CHEMICAL EROSION OF SINTERED BORON CARBIDE
DUE TO H+ IMPACT

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Abstract

The production of hydrocarbons and boron hydrides due to H$^+$ bombardment of sintered B_4C has been investigated as a function of sample temperature and incident ion energy. While hydrocarbon production was observed, the yields were approximately two orders of magnitude smaller than observed for graphite. There was no evidence to indicate the production of any volatile boron-containing compounds.

Introduction

While graphite has many desirable characteristics for first-wall use in tokamaks, its major drawback is its erosion (chemical,[1] radiation-enhanced sublimation[1] and chemically-enhanced self-sputtering[2]) under plasma exposure. Attempts at reducing carbon's erosion involve the development of carbon-based materials by the addition of low-Z elements, e.g., boronization in TEXTOR[3] and B-doped graphites.[4,5] The present study was undertaken as a first step in the development of boron-doped graphites. Once doping levels exceed the solubility concentration of B in carbon, the excess boron will precipitate in the form of crystallites of B_4C. Thus, the object of our

work was to investigate the chemical erosion of B_4C under exposure to energetic hydrogen ions.

Three previous experiments with boron carbide samples have produced apparently conflicting results. Veprek et al, using a low-energy radio-frequency discharge as a source of reactive hydrogen atoms, found very low levels of erosion, indicating almost complete suppression of hydrocarbon formation on B_4C as compared to graphite.[6] On the other hand, Braganza et al showed a clear erosion temperature dependence, with a maximum yield of $Y_m \sim 5.5 \times 10^{-3}$ CD_4/D^+ occurring at $T_m = 480$ K, for 20 keV D^+ ions.[7] Except for shifts in the Y_m and T_m values, the observed erosion temperature dependence was similar to the methane yield observed for D^+ bombardment of graphite. In a study by Bohdansky and Roth[8] for 1 keV D^+ erosion of B_4C, a minor temperature dependence was observed between 775 and 1450K; however there were no data between room temperature and 775K. In our study we have investigated the chemical erosion of B_4C, due to energetic hydrogen impact, for energies of 1 keV to 10 keV and temperatures of 300-1000K.

Experiment

All experiments were performed in our UHV-accelerator facility which includes a low-energy, high-flux mass-analyzed ion accelerator. Beams of H^+ and H_3^+ ions impacted on the specimen surface at an angle of ~30°, with a resulting beam spot of ~0.2 cm². The beam intensity was measured on the sample, with the sample biased to +25 to +100 V (depending on incident ion energy) to suppress secondary electrons.

The sample was made of sintered boron carbide (Tetrabor) supplied by Elektroschmelzwerk Kempton GmbH. According to manufacturer's specifications,

the bulk carbon concentration was 19-21 Atomic %. The sample ($\sim 40 \times 10 \times 2$ mm) was held at both ends by stainless-steel jaws, and was heated resistively. Sample temperature was measured by optical pyrometry, and in some cases it was checked against thermocouple readings.

The hydrocarbon products of chemical erosion were monitored in the residual gas by a differentially pumped Extranuclear quadrupole mass spectrometer, QMS. The QMS was calibrated in situ using known leaks of CH_4, C_2H_4 and C_3H_6 and was operated at a constant total pressure (mainly H_2) in order to maintain a constant conditioning, and thereby a constant sensitivity to CH_4 and other hydrocarbons. Based on previous calibrations[9] for C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8, using the orifice flow method, relative calibrations could be found for other hydrocarbons as well.

Because of the very low erosion yields observed in these experiments, and the minor temperature dependence observed for the 3 keV H_3^+ bombardment, there was concern about the production of hydrocarbons due to backscattered ions reacting on various stainless steel surfaces of the test chamber. By surrounding the sample with a gold-plated shroud, a substantial reduction of background hydrocarbon production was observed. This allowed detection of a temperature dependence in the CH_4 production which could not be observed previously.

