ELSEVIER

Journal of Nuclear Materials 313–316 (2003) 214–218

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Plasma deposition of boron films with high growth rate and efficiency using carborane

O.I. Buzhinskij [a,*], V.G. Otroshchenko [a], D.G. Whyte [b], M. Baldwin [b], R.W. Conn [b], R.P. Doerner [b], R. Seraydarian [b], S. Luckhardt [b], H. Kugel [c], W.P. West [d]

[a] *Troitsk Institute of Innovations and Thermonuclear Researches, 142190 Troitsk, Moscow Region, Russia*
[b] *University of California, San Diego, CA, USA*
[c] *Princeton Plasma Physics Laboratory, Princeton, NJ, USA*
[d] *General Atomics, San Diego, CA, USA*

Abstract

The injection of carborane ($C_2B_{10}H_{12}$) on the PISCES-B linear plasma device has been used to produce boron containing films on various target species. Film growth rates achieved are extremely high (up to 30 nm/s) compared to those typically found for glow discharges (~0.01 nm/s). For low-Z target materials (C and Al) the film production is highly efficient, with the boron film growth rate comparable to the incident ion flux and the injection rate of boron atoms. The boron to carbon ratio is 3.0–3.6 for these films. Similarly high growth rates (~10 nm/s) are obtained with high-Z target (W), but with lower deposition efficiency and higher B/C film ratio. The high film growth rate/efficiency are apparently linked to the high degree of carborane ionization and dissociation caused by the ~40 eV PISCES-B plasma, compared with $T < 1$ eV plasmas of glow discharges. This technique opens the possibility of continuously producing protective B films in thermonuclear devices where net erosion rates approach 10 nm/s.

PACS: 52.40.H
Keywords: Plasma; Boron films; Carborane; High growth; Tokamak; Plasma–wall interaction

1. Introduction

In magnetic confinement fusion devices is widely applied boronization for deposition of boron (B) containing films [1]. The application of boron films allows to improve conditions on the surfaces of vacuum vessels and plasma facing components. Boron enables to reduce a level of plasma impurities, actively gettering oxygen (a pervasive impurity in vacuum systems), and protects a surface contacting to plasma. The application of boronization essentially reduces the contents of carbon (most popular material for protection of the first wall in modern devices) because of the decrease in chemical erosion by means of the deposition of boron containing coatings on the graphite tiles [2]. At the present a low-density helium glow discharge plasma ($n_e < 10^{17}$ m^{-3}, $T_e < 1$ eV) is commonly used for boronization in magnetic confinement devices, although a radio-frequency discharge plasma has also been used [1]. A boron-containing molecule is released in plasma discharge, resulting in a boron film ~100 nm thick in several hours (~0.01 nm/s growth rate) over the large surface area of the device (>10 m^2). There are a number of initial substances that are used for boronization, such as diborane (B_2H_6), borontrimethyl $B(CH_3)_3$, decaborane $B_{10}H_{14}$ and carborane $C_2B_{10}H_{12}$. In general, diborane has proved the most popular due to absence of carbon

* Corresponding author. Tel.: +7-095 334 0538; fax: +7-095 334 5510.
E-mail address: buzh@triniti.ru (O.I. Buzhinskij).

0022-3115/03/$ - see front matter
PII: S0022-3115(02)01482-4

atoms in the molecule. For example, a boron-to-carbon ratio of 9:1 is achieved in the boronization film on all the graphite surface DIII-D tokamak using diborane [3]. The rather slow deposition rate of glow discharge boronization presents substantial limitations in current and future fusion devices. Boronization is performed in pauses between discharges with a frequency dictated by the deterioration of plasma performance and appearance of a significant amount of impurities. Diborane is highly toxic, explosive and hazardous gas that demands special precautionary measures and equipment and is associated with high money costs. The protective ~100 nm boron film is eroded away in only a few discharges ~1–10 s duration at the strikepoint of a tokamak divertor, where typical net erosion rates are ~3–10 nm/s [1]. Such high erosion rate of protective films demands the most effective methods of boronization.

