Non- destructive investigation of a polycrystalline carbonado diamond

TB Moipolai[1], AM Venter[2], TP Ntsoane[2], MAG Andreoli[3]andSH Connell[1]

[1] Department of Physics, University of Johannesburg, Johannesburg, South Africa
[2]Research and Development Division, Necsa Limited, South Africa
[3] Nuclear Liability Management Department, Necsa Limited, South Africa

Corresponding author: Andrew.Venter@necsa.co.za

Abstract. This study reports a non-destructive investigation of a polycrystalline carbonado diamond in its raw as-discovered form. The carbonado has a porous structure and is mostly composed of carbon, oxygen and nitrogen. The carbon is crystallised as cubic diamond, but no specific crystalline oxide or nitride phases were observed. Residual stress values, determined using the $\sin^2\psi$ technique at depths of 240 μm, indicated stress values ranging from -35 ± 85MPa to 135 ± 50 MPa, i.e. within the experimental accuracy and constraints imposed by the surface roughness, the averaged surface stresses are close to zero.

1. Introduction

Diamond, the hardest of the naturally occurring materials, is an allotrope of carbon in which the carbon atoms are arranged in specific lattice symmetries, the cubic one with tetravalent covalent bonds being the one most common in nature. Carbon occurs as a native element in several polymorphs, of which the most familiar are graphite (very soft, hexagonal, black, as anisotropic sheets) and diamond (extremely hard, cubic, various colours, generally translucent). In addition there are the polycrystalline fine-grained aggregates discussed here (carbonado and related forms), and other rare polymorphs [1].

Our research interest is in the characterization of the residual stresses locked in polycrystalline diamonds from different origins to add information towards unravelling their still very controversial origin [2]. With respect to residual stress investigations the only reported study was performed on surface modified (cut and polished) carbonado samples using Raman spectroscopy [3, 4]. Since surface modifications cause stress redistribution we have subsequently adopted a non-destructive approach by investigating the sample in its natural as-discovered form.

Residual stresses in solids result, amongst others, from the conditions prevailing during their formation, i.e. temperature and pressure, as well as the effects of inclusions that contribute differences in coefficients of thermal expansion (CTE).

The typical, primary requirements for natural diamond formation are combinations of high pressures (HP) and high temperatures (HT). Possible mechanisms of formation are [5]:

- Igneous crystallisation from C-rich kimberlite melts in the mantle [HT-HP].
- Solid state conversion from graphite as a result of subduction of oceanic/continental crust to mantle depth [HP-HT].
- Shock-metamorphism in meteorite impact processes [Ultra HT-PT].

- Presolar.

The sample of our investigation, carbonado, generally are a few mm to cm size pebbles from soils/sediments, contain inclusions of foreign phases and may have been formed from any of the above mechanisms. Commonly known as "Black Diamond", carbonado is a natural polycrystalline diamond found in alluvial deposits in the Central African Republic and Brazil [6]. It is a porous aggregate of micron-sized diamond crystals and black or dark grey in colour. It does not seem to occur with normal diamonds in kimberlite pipes, suggesting a very different mode of origin. It is postulated that the hexagonal form of diamond, called lonsdaleite, would result purely from the latter two mechanisms mentioned above [7].

We report results from exploratory non-destructive investigations on a polycrystalline carbonado originating from Brazil. Investigations included scanning electron microscopy for elemental identification and imaging, as well as X-ray diffraction (XRD) for chemical phase identification and residual stress determination of the sub-surface region to a depth in the order of 240 μm.

2. Experimental

Since the sample is of significant scientific value, no surface preparation, apart from surface cleaning with compressed air, has been performed to remove loose deposits. Characterisation investigations have been performed with: Laboratory X-rays for chemical phase identification and residual stress analysis; Supplemented by scanning electron microscopy (SEM) in secondary electron (SE) and backscattered electron (BSE) imaging and energy dispersive X-ray spectroscopy (EDS) for elemental identification to aid in the diffraction characterization. All the investigations have been done at the Necsa facilities within the Research and Development Division.