In order to demonstrate that at least the temperature-dependent part of the erosion signal was not due to reflected hydrogen ions, the B_4C sample was replaced by a piece of tungsten foil, which could be heated in a similar manner. For both 9 keV and 3 keV H_3^+ ion bombardment of W, no significant temperature dependence was observed, and also, no transients were observed in the hydrocarbon production, see discussion below. Based on published reflection coefficients for H on boron and tungsten,[10] we estimate that, at

the most, approximately 50% of the lowest signals observed for the erosion of B_4C may be due to backscattered ions reacting on other surfaces.

Results and Discussion

Experiments were performed with 3 keV H_3^+, 9 keV H_3^+ and 10 keV H^+ ions over a temperature range of 300-1000K. The methane yield as a function of temperature is shown in Fig. 1 for the case of 3 keV H_3^+ (i.e., 1 keV/H). During initial bombardment of the sample a gradual decrease in the erosion yields with time was observed. The upper curve (x) in Fig. 1 represents the first set of erosion measurements. The lowest curve (o) shows the final set of data after many days of experiments. A similar behaviour was observed for the 9 keV/H_3^+ case, however, the effect was reduced, probably as a result of conditioning by the 3 keV H_3^+ runs. Compared with pyrolytic graphite,[9] the chemical erosion yield of B_4C is about two orders of magnitude lower, see Fig. 1.

In Fig. 2 we show the production of methane as a function of temperature for the different ion energies studied. The peak in the erosion yield for 1 keV/H impact occurs at ~700K, with a trend to lower peak temperatures with increasing ion energy. There also appears to be an increase in the maximum yield for the 10 keV H^+ case (present data) and the 20 keV D^+ results of Braganza et al.[7] It is likely that these high erosion yields may be due to transients; because of the deep ion ranges associated with high ion energies, many hours of bombardment may be required to reach true steady state conditions, see below.

Very large, and long duration transients in the CH_4 production were also observed for some conditions, even with the well conditioned sample. For example, heating the sample to 1000K for 20 minutes, followed by 9 keV

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H_3^+ bombardment at 650K resulted in an erosion yield initially 35 times larger than the steady-state value. Examples of transient erosion yields are shown in Fig. 3. Figures 3a, b and c show traces where the specimen temperature was systematically increased from run to run. The traces in Figs. 3d and e represent runs where the sample was preheated to 1000K prior to establishing the test temperature for subsequent hydrogen ion impact. Very large initial transients are observed for the latter cases.

The gradual decrease of the erosion yield with continued H^+ bombardment perhaps is an indicator that carbon is being depleted from the ion range, resulting in a boron-rich surface layer. The fact that heating to 1000K is able to induce a large transient erosion yield indicates a possible replenishment of carbon in the ion implantation zone.

To confirm that changes in the near-surface composition of the B_4C specimen were occurring, the sample was analyzed by Auger Electron Spectroscopy (AES). This was performed after several months of atmospheric exposure, subsequent to an H^+ impact experiment which had reached steady state CH_4 production for 9 keV H_3^+ at 650K temperature. Initial AES analysis showed large concentrations of C on the beam spot with considerably larger amounts being found off the beam spot. While surface contamination during atmospheric exposure is expected to account for some of the observed C, the difference in the off-spot and on-spot concentrations (~10 times the stoichiometric C/B ratio) is a definite indication that carbon had segregated to the surface during the 1000K preheating cycles. While such segregated carbon was depleted from the beam spot by H^+ impact, it continued to accumulate on off-spot surfaces. Sputtering with 2 keV Ar^+ ions enabled us to do AES depth profiling. In the ion implantation zone (~500Å deep) a somewhat lower amount of C was observed on-spot compared with off-spot,

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again being consistent with the above H^+-induced carbon deletion hypothesis. Beyond the implantation zone, both on-spot and off-spot C concentrations were stoichiometric, viz, C/B $\approx$ 0.25. In-situ heating of the specimen at 1000K for 20 minutes, as was the case for some of the H^+ impact experiments, resulted in an increase in the near-suface C concentration for both on-spot and off-spot cases to C/B $\sim$ 0.7. After sputtering away $\sim$50Å the C/B ratio was again near-stoichiometric.