In the present work an alternative boronization technique based on the use relatively high flux hot plasma ($T_e \sim 40$ eV) in the PISCES-B linear plasma device is described. As a result the film growth rates >10 nm/s are measured, a factor of 1000 improvement on the growth rates found for glow discharge deposition. The plasma parameters used in the experiments closely resemble those of the DIII-D tokamak divertor plasma. This implies that this boronization technique would work equally well on the modern large-scale tokamaks and provide protective boron film at a rate comparable or greater than the highest net erosion rate of the divertor region. An additional benefit of the described technique is the use of non-toxic, non-explosive, non-hazardous and relatively cheap carborane.

2. Experiment

PISCES-B is a steady-state reflex arc plasma device [4] and is shown schematically in Fig. 1. The plasma operates with a constant axial magnetic field ~100–300 G. The ~1 m length cylindrical plasma is defined by the cathode and extraction anode (radius = 30 mm). The source consists of a heated LaB_6 cathode and a water-cooled copper anode. A target sample is placed at the end of the plasma to receive parallel ion flux. The retractable target holder of 20 mm radius is centered on the plasma and can be actively biased and cooled. Adjusting the cooling rate of the target, which is heated by the plasma contact, varies the sample temperature.

PISCES-B has a large operational range, but the present experiments are restricted to the following operating parameters. Helium is used as the working gas, where only the source region being evacuate by a turbo-molecular pump. The plasma is operated at the minimum power and discharge current that still allowed stable operation. The resulting plasma parameters are measured with a radially scanning Langmuir probe and

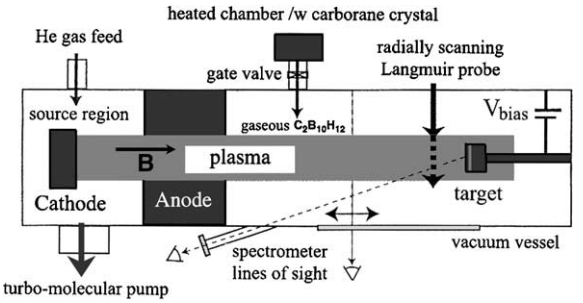

Fig. 1. Schematic of PISCES-B linear plasma device equipped with carborane injection for boron film deposition.

are as follows: $T_e \sim 40$ eV, $n_e \sim 2 \times 10^{17}$ m^{-3}, ion flux $\sim 3 \times 10^{21}$ m^{-2} s^{-1}. The radial profiles indicate a fairly constant T_e and a peaked density/flux profile. In general the target assembly was left floating, with $V_f \sim 160$ V resulting from the high T_e. The floating potential can be considered a good approximation of the incident ion energy at the target. These exposure conditions are similar to the divertor tiles of a low-recycling divertor in a tokamak.

Carborane ($C_2B_{10}H_{12}$) is a non-toxic crystal at room temperature. Its molecular structure is a dodecahedron for the B/C atoms, with H attached externally to each B/C band [3]. Crystalline carborane is placed in a temperature-controlled batcher ($T = 300$–450 K). The batcher is connected to the PISCES-B target region vacuum chamber through a tube equipped with a gate valve. The carborane batcher is not actively pumped. The temperature of the carborane determines the injection rate of gaseous carborane into the PISCES-B chamber (Fig. 2). Carborane has a low melting point (~370 K), readily sublimates, even at room temperature. The connecting tube is heated in order to avoid condensation of the carborane on the tube.

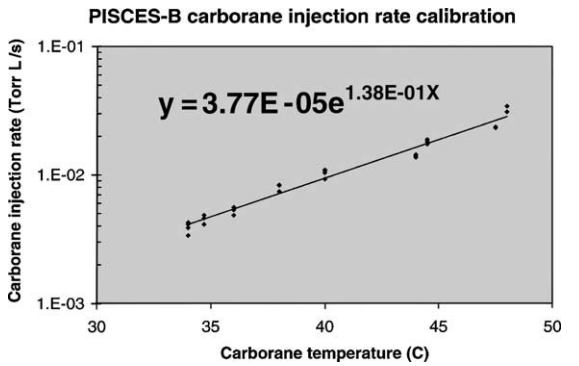

Fig. 2. Measured injection rate of gaseous carborane versus carborane temperature. Solid line indicates least-squares fit to data.

