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Diamond and Related Materials 6 (1997) 450–455

DIAMOND AND RELATED MATERIALS

# Deposition of CVD diamond onto boron carbide substrates

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## Abstract

Boron carbide ($B_4C$) is a hard, lightweight ceramic used in the nuclear and aerospace industries. Depositing a CVD diamond coating onto its surface may increase its wear resistance and hence its value as a structural material in advanced applications, such as gyroscope rotors. Hot filament CVD has been used to deposit 2–4-μm layers of polycrystalline diamond onto polished $B_4C$ blocks. We found that adhesion of the diamond coating was poor, with spontaneous delamination occurring. SEM and scanning Auger microscopy determined that boron from the surface of the $B_4C$ was diffusing into the CVD diamond to a depth of about 0.1 μm. This left a B-depleted, C-rich layer at the diamond/$B_4C$ interface which caused the delamination of the doped diamond film. © 1997 Elsevier Science S.A.

*Keywords:* CVD diamond; Boron carbide substrates; Delamination

## 1. Introduction

Boron carbide, $B_4C$ (known by the trademark *Tetrabor* [1]), is a shiny black, lightweight ceramic characterised by its extreme hardness (Knoop 3000 kg mm$^{-1}$, Mohs 9.5+). Some properties of $B_4C$ are given in Table 1. As a loose powder $B_4C$ is used for lapping and grinding hard metals [2], corundum and glass. Sintered pieces are produced by hot pressing fine $B_4C$ powder at high temperature and under high pressure using an induction furnace and graphite moulds. This method allows the fabrication of geometrically simple shapes, such as blocks, tubes and cylinders, with low density (2.51 g cm$^{-3}$), for use in sand blasting nozzles, hand-lappers, mortars, armour plates, bearing surfaces, etc. In the nuclear industry, $B_4C$ is used as a neutron absorber, owing to the high neutron capture cross-section of B. $B_4C$ is also used as a basic material for the production of other boron compounds, such as boron halides, boron nitride, etc., and for diffusing boron into metal surfaces (a process called boriding) [3], to make hard, wear-resistant coatings of the metal boride on machine tools and workpieces.

One recent application of sintered blocks of $B_4C$ has been as gas bearings and rotor housings in miniature gyroscopes for use in aircraft [4]. The $B_4C$ forms the rotor, and is fabricated as a sintered disk which rotates within the $B_4C$ gyroscope housing at speeds of several thousand rev s$^{-1}$. The excellent mechanical properties and wear resistance of $B_4C$ result in extremely long operational life, resistance to inadvertent high speed rotor touch-down, and allow for lubricant-free operation. However, diamond, being even harder than $B_4C$, has been suggested as offering a possible improvement on this performance. Coating a $B_4C$ rotor with a CVD diamond film might be the way to combine the additional mechanical properties of diamond with the low density, lightweight supporting structure of $B_4C$.

At first sight, the deposition of a CVD diamond coating onto $B_4C$ might seem a good prospect, since the latter material possesses a number of the necessary properties that make it compatible with diamond CVD. It can easily survive the deposition temperature, and it has a very low thermal expansion coefficient. Because $B_4C$ is a carbide, and by analogy with the results from diamond CVD onto other carbides (WC [5], SiC [6]), we should expect that the deposited diamond would nucleate readily and adhere strongly to the substrate surface. In this paper, we present the results of our

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0925-9635/97/$17.00
*PII* S0925-9635(96)00635-8

Table 1
Selected properties of boron carbide (from Ref. [1])

| | |
|---|---|
| Formula | $B_4C$ |
| Boron, carbon content | 77.28, 21.72% by weight |
| Crystal structure | rhombohedral |
| Density | 2.51 g cm$^{-3}$ |
| Colour | shining black |
| Melting point | 2450°C |
| Boiling point | 3500°C |
| Neutron capture cross-section | 600 barn or $6 \times 10^{-22}$ cm$^2$ |
| Molar heat capacity | 52.3 J mol$^{-1}$ K$^{-1}$ |
| Thermal expansion (20–800°C) | $5 \times 10^{-6}$°C |
| Thermal conductivity at 25°C | 0.29–0.67 J cm$^{-1}$ s$^{-1}$ °C$^{-1}$ |
| Electrical resistivity at 25°C | 0.1–10 Ω · cm |
| Hardness (Knoop 100 g load) | 3000 kg mm$^{-2}$ |
| (Mohs) | 9.5+ |
| Young's modulus | 45 000 kg mm$^{-2}$ |
| Chemical reactivity | inert to most common mineral acids and alkalis |

investigation into depositing CVD diamond onto $B_4C$ substrates. The viability of using diamond-coated $B_4C$ in applications requiring high toughness, lightness and wear resistance is discussed in the light of the results obtained.