CH_4 was the primary hydrocarbon product observed in the erosion process. Small amounts of C_2H_x and C_3H_x hydrocarbons were observed for most measurements, however, they usually contributed only 5-10% to the total carbon removal rate. From the observed mass spectra (M/e $\leq$ 45) there was no evidence of any boron-containing reaction products. Boron hydrides, e.g., B_2H_6, should be clearly observable through a cracking pattern which would include signals at M/e of 10 and 11. No signals were observed at these masses. Hydrocarbons and background impurities would effectively mask small signals at higher mass numbers.

If the chemical removal of carbon in steady-state is limited by the physical sputtering of the boron component, then based on published sputtering data,[11] the maximum hydrocarbon yields would be limited to the following:

$$\text{for } 1 \text{ keV H:} \quad 1.1\times10^{-2} \text{ atoms/H} \div 5 = 2.2\times10^{-3} \text{ C/H}$$

$$\text{for } 3 \text{ keV H:} \quad 6\times10^{-3} \text{ atoms/H} \div 5 = 1.2\times10^{-3} \text{ C/H}$$

$$\text{for } 10 \text{ keV H:} \quad \sim2.5\times10^{-3} \text{ atoms/H} \div 5 = 5\times10^{-4} \text{ C/H}$$

For the 1 and 3 keV/H^+ (3 keV H_3^+ and 9 keV H_3^+) cases, the final steady-state values measured are within this 'upper limit', however, the 10 keV H^+ results are not. It is suspected that, because of the deep ion range, many hours of bombardment would be required to reach true steady-state in this case.

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Conclusions

Chemical erosion of B_4C occurs throughout the entire temperature range studied (300-1000K), however, the peak methane yields are about two orders of magnitude lower than that of pyrolytic graphite. No boron-hydrogen compounds were detected in the residual gas. Initial bombardment of the sample resulted in erosion yields larger than those eventually obtained, indicating a possible depletion of carbon from the ion range. Heating of the sample to 1000K resulted in large transient erosion rates, possibly due to the replenishment of the carbon component in the near-surface region.