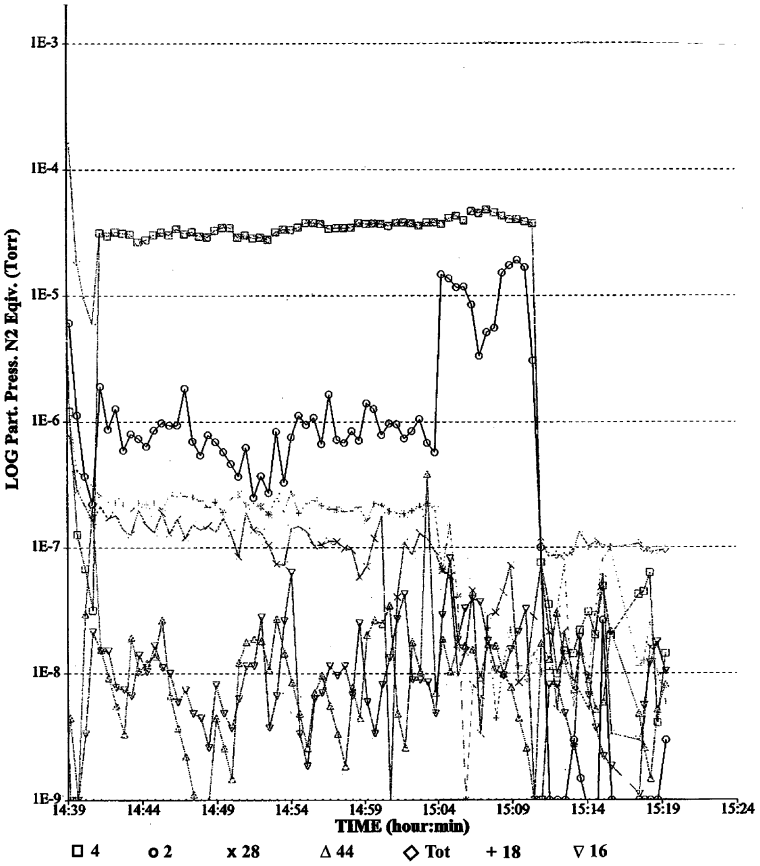

Fig. 3. Mass spectrum of gas in the PISCES-B chamber at boronization.

After boronization experimental target species were investigated in situ directly in the PISCES-B discharge chamber. Deposited coatings were analyzed by usual diagnostic procedures for the surface analysis: AES, SEM, SIMS, RSA etc. Experiments were carried out on seven types of targets, including low-Z target materials (C and Al) and high-Z targets (W and Mo). Temperature of targets is varied from room up to 700 K and exposure time from 2 up to 30 min. Film growth rate was determined by measurement of carborane injection duration (see Fig. 3) and B/C film depth after boronization.

3. Results of experiment and discussion

Carborane has an immediate effect on discharge plasma forming as shown by dramatic decrease of $M = 28$ in mass spectrum (Fig. 3). Also shown, that carborane provides 'significant' plasma fueling (see He/H_2 ratio). Spectroscopic measurements of plasma confirm these results. The carborane leads to hydrogenic fuelling of the plasma, at that He and H densities are comparable. H_2 behave exactly like H, this suggests that the carborane molecules have H atoms 'stripped' from them. BH complexes also are measured, but they appear to be a small fraction of the density compared to H. This suggests that while significant dissociation of the carborane molecule occurs, the resulting molecules have atoms $N > 2$. The axial profiles of the H and BH resulting from carborane injection are uniform. This suggests that the carborane has become a fuelling species and leads to significant recycling in the target chamber which is not pumped during experiment, therefore the He gas feed needs to be reduced to maintain the same ion flux the target when the carborane valve is open. The carborane molecules become well dissociated but not predominately to very small mass molecules. These effects are made possible by the highly ionizing and dissociating hot plasma of PISCES-B.

