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The allotropic transformation of polycrystalline cubic boron nitride structures resulting from the thermal effects of pulsed laser ablation

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ABSTRACT

Cubic boron nitride, being only second to diamond for its hardness and possessing superior thermal stability is suitable for a wide range of applications. In particular, the versatility of this material and its polycrystalline cubic boron nitride composite form can be extended by micro processing enabling its use in advanced manufacturing applications. By employing a pulsed laser ablation technique for the micro texturing of this material, this paper presents for the first time the thermal response of polycrystalline cubic boron nitride incorporating a ceramic binder to the laser ablation process. Combined FIB/TEM/EELS/EDX techniques have been used to characterise a cubic boron nitride based material and its Titanium Carbide binder at nanometric resolutions after the surface has been ablated via an Nd Yag laser. Allotropic transformations of the cubic boron nitride into amorphous boron nitride immediately below the ablated surface and into hexagonal boron nitride down to depths exceeding 300 nm have been identified in a site exposed to high thermal excitation while the boundaries between boron nitride and the primary binder constituents remained definitive. Importantly, the structural integrity of the studied PCBN remained intact below the regions of phase transformations.

Prime novelty statement: The paper presents for the first time an evaluation of laser ablated polycrystalline cubic boron nitride surfaces and substructures at nanometric resolution. A novel procedure for the focus ion beam preparation of circa 100 nm thick lamella using multi surface protection coatings and stabilising straps is presented, allowing and HRTEM imaging and EELS analyses of this fragile structure.

1. Introduction

Boron nitride is a chemical compound with a carbon like structure existing in different crystalline forms; in particular it has several BN phases (r-BN, w-BN, h-BN, c-BN). Among these, the only two equilibrium phases are the hexagonal sp^2-bonded structure known as h-BN which represents the soft phase, having a layered structure similar to graphite and the cubic sp^3-bonded structure known as c-BN which is the hard phase, comparable to the diamond phase of carbon [1].

It has been demonstrated that the transition from sp^2 to sp^3 bonding to effect the h-BN to c-BN phase change requires a large reaction energy to overcome the impeding kinetic barrier at ambient conditions [1]. The transion energy can be provided by high pressure and temperature synthesis. C-BN is produced by a conversion of a mixture of h-BN and catalysts (lithium nitride, magnesium nitride, calcium nitride) under pressures and temperatures, in the order of 4–6 GPa and 1000–1500 K respectively [2]. In addition, quantities of boron oxide can also be used in the process to decrease the pressure at which c-BN synthesis takes place, which would otherwise be in the region of 18 GPa [3].

While the scientific community continues to explore the thermodynamic stabilities of h-BN and c-BN at ambient pressure [4] the currently presented pressure-temperature phase diagrams of Boron nitride show the thermodynamic stability of c-BN in ambient as well as at high pressure and temperature conditions; while h-BN is thermodynamically stable in high temperatures conditions and exists in a metastable form at lower temperatures [4].

During the process of c-BN synthesis there are a number of chemical phenomena occurring, which can also result in the formation of other BN structures such as amorphous BN (a-BN) resulting from thermal gradients and the presence of the catalytic substrates [1,5] and are not normally desirable outcomes from the synthesis of BN.

To widen the applications fields beyond those for c-BN, the synthesis of polycrystalline cubic boron nitride (PCBN) has been developed which allows the production of large size solid structures (area up to 0.01 m^2). PCBN is produced by sintering grains of c-BN in a high pressure (7 GPa) and high temperature (1200–1400 K) environment, with different types of binders (TiC, TiN, Al, WC–Co, Ti, TiN–Al). While some grades of PCBN can offer a higher fracture toughness to c-BN, the presence of the binder phase, e.g. TiC TiN, reduces the thermal conductivity of the bulk structure to around 50% of that of pure c-BN [6].

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Table 1
Atomic centre-to-centre separation of single crystal BN and binder of PCBN [1,7].

BN phase	d spacing (nm)	Lattice direction	Binder phase	d spacing (nm)
h-BN	0.333	002	TiC	0.25
c-BN	0.209	111		

The atomic centre-to-centre B to N d spacing of hexagonal and cubic BN for specific lattice directions and for a TiC binder are provided in Table 1.

Due to its exceptional hardness (Vickers hardness 500 $kg \cdot mm^{-2}$ [8]) and thermal stability, PCBN finds suitable fields of application in the manufacturing industry, predominantly as machine tooling. In addition c-BN based tools offer increased chemical stability over diamond tools, thus increasing their attractiveness for the machining of carbon reactive materials (e.g. steels, cast irons and chromium, nickel, titanium alloys). The expanding use of PCBN in precision engineering has led to increased scientific research on the manufacturing processes of ultrahard tools for defined edge applications (e.g. drilling, milling). Depending on the dimensions of the cutting tool, different processes are used for the generation of tool geometries and profiles. While mechanical processes e.g. grinding, electro-discharge machining are suitable for macro tools, pulsed laser ablation has been found to provide distinct advantages for micro tools [9], particularly when produced from ultrahard materials such as PCD and PCBN that are difficult/not possible to processes by other methods.