The low steady-state carbon erosion yields observed indicate that after sufficient bombardment to remove transient effects, the chemical erosion of boron carbide will be small compared to physical sputtering, and in fact, may be rate-limited by physical sputtering of the boron component.
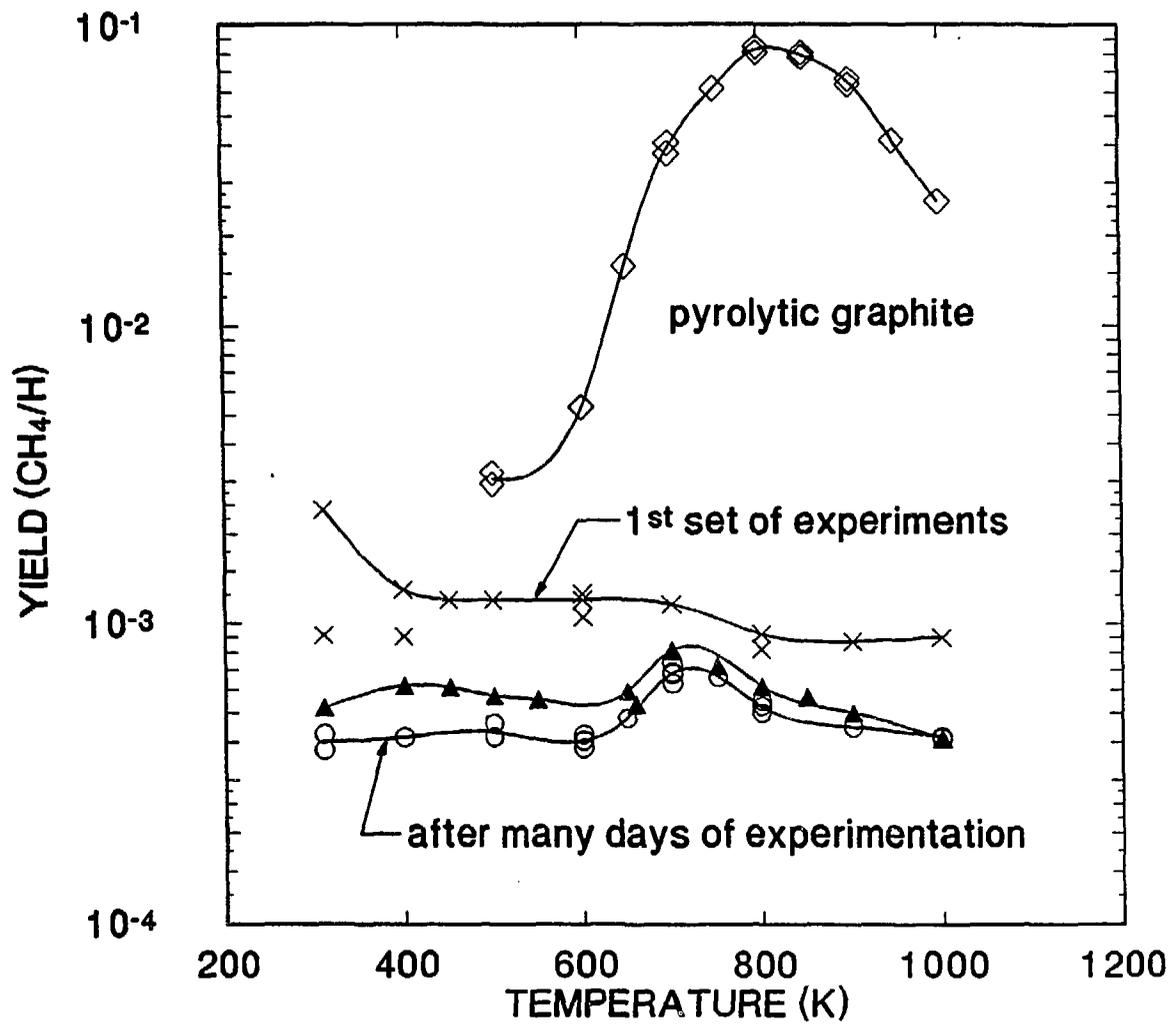
Acknowledgements

References

1. J. Roth, E. Vietzke and A. A. Haasz, "Erosion of Graphite due to Particle Impact", Nucl. Fus., to be published.

2. J. W. Davis and A. A. Haasz, "Chemically Enhanced Self-Sputtering of Carbon", Appl. Phys. Lett., to be published.

3. F. Waelbroeck et al, Plasma Physics and Controlled Fusion 31 (1989), 185.

4. J. Roth, J. Nucl. Mater. 145-147 (1987), 87.

5. Y. Hirooka et al, J. Vac. Sci. Technol. A8 (1990), 1790.

6. S. Veprek, M. R. Haque and H. R. Oswald, J. Nucl. Mater. 63 (1976), 405.

7. C. Braganza, G. M. McCracken and S. K. Erents, Proc. Int. Symp. Plasma-Wall Interaction, Jülich (1976), p. 257.

8. J. Bohdansky and J. Roth, J. Nucl. Mater. 122&123 (1984), 1417.

9. J. W. Davis, A. A. Haasz and P. C. Stangeby, J. Nucl. Mater. 155-157 (1988), 234.

10. W. Eckstein and H. Verbeek in "Data Compendium for Plasma-Surface Interactions", Nucl. Fus. Special Issue (1988), p. 12.