Produced boron containing films are sufficient thick (Fig. 4(a) and (b)), from 0.2 up to 20 μm, their thicknesses depend on a substrate material and discharge duration (Table 1). Coatings produced by boronization have exhibited a good adhesion to the substrate and high strength. The B/C ratio is 3.0–3.6 for films with

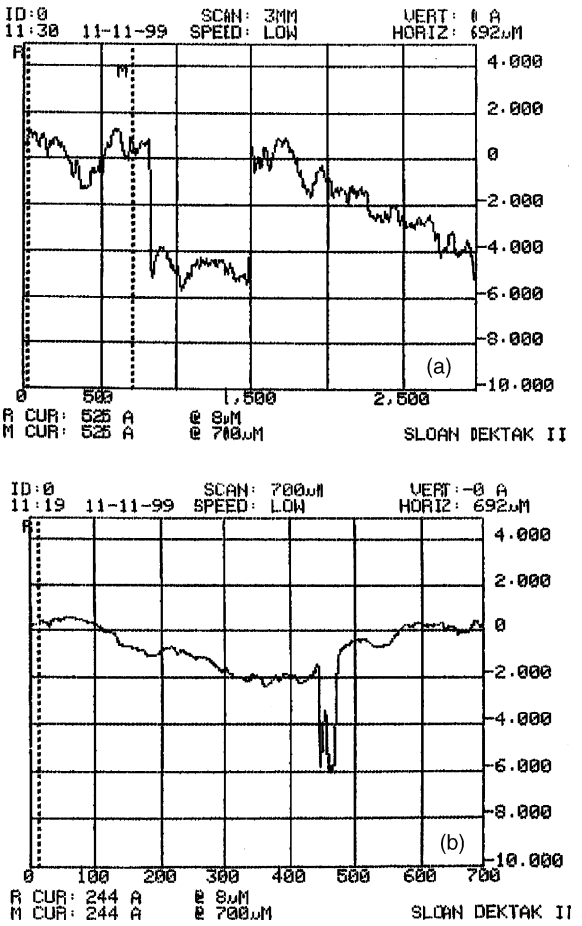

Fig. 4. Thickness of boron film in various regions of W target at scanning of 3 mm (a) and 0.7 mm (b) areas.

Table 1
Summary of boron film deposition using carborane on PISCES-B

Target	Carborane rate ($\times 10^{17}$ molecules/s)	Film depth (nm)	Film growth rate (nm/s)	B/C ratio in film
C	1.5	3500	33	3
Al	1.5	2×10^4	11	3.6
Al	1.5	2000	17	3.2
Al*	1.5	4000	0.56	3
W	18	250	2	
W	13	400	12	9.3

Plasma conditions: incident flux $\sim 3 \times 10^{21}$ $m^{-2}\,s^{-1}$, electron temperature ~40 eV (Al* – without plasma).