## 2. Experimental

The substrates used in this study were cut from rotor disks made of *Tetrabor* [1] sintered $B_4C$. The bearing surface had been patterned using ion-beam milling to produce spiral grooves necessary to allow the rotor to become airborne and spin during operation (see Fig. 1). The surfaces were manually abraded prior to diamond deposition using 1–3-μm diamond grit. Diamond deposition was performed in a standard hot filament reactor [7] using typical CVD conditions (1% methane in $H_2$, 200 sccm gas flow, 20 Torr pressure, substrate temperature, 900°C, Ta filament temperature, 2200°C), which gave a deposition rate of around 0.5 μm h$^{-1}$. Deposition times were typically 7 h, producing continuous diamond coatings of 3–4 μm thick. After deposition, the coating and $B_4C$ substrate were analysed using scanning electron microscopy (SEM) and scanning Auger microscopy (SAM).

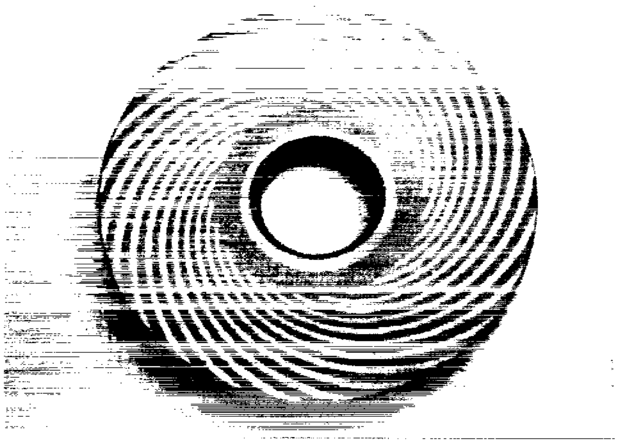

Fig. 1. A planar view of one of the $B_4C$ rotor bearings used as a substrate. The spiral grooves were created by ion beam milling (courtesy of Smiths Industries [4]).

## 3. Results

Examination of the diamond coating showed that diamond nucleated readily on the abraded $B_4C$ surfaces and formed a continuous coating after around 90 min. The films did not exhibit any cracking or show any other signs of stress. However, adhesion was very poor, with delamination of the entire film occurring readily, or even spontaneously, and this delamination served to relieve film stress and prevent cracking.

To investigate the cause of this poor adhesion, SAM analysis was performed at various locations on the coating and the substrate.

### 3.1. *The top surface of the diamond film*

Examination with SEM of the top side of the film revealed a surface morphology which consisted of a mixture of (100)- and (111)-faceted crystals (~1–2 μm). The microcrystalline nature of the film surface, and its propensity for delamination can be seen in the SEM image shown in Fig. 2(a). The SAM spectra recorded from different locations of the sample yielded only an Auger electron peak corresponding to the *KLL* transition line for C. A typical spectrum of the analysed areas is shown in Fig. 2(b), and a detailed examination of the fine structure of the carbon peak (Fig. 2(c)) reveals an sp$^3$-bonding type that is characteristic of the diamond structure [8]. The lack of any other significant peaks indicates that no contamination layers of oxygen and amorphous C (which normally adsorb at the surfaces of samples exposed to air prior to analysis within the UHV chamber of the SAM) were detected. This observation implies a degree of inertness of the deposited CVD diamond film to air.

### 3.2. *The back surface of the diamond film, after delamination*

Analysis of the back side of the delaminated film (originally in contact with the $B_4C$) was also performed by scanning the electron beam over selected areas of ~400 μm$^2$. The first series of recorded spectra from the film surface showed a high intensity signal at 272 eV for