2.1. Sample

A photograph of the carbonado is shown in figure 1. It has a distinctive irregular pebble (stone) shape and of approximate size 13.5 x 10 x 3.5 mm^3, characteristically black in colour with clear crevices and porosity visible with the naked eye.

Figure 1: Photograph of the carbonado. Investigation were performed at the four positions indicated which were selected to be representative of as-flat-as-possible positions on the sample surface. The irregular topography of the sample is clearly evident. Note the bubble-like void appearance covering the entire surface.

2.2 Investigations

XRD investigations were done with a Bruker D8 Discover instrument equipped with a 1/4 Eulerian cradle goniometer stage, highly collimated Cu radiation, incident beam size 0.8 mm in diameter, and an area detector system. In conjunction with the laser video alignment system of the instrument, picking of measurement positions and aligning to the instrument rotation axis were possible to within 20 μm accuracy. The beam penetration depth into carbon by Cu radiation was calculated to be 240 μm. Chemical phase identification was done against the International Centre for Diffraction Database (ICDD) search / match function and residual stress investigations were performed with the $sin^2\psi$ side-inclination technique for ψ angles 0 ° to 70°. The residual stress technique is based on the accurate determination of the (311) Bragg reflection of diamond, typically observed at 2θ = 92.093°, at various sample tilt angles with respect to the fixed incident and diffracted beam paths. Data analysis was done using the software package Leptos version 6 supplied by Bruker AXS. Stress-free d-spacings were taken as the psi = 0° measurement. Since an essential requirement for residual stress analysis by XRD is that the surface needs to be flat to at least 20% of the penetration depth of the X-rays, four positions were selected on the sample surface that offered as-flat-as-possible surfaces for the investigations.

The SEM investigations were done with a Quanta FEI 200 SEM/EDS instrument equipped with a silicon drift detector. The instrument parameters employed were 30kV voltage, 0.67 nA current, working distance WD = 15.00 mm and magnification 500X.

For the XRD investigations the sample was mounted in a sample holder to ensure repeatable sample setup. For the SEM analyses the sample was taped to the sample stage with carbon tape to limit charging. All SEM investigations were done at low vacuum of 0.45 Torr.

2.3 Residual stress analysis

Residual stress is the stress that remains in a solid sample with no external forces applied.

Positive values indicate tensile (expansion) stress whilst negative values indicate a compressive (contraction) state. The deformation per unit length is the strain [8].

The X-ray diffraction method measures macroscopic strains from the interplanar spacings through the application of the $sin^2\psi$ side-inclination technique shown in figure 2. With this technique the lattice plane spacing of a specific *(hkl)* reflection is accurately measured as function of sample tilt angles ψ (inclination angles). The residual stress for a bi-axial (in-plane) condition (assumed with XRD due to the limited penetration depth) is deduced through the equation

$$\varepsilon_{\emptyset} = \frac{d_{\psi} - d_0}{d_0} = \frac{1+v}{E}(\sigma_{\emptyset} sin^2\psi) - \frac{v}{E}(\sigma_{11} + \sigma_{22})$$

where E and ν are the Young's modulus and Poisson's ratio of the material under study, d_{ψ} is the lattice spacing at each ψ, and d_0 is the value of d at $\psi = 0^o$, σ_{11} and σ_{22} are the in-plane principal stresses and σ_{33} the normal stress component. S_1, S_2 and S_3 represent these principal stress components in the sample coordinate system. This strain equation describes a linear dependence for data plots of ε versus $sin^2\psi$ with the in-plane stress σ_{ϕ} determined from a least squares fit of the curve gradient. For the principal stress to be resolved, measurements need to be performed for at least 3 (azimuthal) phi rotations.

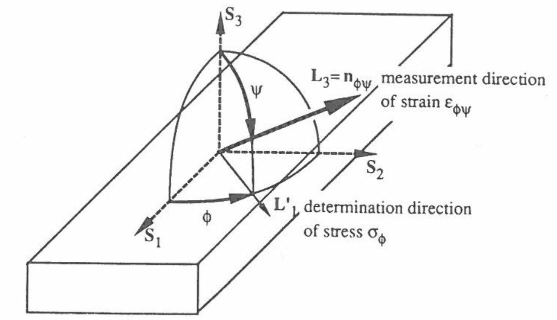


Figure 2: XRD residual stress measurement geometry [9].