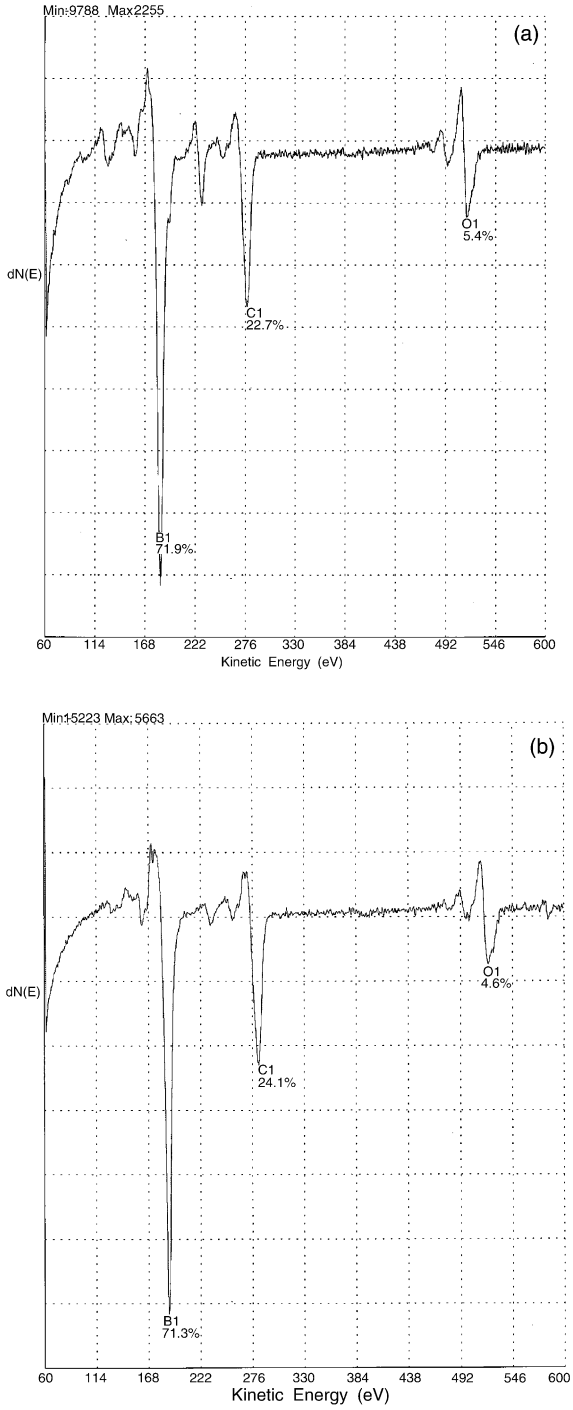

Fig. 5. AES survey of Al target (a) and C target (b) exposed to carborane for 2 min.

low-Z target materials (C and Al) (Fig. 5(a) and (b)), for high-Z target (W) its ratio is ~9:1 (Table 1). Film growth rates achieved extremely high (up to 30 nm/s) magnitude, that exceed by a factor of 1000 the growth rates for glow discharge deposition. The such high film growth rates and density can be explained the high degree of carborane ionization and efficient dissociation of the

large molecules caused by the ~40 eV PISCES-B plasma with high density, compared with $T_e < 1$ eV plasmas of glow discharges. For low-Z materials (C and Al) the film production is highly efficient, the boron film growth rate comparable to the incident ion flux and the injection rate of boron atoms. High film growth rates are obtained and with high-Z targets (W, Mo), but with lower deposition efficiency. Proposed technique opens the possibility of continuously producing renewable protective B films in magnetic confinement fusion devices where net erosion rates approach ~10 nm/s.

4. Conclusions

1. Alternative boronization technique with using carborane immediately in the PISCES-B plasma, whose parameters resemble those of the DIII-D tokamak divertor plasma, is proposed.
2. For low-Z targets (C and Al) film growth rates achieve of tens nm/s and are defined high deposition efficiency, B/C films ratio is 3.0–3.6.
3. For high-Z targets (W, Mo) film growth rate ~10 nm/s and high B/C ratio (9:1) are observed.
4. High growth rate and efficiency are agreed upon the high degree of carborane ionization and dissociation in ~40 eV electron temperature plasma with relatively high density.
5. Proposed technique opens the possibility of continuously producing renewable protective boron containing coatings in fusion devices.

References

[1] O.I. Buzhinskij, Yu.M. Semenets, Fusion Technol. 32 (1) (1997) 1.
[2] V.Kh. Alimov, D.B. Bogomolov, M.N. Churaeva, A.E. Gorodetsky, S.L. Kanashenko, A.I. Kanaev, S.Yu. Rybakov, V.M. Sharapov, A.P. Zakharov, R.Kh. Zalavutdinov, J. Nucl. Mater. 196–198 (1992) 670.
[3] G.L. Jackson, J. Winter, K.H. Burrell, J.C. DeBoo, C.M. Greenfield, R.J. Groebner, T. Hodapp, K. Holtrop, A.G. Kellman, R. Lee, S.I. Lippmann, R. Moyer, J. Phillips, T.S. Taylor, J. Watkins, W.P. West, J. Nucl. Mater. 196–198 (1992) 236.
[4] Y. Hirooka, R.W. Conn, T. Sketchley, W.K. Leung, R. Doerner, J. Elvurm, G. Gunner, M. Khadagel, R. Lehmer, P. Luong, Y. Ra, L. Schmitz, G. Tynan, J. Vac. Sci. Technol. A 8 (1990) 1790.