ELSEVIER

Journal of Nuclear Materials 256 (1998) 207–212

journal of nuclear materials

Microstructure of boron nitride coated on nuclear fuels by plasma enhanced chemical vapor deposition

Hasan H. Durmazuçar [a], Güngör Gündüz [b,*], Canan Toker [c]

[a] Kimya Mühendisliği Bölümü, Cumhuriyet Üniversitesi, Sivas 58140, Turkey
[b] Kimya Mühendisliği Bölümü, Orta Doğu Teknik Üniversitesi, Ankara 06531, Turkey
[c] Elektrik-Elektronik Mühendisliği Bölümü, Orta Doğu Teknik Üniversitesi, Ankara 06531, Turkey

Received 14 June 1997; accepted 1 April 1998

Abstract

Three nuclear fuels, pure urania, 5% and 10% gadolinia containing fuels were coated with boron nitride to improve nuclear and physical properties. Coating was done by plasma enhanced chemical vapor deposition technique by using boron trichloride and ammonia. The specimens were examined under a scanning electron microscope. Boron nitride formed a grainy structure on all fuels. Gadolinia decreased the grain size of boron nitride. The fractal dimensions of fragmentation and of area–perimeter relation were determined.

1. Introduction

There has been important developments in burnable absorber fuels within the last two decades. Two absorbers have been of commercial importance, one is the use of gadolinia (Gd_2O_3) within the fuel, and the other is to coat the fuel with zirconium diboride (ZrB_2). The mixing of gadolinia with urania can be accomplished either by conventional powder mixing or sol–gel process [1–3]. The deposition of ZrB_2 onto the fuel is done by sputtering technique [4,5] which is quite complicated. Gadolinia has some disadvantages: (i) it depletes very fast; (ii) it lowers the thermal conductivity of the fuel; and (iii) it reduces the melting point of the fuel when its content is above 10%. The use of ZrB_2 has mainly the disadvantages of (i) difficult fabrication and reprocessing, and (ii) low moderator temperature coefficient control.

When both absorbers are used together in the same fuel their disadvantages can be somewhat decreased, and the change of gadolinia/boron content gives the flexibility of fuel design upon the desired requirements. To overcome the problems of ZrB_2 coating, recently a new technique of coating has been suggested [6,7]. This is boron nitride (BN) coating of fuels by chemical vapor deposition (CVD). Boron nitride has excellent physical and chemical properties; it is chemically inert, withstands high temperatures and pressures, and has a thermal conductivity comparable with stainless steel. The CVD of BN was done by using two different sources. One is from the interaction of boron trichloride (BCl_3) with ammonia (NH_3), and the other from the decomposition of borane trimethyl amine complex (BTMA). Different analyses such as infrared spectrum, X-ray diffraction, and scanning electron microscopic examination showed that both BCl_3 and BTMA could be used as BN precursors for coating nuclear fuels.

The CVD of BN can be achieved above 875 K and hardening of it needs temperatures around 1400 K. This is a time consuming method, and a much faster technique is to use plasma enhanced chemical vapor deposition (PECVD). By this technique it is possible to ionize the precursor materials very efficiently at high plasma powers and thus the formation of even cubic BN which is the second hardest substance after diamond can be realized [8–13]. The IR spectra of BN obtained from CVD and PECVD are similar, and the characteristic B–N stretching appears as a wide peak at 1400 cm^{-1} in both cases [7,14,15]. Different variety of precursors such as boron trichloride, diborane (B_2H_6), and cyanoborane $(CNBH_2)_n$ are used [14,16].

* Corresponding author.