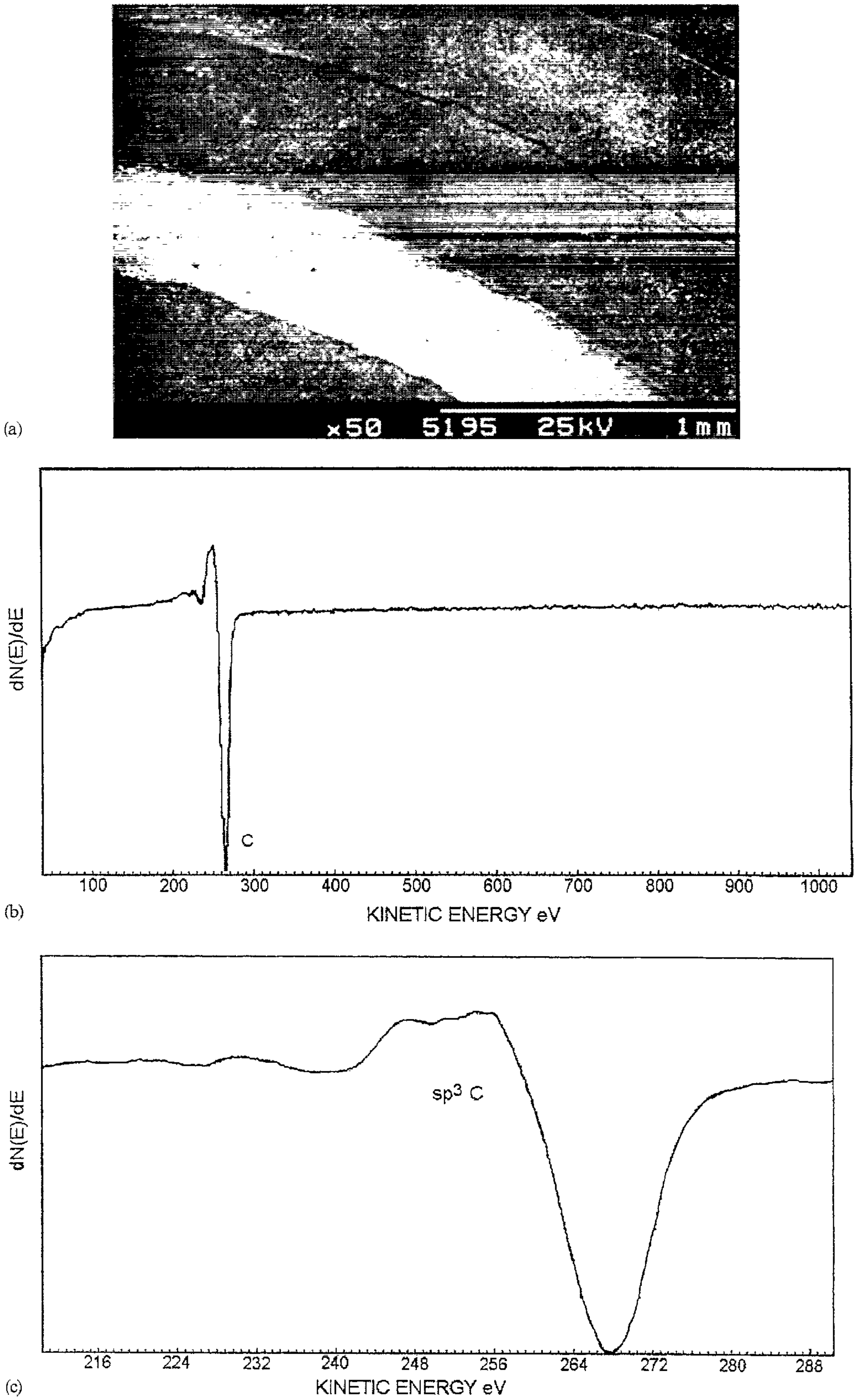

Fig. 2. Low magnification SEM image of diamond film on top of the grooved $B_4C$ substrate. The film has delaminated from one of the grooves. (b) Typical Auger electron spectrum taken from the top surface of the CVD diamond film. (c) Fine structure of the *KLL* carbon peak characteristic of the diamond structure.

C and relatively smaller ones at 179, 379 and 508 eV corresponding to B, N, and O, respectively. The shape and fine structure of the C peak suggested a mixture of amorphous and diamond forms of C.

In order to remove possible contaminant species from the analysed surface areas, a controlled sputter etch using an Ar ion beam was performed. The spectra obtained following the etching of ~50 Å from the top surface layers exhibited higher peak intensity for B and N with no peak for O (see Fig. 3(a)), indicating that the O was a contaminant resulting from prior exposure of the film to air. The N is believed to originate from the $B_4C$ substrate (see later). The average atomic concentrations of the detected elements from the Auger data were found to be: C 88%, B 9% and N 3%.

The results of further sequential etching and SAM analysis of four selected areas showed that both elements B and N had diffused into the diamond film to a distance of ~0.1 μm from the diamond–substrate interface. Deeper than this, the film was found to contain only C, with a peak fine structure which indicated $sp^2$ bonding (see Fig. 3(b)). This was due to graphitisation of the diamond by the Ar ion bombardment.

