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BORON COATINGS ON GRAPHITE FOR
FUSION REACTOR APPLICATIONS*H. O. Pierson and A. W. Mullendore
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ABSTRACT

This study is an experimental investigation of boron coatings on graphite and the preliminary determination of some of their physical and nuclear related properties. The boron was obtained by the decomposition of diborane in argon at 500°C and one atm. Adhesion to the graphite (POCO AXF-5Q) was good if a slightly abraded surface was provided. The boron was pseudo-amorphous, had high purity with no visually observable porosity and the fractured surface showed no growth features. It was very hard ($VHN_{25} = 2400 \text{ kg/mm}^2$) and had good resistance to hydrogen ion erosion and arcing. It may, therefore, be a suitable candidate for first wall and limiter coatings in tokamak fusion reactors.

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INTRODUCTION

Boron is a very hard, refractory element with a melting point of 2200°C. It has a low atomic number and two stable isotopes with widely different thermal neutron cross sections (3838 barns for B¹⁰ and less than 0.05 barn for B¹¹ at 0.025 eV). Because of these properties, it is one of the most important nuclear materials in fission reactors, and a prime contender for first wall and limiter coatings in tokamak fusion reactors.¹

Boron coatings can be applied by chemical vapor deposition (CVD) by the hydrogen reduction of boron trichloride above 1000°C. This reaction has been used for several years to produce boron fibers.² Another possible reaction is the thermal decomposition of diborane.

This reaction has been used in the production of boron powder but has yet to be extensively investigated for coatings.^{3,4} Yet, it has major advantages over the chloride reduction since it can proceed at much lower temperatures and produces no HCl to react with the substrates.

These considerations led to this study which is a preliminary, experimental investigation of boron coatings from diborane for fusion reactor applications.

EXPERIMENTAL

Apparatus and Process

The reactor shown in Figure 1 was evacuated, then back-filled with one atm of argon and heated to the desired temperature.

The graphite substrate consisted of disks 2.5 cm in diameter and 0.5 cm high, made from POCO AXF-5Q (Union Oil Co.) with a thermal expansion of $7.7 \times 10^{-6}/^{\circ}\text{C}^{-1}$ and a density of 1.84 g/cm^3 .⁵ The surface of each disk was lightly abraded with a 150 μm glass beadblast. They were then ultrasonically cleaned in a solvent and vacuum dried at 200°C .

Analytical Procedure

The structure of the coatings was examined by x-ray diffraction using a Guinier-Hagg focusing camera, by scanning electron microscopy and by optical metallography.

The impurity content was determined by emission spectroscopy and was examined qualitatively by Auger spectroscopy. The adhesion to the substrate was evaluated in a pulsed electron beam apparatus described elsewhere.⁵ Resistance to hydrogen ion erosion was tested in a Kaufman ion source chamber.⁶

RESULTS AND DISCUSSION

Structure and Composition

Coatings were deposited between 400 and 900°C . At 400° they scratched easily and were not coherent. At 500°C they were hard, and had uniform thickness which averaged $60 \mu\text{m}$ for one hour deposition. Above 500°C , the deposition rate dropped rapidly and was negligible at 900° .

Figure 2a shows a fracture surface of a 500°C coating and Figure 2b shows a polished cross section of the same coating. The fracture is conchoidal with no discernable growth features. The thickness is uniform and reproduces the irregularities of the graphite substrate.

The coating shows no evidence of macroscopic porosity and appears close to 100% dense. X-ray diffraction patterns were obtained from coatings deposited at 400, 500 and 600°C. The graphite substrate was removed from the coating by abrasive paper grinding and transmission diffraction patterns of the coating were obtained in a focussing Guinier-Hagg camera. In each case only broad, diffuse diffraction halos were observed. These were found to correspond very well to the diffraction results of Wawner and Lewis⁷ for a low temperature form of boron deposited on a heated tungsten wire from a boron halide. They interpreted their patterns in terms of a defected or poorly crystallized phase and were able to index the halos to a body centered cubic cell. A sample of coating formed at 500°C was vacuum annealed at 1200°C for 30 minutes and was found to transform to the β rhombohedral⁸ high temperature polymorph of boron.

The results of emission spectrographic analysis for coating impurities are shown in Table 1.

TABLE 1

EMISSION SPECTROGRAPHIC ANALYSIS OF BORON COATING IMPURITIES

Element	Concentration in ppm	
	500°C deposit	600°C deposit
Ca	<5	<5
Al	2	<1
Mg	1	1
Mn	<1	<1
Si	200	130
Fe	<1	<1

They indicate a very low level of impurity. Auger spectroscopy was also performed to detect low Z impurities. Oxygen and

carbon were detected on the surface but decreased markedly with sputter removal of $\sim 100 \text{ \AA}$ from the surface.

Physical and Nuclear Related Properties

Microhardness measurements gave a Vickers hardness number of $\text{VHN}_{25} = 2400 \text{ kg/mm}^2 \pm 2\%$ (25 g load, average of seven indentations). This is in good agreement with other reported values.⁹ After fifty successive 0.7 sec. electron beam pulses at 2 kW/cm^2 , there was no evidence of adhesion failure nor any changes in the appearance of the coating. This indicates excellent adhesion to the graphite and good thermal stability of the coating.

Arcing studies of conductive surfaces typically show unipolar arc spots in the test chamber when no bias is applied and develop high energy moving arcs which erode the surface when the bias is applied.¹⁰ The boron coatings are good insulators at room temperature and only showed faint low energy arcs even with biasing. When the boron coating was disrupted by scratching, high energy plasma arcs developed which eroded the graphite substrate and melted the edges of the boron coating. There was no evidence of spall (Fig. 3).

Figure 4 shows the low energy hydrogen erosion yield of a boron coating in comparison with the yield of other refractory materials.¹⁰

CONCLUSIONS

The boron coatings obtained by the decomposition of diborane on graphite are very hard pseudo-amorphous structures

with essentially no porosity and with excellent adhesion to the substrate. The coatings are of good purity, have excellent resistance to hydrogen ion erosion and they display resistance to the formation of electrical arcs. These preliminary results indicate that CVD boron may be suitable for fusion reactor coating applications.

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FIGURE 1

SCHEMATIC OF CVD REACTOR

Fig. 2. Photomicrograph of boron coating deposited at 500°C.
a) fracture surface, b) polished surface (with hardness indentations).

Fig. 3. Arc track on boron coating. Note scratch.

FIGURE 4

YIELDS HYDROGEN ION EROSION