PII: S0022-3115(98)00058-0

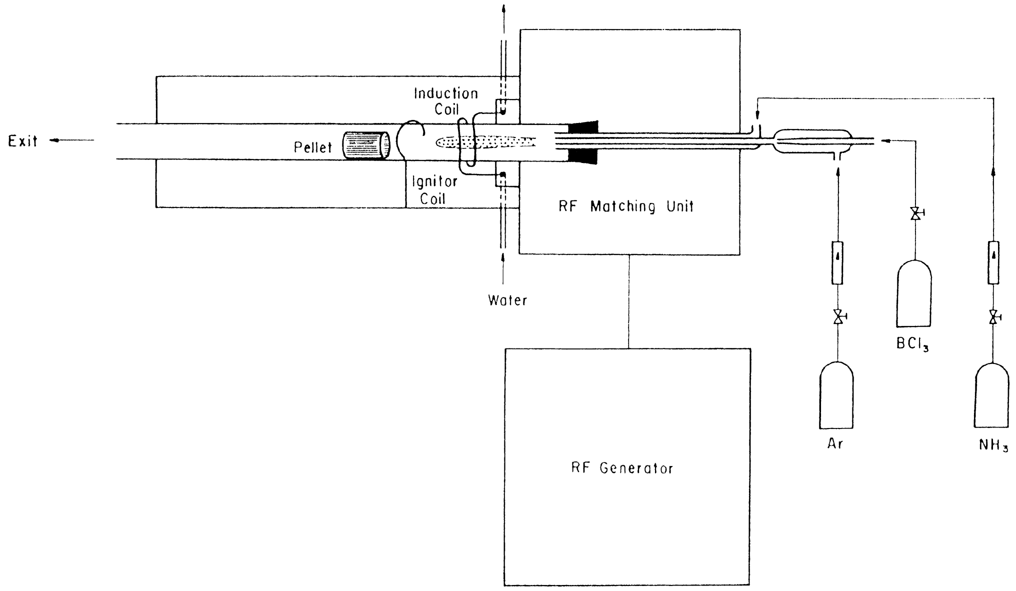

Fig. 1. PECVD system.

The aim of this work was to coat nuclear fuels by BN by the use of PECVD technique, and study its microstructure.

2. Experiments

In the experiments BN was deposited from gaseous BCl_3 and ammonia (NH_3). Fig. 1 shows the experimental set up for plasma coating. It consists of a radiofrequency (RF) generator connected to a matching unit. The wave produced has a frequency of 27.12 MHz, and its energy is inductively discharged onto the gases passing through a quartz tube at atmospheric conditions. The operating power was 750 W. The plasma was created by argon (Ar) gas, and BCl_3 and NH_3 molecules decompose in the ionized Ar gas. BCl_3 was carried into the reaction zone by Ar as seen in Fig. 1.

Water runs through the discharge tube to eliminate excessive heating. The NH_3/Ar ratio was critical for the formation of plasma, and it was kept at 1/12 by volume. The fuel pellet was kept 3 cm away from the torch to minimize the possible effects of ionized gases on the fuel.

Three different nuclear fuels were used in the experiments; (i) pure uranium dioxide (UO_2-only); (ii) uranium dioxide (95%)–gadolinium oxide (5%) (UO_2–5% Gd_2O_3); and (iii) uranium dioxide (90%)–gadolinium oxide (10%) (UO_2–10% Gd_2O_3). These fuels were prepared by sol–gel method. Their production and physical properties are described elsewhere [2,3].

The specimens were examined by using a scanning electron microscope (JSM, Model: 6400).

3. Results and discussions

The photographs of UO_2-only, UO_2–5% Gd_2O_3, and UO_2–10% Gd_2O_3 are shown in Figs. 2–4, respectively. BN coatings on these fuels are shown in Figs. 5–7 at two different magnifications of ×3000 and ×13 000 in each case. It is seen that BN forms grains and they are much smaller than fuel pellet grains in all cases. The substrate does affect the grain size. The grains formed on UO_2-only are larger than those formed on gadolinia containing fuels. Gadolinia decreases the grain size,

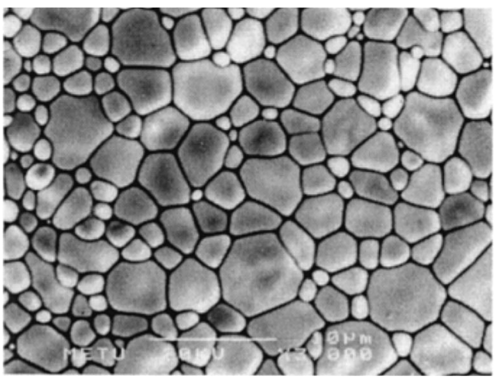

Fig. 2. Uncoated UO_2-only (×3000).