11. J. Roth, J. Bohdansky and A. P. Martinelli, Rad. Effects 48 (1980), 213.
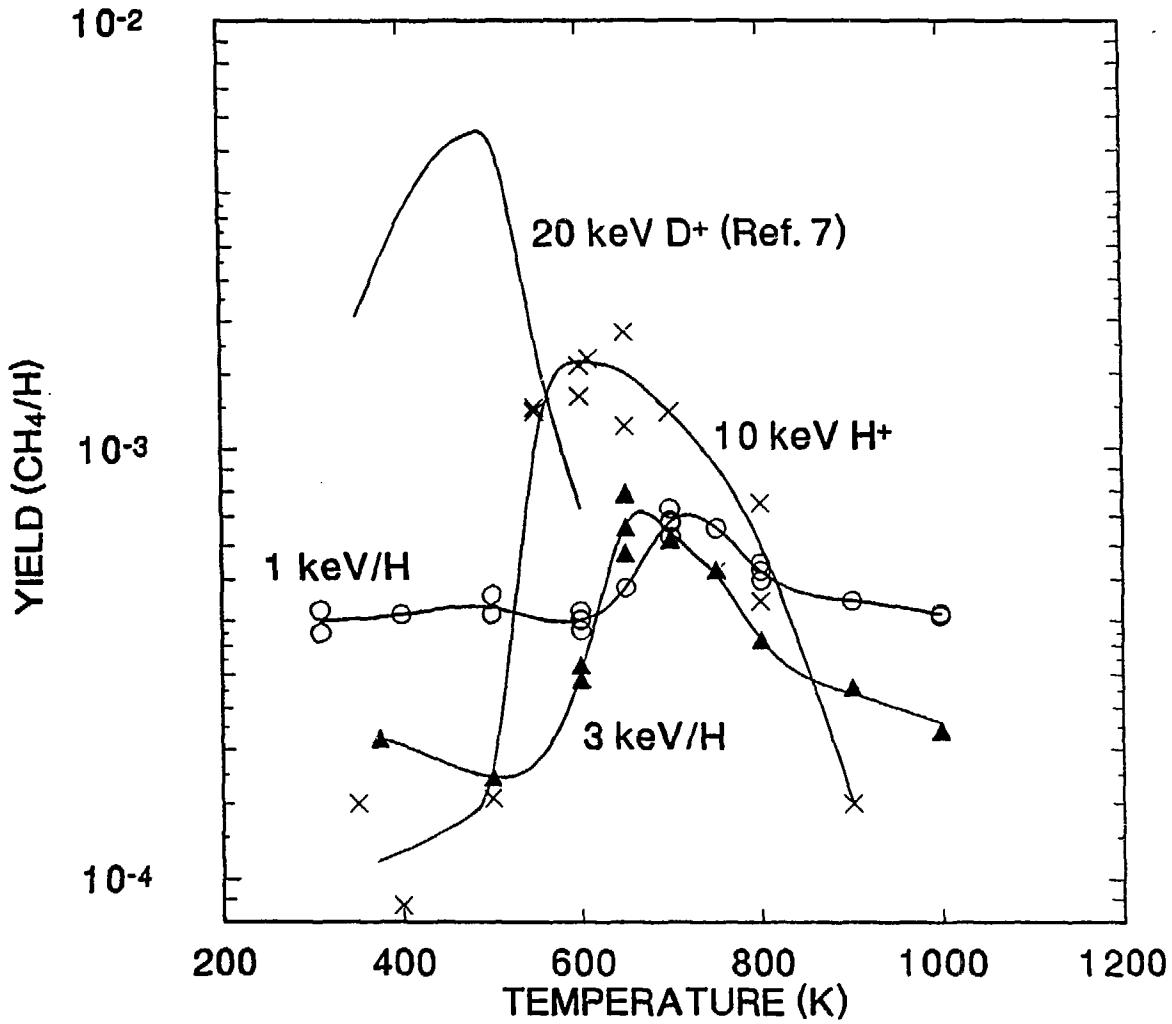
Figure Captions

Figure 1: CH_4 production due to 3 keV H_3^+ (~6×10^{15} H/cm^2s) bombardment of B_4C as a function of temperature. The three curves represent a conditioning of the sample, with the upper curve (x) being the initial experiments, and the lower curve (o) being the final data The erosion yield of pyrolytic graphite under similar bombardment conditions is also shown (Ref. 9).

Figure 2: CH_4 production due to 3 keV H_3^+ (~6×10^{15} H/cm^2s), 9 keV H_3^+ (~1.5×10^{16} H/cm^2s) and 10 keV H^+ (~3×10^{15} H/cm^2s) bombardment of B_4C as a function of temperature. CD_4 production for 20 keV D^+ on B_4C (Ref. 7) is also shown. A shift in peak erosion temperature is noted.