3. Results

Figure 3 shows SEM secondary electron (SE) images taken at each of the measurement positions. The porosity of the sample with distinctive crevices is clearly evident. The carbonado surface is quite complex: a spot analysis has identified the dark areas in the SE image as carbon and the paler regions indicative of heavier elements. The pore sizes are estimated to be 40 – 100 µm with no visible partially closed cavities within which foreign material could be entrapped.

Figure 4 shows the elemental and chemical phase analyses results taken at the four measurement positions and summarized in table 1.

Figure 5(a) displays the *strain* versus $sin^2\psi$ results that were measured at the four positions. It is clear that the residual stress analyses are adversely affected at large sample ψ-tilt angles by the severe surface roughness of the sample, leading to deviation from a linear trend. This is ascribed to the surface roughness leading to partial screening of the incident and diffracted beam paths causing anomalous absorption of the beam, with the resulting peak determination of the altered peak leading to artifacts and shifts in the perceived beam centre. Since the $sin^2\psi$ is based on a linear dependence, data analyses were subsequently limited to $sin^2\psi$ values smaller than 0.7 for which a linear dependence does exist as shown in figure 5(a). To demonstrate the feasibility of the $sin^2\psi$ technique overall, figure 5(b) shows results measured on our equipment from a polycrystalline diamond (PCD) compact that has a flat smooth surface, that is ideally suited for stress analyses up to $sin^2\psi$ values of 0.9. The latter result is indicative of a stress of -836 ± 78 MPa.