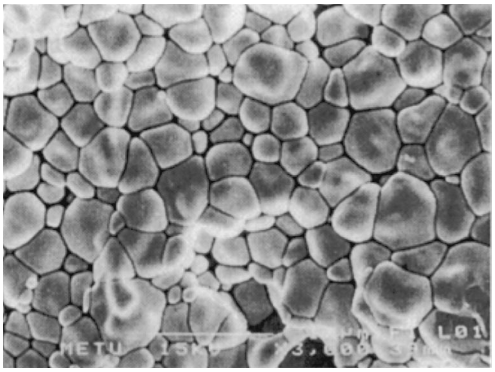

Fig. 3. Uncoated UO_2–5% Gd_2O_3 (×3000).

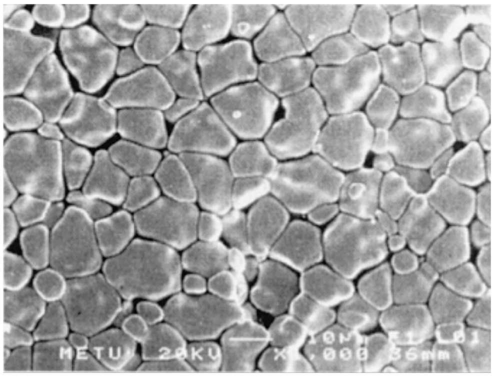

Fig. 4. Uncoated UO_2–10% Gd_2O_3 (×3000).

and the smallest grains were formed on UO_2–10% Gd_2O_3 fuel.

In order to make a quantitative comparison of BN grains formed on the three substrates, the fractal analysis of BN grains were carried out. The information obtained from this analysis shows the route of the formation of that material and the way by which its morphology is formed. Two different fractal dimensions were determined, one is the fragmentation fractal dimension and the other the fractal dimension of the area–perimeter relation [17].

The growth of a BN grain is limited by the presence of other grains in the neighborhood. Therefore the self-similarity is bounded by the upper and lower limits of the grains. Under these conditions the parameter used for fractal analysis is estimated from a logarithmic averaging formula suggested by Gelleri and Sernetz [18],

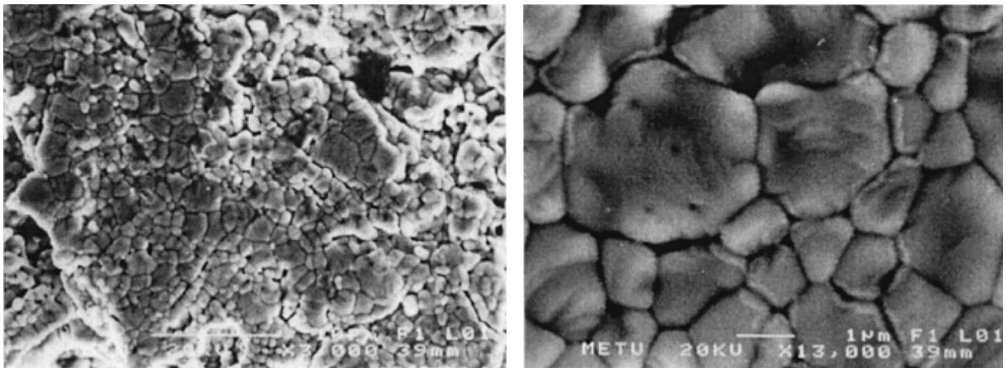

Fig. 5. BN coated UO_2-only; left: (×3000), right: (×13 000).