Figure 3: A comparison of the QMS mass 15 signals during bombardment of B_4C by 9 keV H_3^+ ions at various temperatures, without (a, b, c) and with (d, e) preheating to 1000K.
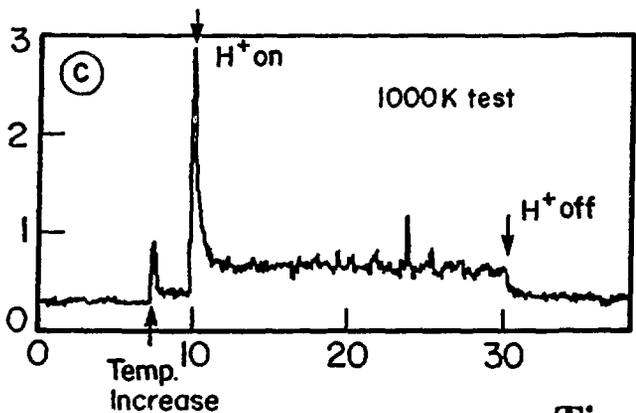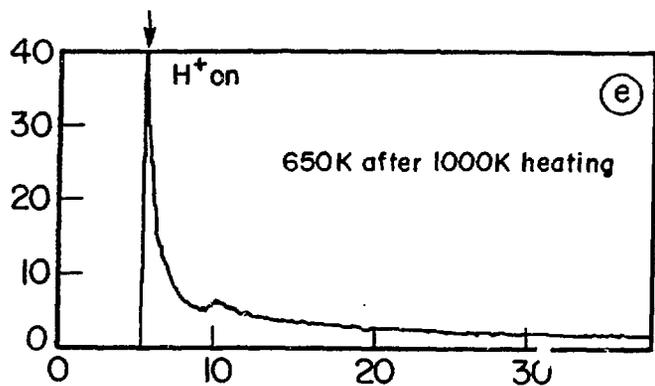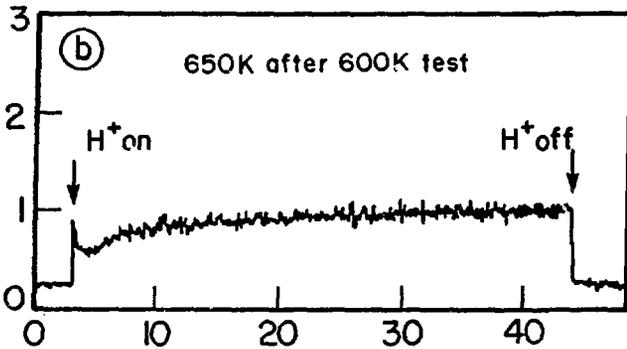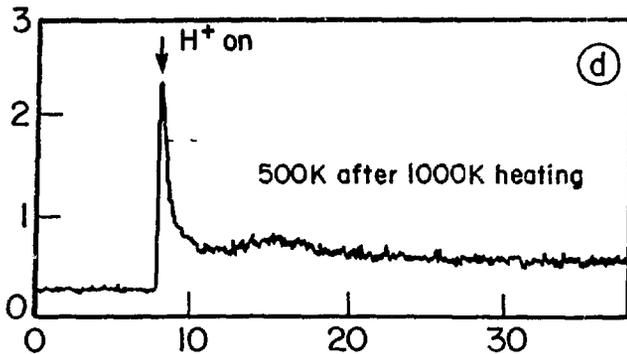
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Figure showing YIELD (CH_4/H) versus TEMPERATURE (K), with curves labeled "pyrolytic graphite", "1st set of experiments", and "after many days of experimentation".

Davis & Haasz Fig1

10-2

20 keV D+ (Ref. 7)

10 keV H+

1 keV/H

3 keV/H

10-3

YIELD (CH4/H)

10-4

200   400   600   800   1000   1200

TEMPERATURE (K)

Davis & Haasz Fig 2

Davis & Haas Fig 3