In the context of laser generated structures, it is particularly important to understand the thermal response of the material to ablation in order to achieve a high degree of process control. Using specifically developed Focus Ion Beam (FIB) lamella preparation procedures for High Resolution Transmission Electron Microscopy (HRTEM) and Electron Energy Loss Spectroscopy (EELS), recent studies have identified the specific behavioural characteristics of solid diamond and related structures to the thermal effects of laser ablation. In the case of monocrystalline CVD diamond, distinct bands of amorphous carbon, graphitised carbon followed by an undisturbed diamond structure, characterised by abrupt transition boundaries, were identified as depths increased below the ablated surface [9]. In the case of PCD a more complex response to the intense thermal exposure was revealed. Sites containing amorphous carbon and graphitic structures were identified immediately below surfaces ablated at two different fluence levels, which formed an abrupt interface with the undisturbed polycrystalline diamond below [10]. Furthermore partially evacuated pockets containing traces of the Cobalt binder were identified within the amorphic/graphitic regions of the lamella which strongly indicated the partial vaporisation of the binder constituents in this region [11].

This work has provided a valuable insight not only to the residual diamond based structures processed by laser ablation, but have allowed an understanding of the mechanisms by which material is removed/modified by this intense thermal activity, namely though the vapour phase, solid to liquid and solid to solid allotropic phase changes. PCBN is generally a more fragile material than solid diamond or PCD structures due to its seceded (non-intergrown) granular structure, [12] and therefore poses more of a challenge to employ such investigatory methods using very thin lamella (100–150 nm) for TEM investigations. Nonetheless, the potential advantages offered by laser ablation in the texturing and generation of micro features/geometries in PCBN and the lack of understanding of the thermal response of this material to the intense thermal activity produced by pulsed laser ablation and the potential for enhancement's to FIB lamella stabilisation and extraction procedures provides an ideal opportunity to explore these thermal responses down to nanometric resolutions.

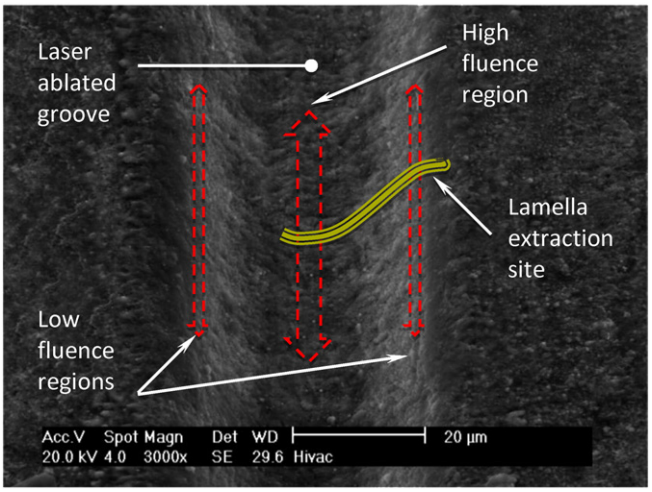

Fig. 2. ESEM images of the laser ablated groove in the PCBN showing the regions exposed to high and low fluence and the selected site for FIB lamella extraction.

1.1. Scope of the paper

This paper studies the thermal response of a polycrystalline cubic boron nitride material to a pulsed laser ablation process, and by primarily using nanometric characterisation techniques (high resolution transmission electron microscopy/electron energy loss spectroscopy) it focuses on the following aspects:

- An identification of the depth of the material's thermal response to high and low fluence levels of laser irradiation and a determination of the crystallographic integrity of the underlying substructure.

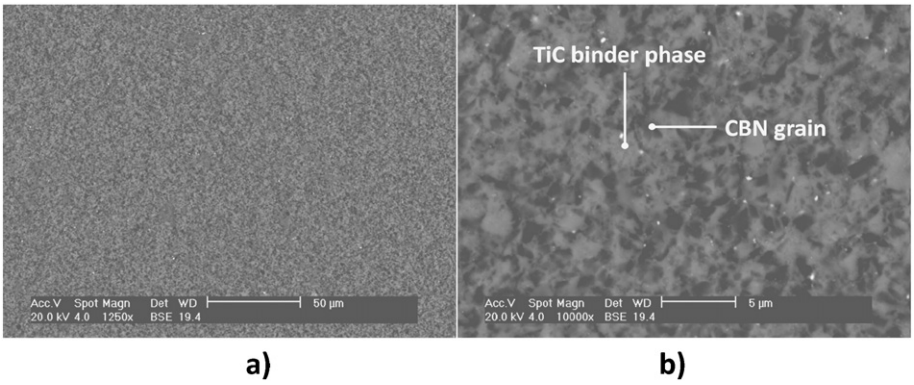

Fig. 1. Backscatter ESEM imaging of a polished surface of the DCC500 fine grained PCBN before exposure to pulsed laser ablation: a) low magnification image of the specimen showing the c-BN/binder structure (50% c-BN by volume), b) enlargement of the structure showing the c-BN granular (dark areas) and the ceramic binder (light areas).