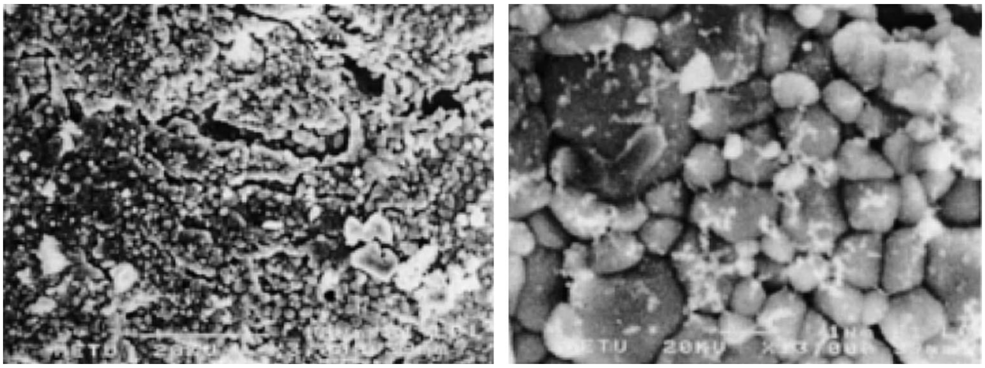

Fig. 6. BN coated UO_2–5% Gd_2O_3; left: (×3000), right: (×13 000).

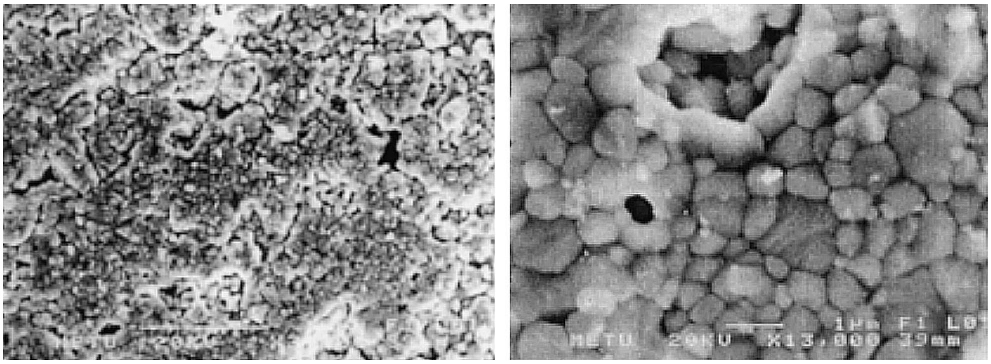

Fig. 7. BN coated UO_2–10% Gd_2O_3; left: (×3000), right: (×13 000).

$$y_{logit} = \ln\frac{y_i - y_L}{y_U - y_i},$$

where y_i is the experimental value of the measured quantity, y_L and y_U are its lower and upper bounds, respectively. y_{logit} is called log-logistic value used in determining fractal dimension.

In Fig. 8 the ordinate represents the number of BN grains on an examined photograph in terms of y_{logit} values while the axis represents the area of grains. The fractal dimensions were found directly from the slopes as 1.3822, 1.2352, and 1.1761 for BN grains on UO_2-only, UO_2–5% Gd_2O_3, and UO_2–10% Gd_2O_3 fuels, respectively. It is seen that as the gadolinia content in the fuel increases the fractal dimension of BN decreases. The size distribution of BN grains on pure UO_2 is the most random among all fuels.

The determination of fractal dimension of area–perimeter relation is based on the relation $p \approx \left(\sqrt{A}\right)^d$

