temperature coating experiments. These optical pictures and other details are given in elsewhere (7).

The optical pictures showed that coating at 1000 °C yielded brown-shelled boron rich boron carbide while the coating obtained at 1100 °C had a brown dominant brown-black particulate structure. The coating performed at 1175 °C was composed of light-black homogeneous crystals having bigger cell morphology very similar that of thermodynamically stable B4C.

Surface morphology

The surface morphology of UO2 and UO2-Gd2O3 fuel pellets coating at 1175 °C were investigated by scanning electron microscopy (JSM, Model 6400). The particle size of the fuel pellets affects the rate of production of fission gases. The retention time of the fission gases that relatively depended on the porosity and particle size of fuel pellets are critical parameters for its performance. Long retention of the fission gases in the fuel causes cracking problems in it.
Figure 1 SEM pictures of uncoated: (a) pure UO$_2$, (b) UO$_2$-Gd$_2$O$_3$ 5% gadolinia.

(a) SEM pictures of EBM

(b) SEM pictures of EBM

Figure 2 SEM pictures of B$_4$C coated pure UO$_2$.

(a) SEM pictures of EBM

(b) SEM pictures of EBM

Figure 3 SEM pictures of B$_4$C coated UO$_2$-Gd$_2$O$_3$ 5% gadolinia.
The average particle diameter of the coated pure UO₂ fuels observed about 5 um. The mean particle diameter of urania-gadolinia 5% and urania-adolinia 10% fuels however ranged between 5-12 um in size. Figure 1a and b indicate the SEM pictures of uncoated pure urania. (UO₂) and UO₂-Gd₂O₃ 5% respectively. SEM pictures of spherical uncoated fuels are pictured with magnifications of 4.000 times, and having an average particle diameter in the range of 5 um in Fig.1. Figure 2a and b display SEM pictures of boron carbide coated pure UO₂. The B₄Ccoating in Fig.2a having magnification of 800 times has a particle dominant, but some thin rod-shaped structures have been observed near center of the picture. Figure 2b shows that B₄C coating on pure UO₂ having magnification of 4.000 times and has a glassy coating structure. Figs. 3a and b indicate SEM pictures of B₄C coating on urania-gadolinia (5%) fuel with magnifications of 1600 and 4000 times respectively. Coating on Fig. 3a is formed in the form of a short pile of rod structures. However, as seen in Fig. 3b, coating is formed in the form of big pieces of glassy structures. Figure 4a and b show that SEM pictures of B₄C coating on urania-gadolinia (10%) fuel with times 8000. Coating in Fig. 3a has in the form of plate and rod-like shaped structures. On the other hand, coating in Fig. 3b is relatively deposited on the pellets in the form of glassy-pile structures. The cross-sectional views of B₄C coating with three different fuel compositions are pictured in Figure 5. Fuel pellets used as substrates are cracked axially.
B₄C coating forms only on the surface with no penetration into the fuel as seen from the interface layers. Coating is formed in a layered manner and the mean thickness of it is measured as about 5µm.

**XRD spectra**

Rhombohedral boron carbide yields C-B-C and C-B-B chain concentrations in the mode of central atom. Distribution of carbon atoms, and its modification in the homogeneity range (B₂₅C-B₇₂C) are unknown. But carbon distribution influences on the physical properties are well known \(^{(5)}\). The x-ray diffraction spectra of coated boron carbide are given in Figure 6. The XRD spectra of coated boron carbide showed peaks with interatomic distances of d=2.57 Å [003] and d=2.57 Å [104]. Graphite peaks appeared at 2θ=28.5° and 45°. The XRD peaks become apparent when the carbon content is increased in boron carbide. The XRD peaks however weakened in boron rich B₄C. The characteristic peak of B₄C appeared at 2θ=36° and [104] space coordinates. There was another peak observed at the space coordinates of [003] with 2θ=35.5°.

![XRD spectrum of B₄C coating reaction from BCl₃+CCl₄+H₂.](image)

**CONCLUSION**

The coating of fuel pellets with ZrB₂ performed by spattering techniques, which is complicated and more expensive compare to CVD. On the other hand, there is a relatively new technique of boron nitride coating, which is more advantageous than ZrB₂ coating method. However, the nitrogen element in compound BN reacts with neutron and convert into radioactive nitrogen-15.
\(^{(14}\text{N}(n,\gamma)^{15}\text{N})\), this is an undesirable effect. As a result, coating fuel pellets with B\(_{4}\)C can eliminate the above problems.

Acknowledgements

The author expresses his thanks to Prof. G. Gündüz for suggestions and supporting while performing this experimental study. He expresses special thanks to Dr. B. Kopuz and Dr. A. Aksit and other colleagues in Nuclear Fuel Department of the Çekmece Nuclear Research and Training Center, TAEA, for sinterization and processing of the fuel pellets. The author also thanks to Dr. A. Tanrikut and Assoc. Prof. I. Uslu for their appreciations.

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