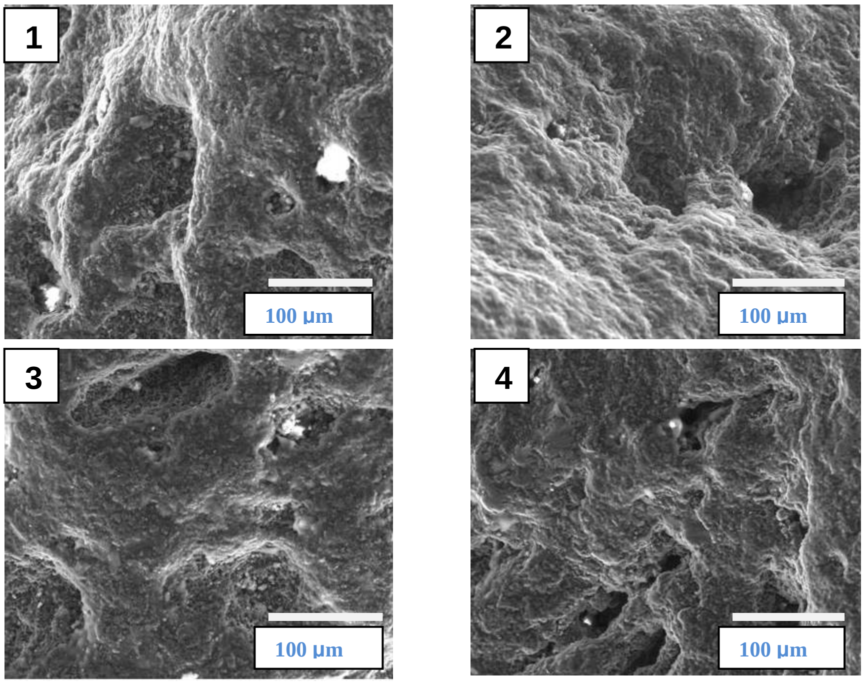
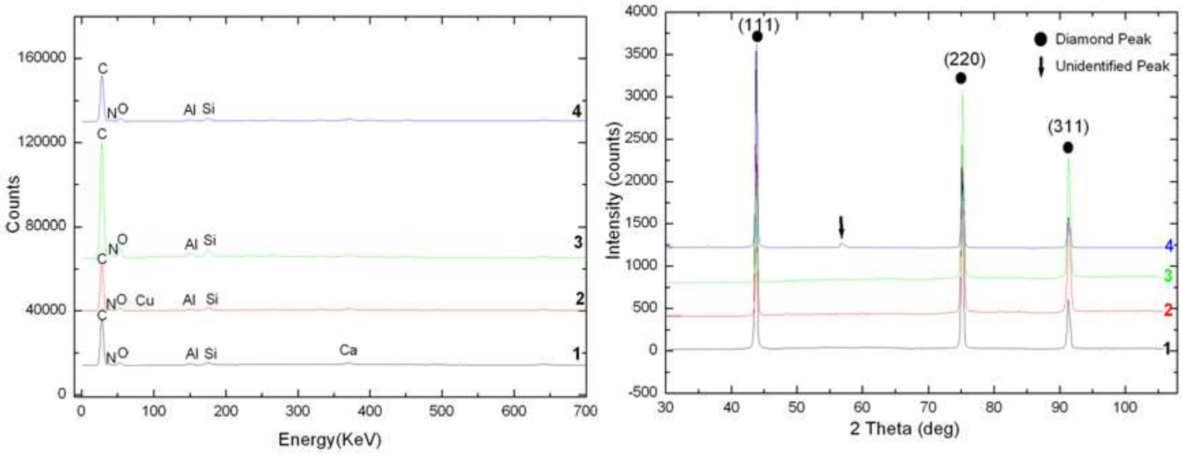
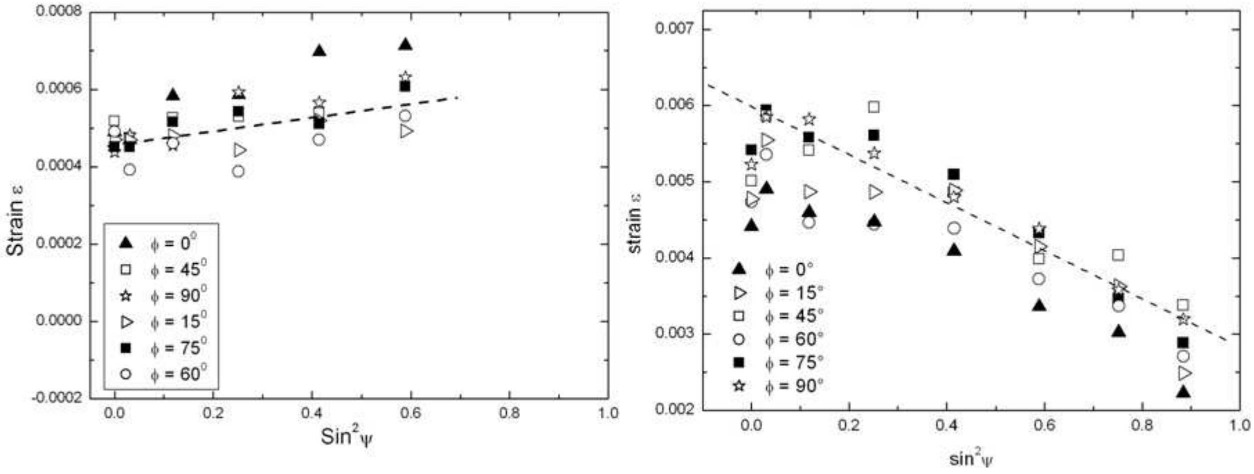


Figure 3: Secondary electron images for the carbonado sample at the four positions of interest.



(a) **(b)**

Figure 4: Analyses results obtained at the four positions of interest on the carbonado sample: (a) Elemental composition determined with the EDS function of the SEM unit; (b) Chemical phase identification using XRD.



(a) **(b)**

Figure 5: *Strain* versus *sin*$^2\psi$ curves (a) Carbonado sample; (b) PCD compact sample as control. The large variation of curves (a) at 0.9 is anomalous and ascribed to the sample roughness. Only values up to 0.7 were subsequently used for the determination of the gradients and thus the stress values. The dotted lines in both curves give the linear trends of the data analysis.