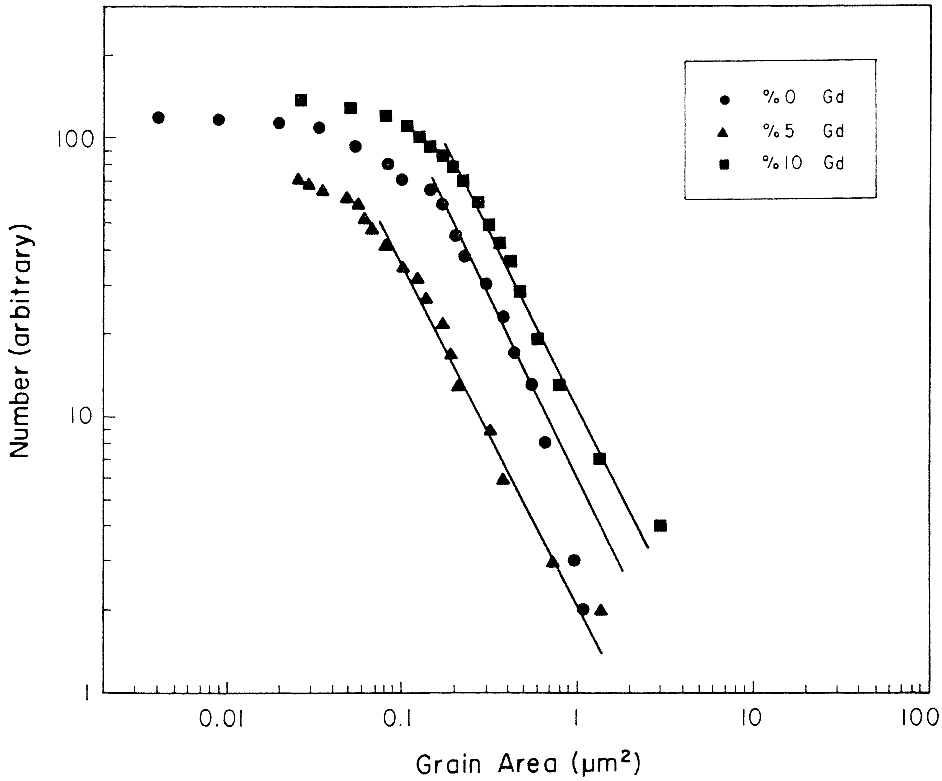

Fig. 8. Log-logistic plot of size distribution of BN grains with area.

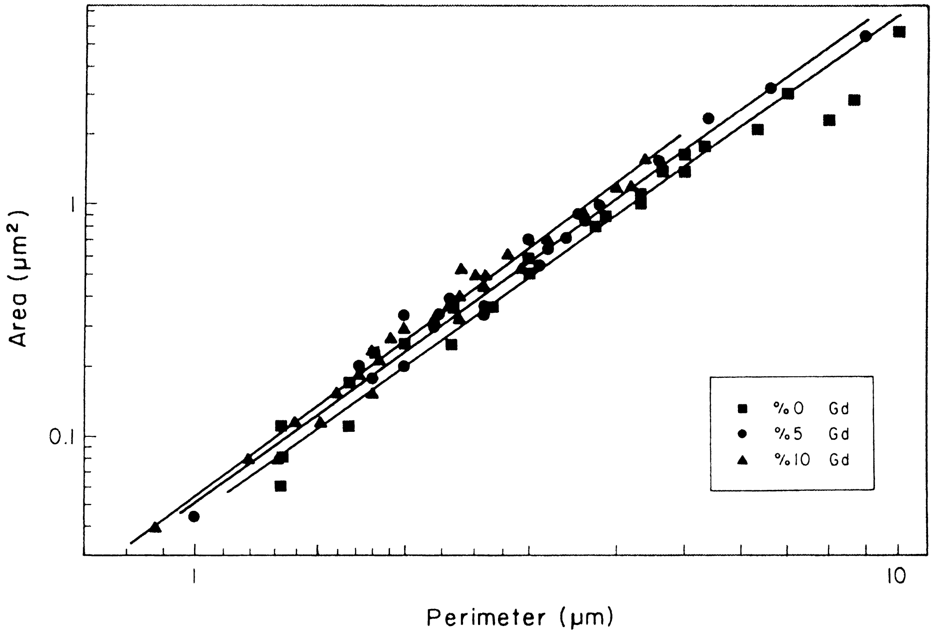

Fig. 9. Area–perimeter plots of BN grains.