### *3.3. The top surface of the $B_4C$ after delamination of the diamond film*

The substrate surface was found to be covered with a C-rich layer that hindered detection of B. Removal of ~150 Å from the surface by sputter etching, followed by SAM analysis showed that the only detectable elements were C, B, and N (see Fig. 4). The concentrations

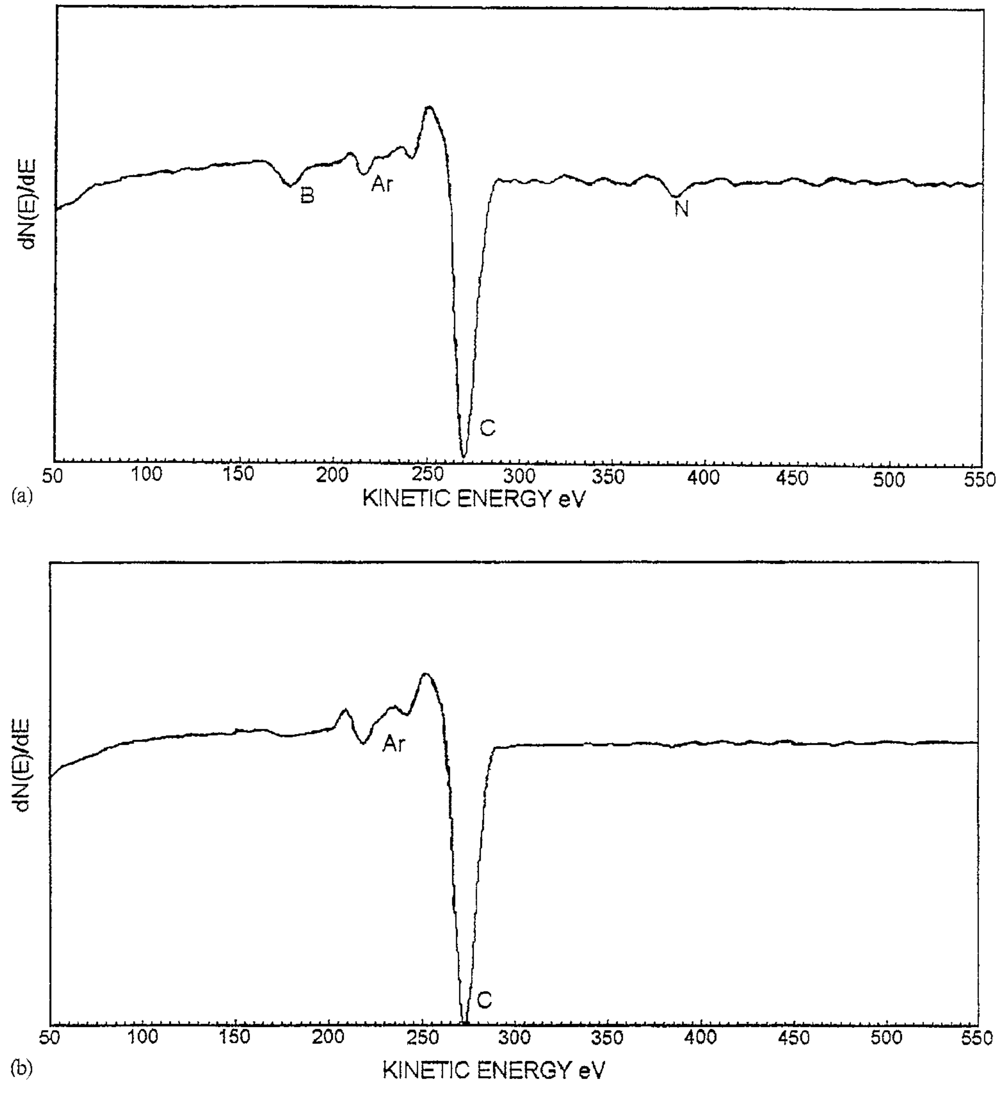

Fig. 3. (a) Typical SAM spectrum from the back side of the delaminated diamond film following Ar ion etching of 50 Å from the surface, showing the presence of C, doped with both B (179 eV) and N (379 eV). An Ar peak is also present due to implantation during the etching. (b) SAM spectrum obtained at a depth of ~0.1 μm from the top surface of the back side of the delaminated diamond film. There is no longer any B or N present.