The experimental results obtained from the various analyses at the four positions are summarized in table1. The stress analysis excluded the data points at *sin*$^2\psi$ > 0.7 since these values were inconsistent with a linear trend. As a control, a flat surface PCD was also measured and the trend shown as reference. The EDS results indicated the major elements carbon, nitrogen and oxygen. The XRD patterns primarily show diamond in its cubic structure.

Table 1: Summary of experimental results

Measurement position	Elemental content (EDS)		Chemical phase content (XRD)	Residual stress σ_φ [MPa]
	Major	Minor		
1	C (56%) O (21%) N (12%)	Si (1.5%) Al (1.1%) Mg (0.9%)	Diamond: Cubic	55 ± 42
2	C (67%) O (16%) N (14%)	Si (1.2%) Al (0.7%) Cu (0.7%)	Diamond: Cubic	-5 ± 42
3	C (67%) O (16%) N (14%)	Si (1.3%) Al (0.8%)	Diamond:Cubic	-34 ± 85
4	C (68%) O (16%) N (13%)	Si (1.6%) Al (1.2%)	Diamond:Cubic	135 ± 50
PCD	-	-	Diamond:Cubic	-836 ± 78

Notwithstanding the literature reports of entrapments and speculation on the possible presence of the hexagonal phase of diamond, lonsdaleite, and amorphous carbon, our results do not indicate the presence of any of these. Presence of amorphous phases would manifest as a broad increase in the background of diffraction patterns at angles below 40º 2θ. The carbon versus oxygen ratios observed in this investigation does not correlate with that of normal atmospheric conditions. This in conjunction with the sample being under a partial vacuum during the SEM analyses indicates that these gases may be present in an entrapped form (N is trapped in as a lattice impurity and O as a termination species). It is known from the literature, that minerals from the environment where the carbonado samples have been discovered, and gases such as N_2 and O_2, can be entrapped in the pores [6].

Conclusion

Notwithstanding the irregular sample shape and severe surface roughness of the carbonado, an estimate of the surface residual stress was possible by careful selection of the site of measurement and objective data analysis. Within the measurement accuracy of the X-ray technique, constrained by the sample surface roughness contributions, the stress values are generally low. The SEM results indicated the presence of large O and N contents, which could not be identified as specific chemical phases with the XRD analyses. No presence of the hexagonal lonsdaleite, or amorphous carbon was observed.

Acknowledgements

Access and personnel assistance with the XRD and SEM instruments of Necsa Limited, with special thanks to Mr.R van der Merwe and Ms. J Kabini, who assisted with the SEM analyses, as well as financial support from the NRF Internship and SANHARP student support programs are acknowledged. Prof F Viljoen, University of Johannesburg Geology Department is specifically thanked for providing the carbonado.

References

[1] *Diamond Deposits*, Eds. EI Erlichand WD Hausel, Society for Mining, Metallurgy and Exploration, Inc. USA (2002) ISBN 0-87335-213-0

[2] Y.A Litvin 2009 *Russian Geology and geophysics***50**1188-1200

[3] H. Kagi and S. Fukura . Infrared and raman spectroscopic observations of central African carbonado and implications for its origin. European Journal of mineralogy **20** (2008), 387-393

[4] S. Fukura , T. Nakagawa, and H. Kagi. High spatial photoluminesce and raman spectroscopic measurements of a natural polycrystalline diamond, carbonado. Diamond and Related Materials, **14** (2005), 1950-1954.

[5] G Kletetschka, PT Taylor, PJ Wasilewski, H.G.M. Hill 2000 *Earth and Planetary Science* Letters **181** 279-290

[6] J. Garai, S.E. Haggerty, S. Rekhi and M. Chance 2006 *The Astrophysical Journal* **653** L153-L156

[7] S De, PJ Hearnay, EP Vincenzi, J Wang 2001 *Earth and Planetary Science Letters***185** 315-330

[8] *Fundamentals of solid mechanics*, Ed. ML Gambhir, PHI Learning Private Limited, New Delhi (2009) ISBN 978-81-203-3870-8

[9] *Handbook of measurement of residual stress*, Ed. J Lu, The Fairmont Press Inc. USA (1996) ISBN 0 88173-229-X, Chapter 5 pp71 – 131.