where p is the perimeter, A the area, and d the fractal dimension. The graphs of ln A versus ln p are shown in Fig. 9, and the slopes (B') were obtained as 2.1341, 2.2390 and 2.3035 for BN grains formed on UO_2-only, UO_2–5% Gd_2O_3, and UO_2–10% Gd_2O_3 fuels, respectively. The fractal dimensions were found from the formula [19]

$$d = 3 - B'/2$$

as 1.9329, 1.8805, and 1.8482 for the three fuels, respectively. As the wiggliness of the perimeter increases d approaches the value 2. It is seen that as the amount of Gd_2O_3 in the fuel increases, the fractal dimension of area–perimeter relation of BN grains decreases. In other words the increase in gadolinia content decreases the perimeter chaoticity of BN grains.

4. Conclusions

1. PECVD yields grainy BN on all types of fuels.
2. Gadolinia decreases the grain size of BN coating and the smallest grains were obtained on UO_2–10% Gd_2O_3 fuel.
3. BN grains formed on UO_2-only show the most random distribution, giving highest fragmentation fractal dimension.
4. The fractal dimension of area–perimeter relation is the highest in UO_2-only fuel, and gadolinia decreases the perimeter chaoticity.

References

[1] Characteristics and Use of Urania–Gadolinia Fuels, International Atomic Energy Agency, IAEA-TECDOC-844, 1995.
[2] G. Gündüz, İ. Uslu, I. Önal, H.H. Durmazuçar, T. Öztürk, A.A. Akşit, B. Kopuz, F. Can, Ş. Can, R. Uzmen, Nucl. Tech. 111 (1995) 63.
[3] G. Gündüz, İ. Uslu, J. Nucl. Mater. 231 (1996) 113.
[4] J.E. Prithchett, D.E. Mueller, Trans. Amer. Nucl. Soc. 55 (1987) 117.
[5] R.L. Simmons, N.D. Jones, F.D. Popa, D.E. Mueller, J.E. Prithchett, Nucl. Tech. 80 (1988) 343.
[6] G. Gündüz, İ. Uslu, C. Töre, E. Tanker, Boron nitride coated uranium dioxide–gadolinium oxide fuel, International Atomic Energy Agency. Technical Committee Meeting on Water Reactor Fuel Element Modelling and its Experimental Support, Windermere, UK, 19–23 September 1994.
[7] G. Gündüz, İ. Uslu, H.H. Durmazuçar, Nucl. Tech. 116 (1996) 78.
[8] H. Saitoh, W.A. Yarbrough, Appl. Phys. Lett. 58 (1991) 2228.
[9] H. Saitoh, W.A. Yarbrough, Appl. Phys. Lett. 58 (1991) 2482.
[10] S. Komatsu, Y. Moriyoshi, M. Kasamatsu, K. Yamada, J. Phys. D 24 (1991) 1687.
[11] F. Qian, V. Nagabushnam, R.K. Singh, Appl. Phys. Lett. 63 (1993) 317.
[12] A. Chayahara, H. Yokohoma, T. Imura, Y. Osaka, M. Fujisavan, Appl. Surf. Sci. 33&34 (1988) 561.
[13] W. Wang, R. Ji, J. Gao, K. Liao, X. Zhang, Phys. Stat. Solid. A 136 (1993) K89.

[14] T.H. Yuziriha, D.W. Hess, Thin Solid Films 140 (1986) 199.
[15] H. Miyamoto, M. Hirose, Y. Osaka, Jpn. J. Appl. Phys. 22 (1983) L216.
[16] L. Maya, J. Amer. Ceram. Soc. 75 (1992) 1985.
[17] B.B. Mandelbrot, The Fractal Geometry of Nature, Freeman, San Francisco, 1982.
[18] B. Gelleri, M. Sernetz, Anal. Chim. Acta 163 (1984) 17.
[19] B.B. Mandelbrot, D.E. Passoja, A.J. Paully, Nature 308 (1984) 721.