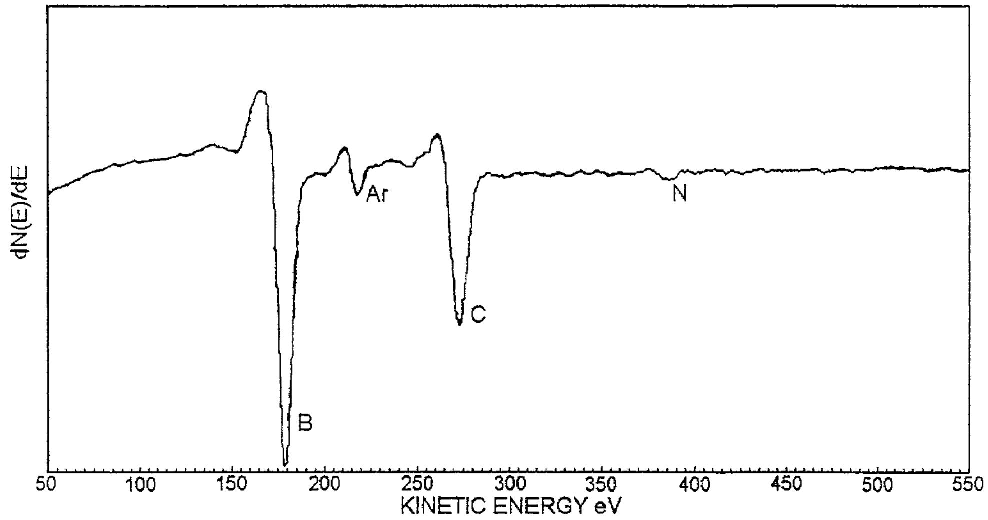

Fig. 4. A representative Auger electron spectrum of the surface of $B_4C$ following removal of the surface carbon layer (~50 Å) by sputter etching.

of these elements as determined from the recorded spectra were B 71.3, C 27.8 and N 0.9 at.%. The N content was the equivalent to that found in the back side of the delaminated diamond film. As N was also found alongside B on both of these analysed surfaces (the $B_4C$ and the back side of the film) it seems most likely that this element had diffused from the substrate into the diamond film upon deposition. The fact that N was only found in the surface layers of the CVD diamond film, but was found the bulk of the $B_4C$, suggests that N is actually a minor constituent of the $B_4C$, and was probably incorporated into the rotor as the $B_4C$ powder was hot pressed during the sintering process.

## 4. Discussion

The results of this study suggest that at the deposition temperature, the diamond acted as a sink for B, dissolving it out of the $B_4C$, and becoming slightly B-doped as a result. This is analogous to the metal boriding process mentioned in Section 1. Under our process conditions, the diffusion rate of B into the diamond was slower than the diamond growth rate. This meant that the top surface of the growing diamond coating remained undoped, while the lower surface, in contact with the $B_4C$, became increasingly more B-doped as deposition proceeded. Meanwhile, the surface of the $B_4C$, became increasingly more depleted in B, and slowly enriched with graphitic carbon. This thin layer of graphite at the interface apparently hindered adherence, and when the sample was removed from the chamber after deposition, the diamond film readily separated from the substrate at this weak interface.

This study shows that it will not be a simple or straightforward procedure to produce a diamond coating on $B_4C$ that has superior properties to the uncoated material. Solutions to the problem of poor adherence may be to coat the $B_4C$ prior to diamond CVD with a suitable metal layer to act as a barrier to B diffusion. We are currently studying the effectiveness of using barrier layers made from 1–2 μm of Ti and/or W. However, this additional coating step adds cost, and therefore may be economically unattractive. An alternative solution, therefore, may be to deliberately deplete the $B_4C$ surface of B before diamond deposition. This might be possible using a suitable heat treatment in a reactive atmosphere, or by selective etching using ion bombardment. Both these approaches are currently under investigation.

One positive aspect to arise from this work is that it has suggested a simple and effective way to produce doped diamond films using an ex situ heat treatment process. The undoped CVD diamond films just need to be placed in contact with a $B_4C$ block, and positioned in a furnace at temperatures of around 900°C for a few hours. The $B_4C$ may act as a suitable boriding agent for diamond in the same way as it does for metals, and this procedure may prove to be a lot simpler than in situ doping using volatile and potentially hazardous B-containing gases such as $B_2H_6$ and $BCl_3$.

## Acknowledgement

The authors wish to thank the EPSRC and Smiths Industries, Cheltenham, for funding this work. PWM also wishes to thank the Royal Society for the award of a Research Fellowship. The authors also wish to thank other membersof the CVD diamond group at Bristol, in particular Profs. M.N.R. Ashfold and G.C. Allen.

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