Fracture of synthetic diamond

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(Received 10 March 1995; accepted for publication 11 May 1995)

The fracture behavior of synthetic diamond has been investigated using indentation methods and by the tensile testing of pre-notched fracture-mechanics type samples. Specifically, the fracture toughness of free-standing diamond plates, grown by chemically-vapor deposited (CVD) methods, was measured using Vickers indentations and by the use of disk-shaped compact-tension specimens; the latter method provides an evaluation of the through-thickness fracture properties, whereas the indentation method was performed on the nucleation surface of the sample. Measured fracture toughness (K_c) values were found to be approximately 5–6 MPa$\sqrt{m}$ by both methods, indicating that the fracture resistance of CVD diamond does not vary appreciably with grain size (within the certainty of the testing procedures). Complications, however, arose with the fracture-mechanics testing regarding crack initiation from a relatively blunt notch; further work is needed to develop pre-cracking methods to permit more reliable fracture toughness testing of diamond. © *1995 American Institute of Physics.*

I. INTRODUCTION

The unique combination of physical and mechanical properties of synthetic polycrystalline diamond make it a promising material for many structural applications; these include the development of ultra-hard coatings (e.g., for hard disks, bearings or cutting tools), in bioprosthetic devices, and even in the design of monolithic or composite engineering materials. For such applications, the superior properties of diamond include the highest values of hardness, stiffness (Young's modulus), and room temperature thermal conductivity shown by any material, coupled with a low coefficient of friction. However, for most practical uses of diamond, an additional engineering parameter of importance is the resistance to fracture, as characterized by the fracture toughness. As elaborated below, this is a difficult parameter to measure in brittle materials such as diamond owing to its extreme values of hardness and stiffness.

Despite complications in the fracture toughness evaluation of diamond materials, it is important to characterize their fracture behavior because of the variety of microstructures which may be produced by synthetic processing methods. For example, diamond grown by chemical-vapor deposition (CVD) produces columnar microstructures with mixtures of grain orientations, typically with a very large variation in grain size (Figs. 1 and 2); details associated with the growth of diamond by CVD methods are discussed elsewhere.[1] Each microstructural change, such as in grain size, shape and orientation, grain-boundary reaction layers, the presence of inclusions or porosity, may well yield a wide range of fracture toughness values and (strength-limiting) flaw populations. However, to date there have only been limited studies on the fracture toughness of polycrystalline diamond,[2,3] primarily due to the difficulties in toughness measurements, such that the relationships between microstructure and mechanical properties are not understood.

The fracture toughness, K_c, provides the most realistic assessment of the fracture resistance of a brittle material in terms of a measure of the critical stress intensity (i.e., the intensity of the *local* linear-elastic stress and deformation fields) to cause unstable (i.e., catastrophic) fracture from a pre-existing crack (see, for example, Ref. 4). Previous fracture toughness measurements on synthetic diamond have focused on two "approximate" procedures, specifically involving indentation techniques,[2] and a "fracture mirror" method;[3] a summary of results is listed in Table I. The indentation method involves an extension of the hardness test, where the value of K_c is determined from the length of the radial cracks which develop at the corners of the indentation following penetration of the surface of the sample with a sharp pyrimidical (Vickers) indenter under sufficient load.[5] This method is easy to perform, but the measurement accuracy is limited by uncertainties in the magnitude of the residual stresses generated in the vicinity of the intent, specifically involving the material-dependent constant relating hardness to toughness.[6] Fracture mirror measurements, conversely, rely on identifying a critical flaw along the plane where fracture has occurred; this technique typically is difficult to perform for diamond materials as a result of their complex microstructures (see, for example, Figs. 1 and 2).

Accordingly, the objective of this paper is to describe studies to measure the fracture toughness of free-standing CVD diamond (~150–200 μm thick) plates using full-scale fracture mechanics test methods with pre-notched compact-tension specimens;[7–9] results are compared with surface measurements obtained using the approximate indentation techniques, and previously reported[2] indentation data.

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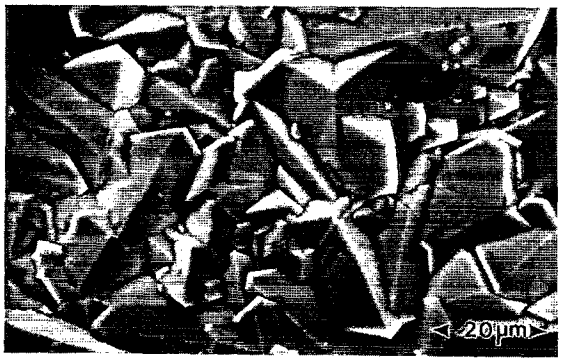

FIG. 1. SEM micrograph of the growth surface of a CVD diamond sample.

II. EXPERIMENTAL PROCEDURES

A. Material

Diamond plates were prepared for this study by growth in a microwave plasma reactor on 50.8 mm diameter [100] polished silicon wafers. Wafers are prepared for deposition by cleaning in solvents and scratching with a fine diamond powder for nucleation enhancement. Diamond growth was achieved at 2.45 GHz excitation in a mixture of ~1% methane in hydrogen at a total flow rate of 200 standard cubic centimeters per minute (sccm). The total chamber pressure was 30–70 Torr and applied (microwave) power was 500–1500 W. Diamond growth proceeded until a thickness of ~ 150 to 200 μm was obtained. A free-standing CVD diamond plate was then derived from the sample by chemical removal of the silicon wafer in acid etchants.[2] The plate contained high quality diamond as evidenced by the sharp characteristic peak of 1332 cm^{-1} in the Raman spectrum with a minimum of non-diamond carbon indicated by the absence of a broad peak at ~1500 cm^{-1} (Fig. 3). In addition, the well-faceted microstructure apparent from the growth surface is characteristic of CVD diamond slabs of a similar thickness (Fig. 1). The through-thickness columnar grain morphology (Fig. 2) revealed grain sizes varying from $\ll 1\mu$m on the nucleation side to ~20 μm on the growth side.

Because of the lack of curvature of the free-standing films, residual stresses were reasoned to be minimal; this was confirmed by Raman spectroscopy measurements which did not indicate any significant shift in relative wave number from the characteristic value.[10]

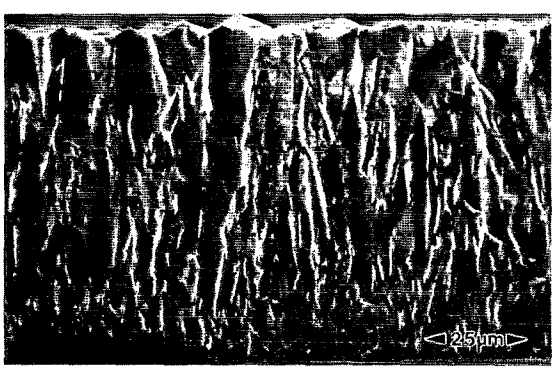

FIG. 2. SEM micrograph of a cross-section of a CVD diamond sample, showing the columnar microstructure with a very wide range of grain sizes from $\ll 1$ μm on the nucleation surface to ~20 μm on the growth surface.

TABLE I. Summary of fracture toughness K_c measurements on diamond.

Method	Average K_c (MPa$\sqrt{m}$)	Reference	Comment
Indentation	5.6	present work	CVD nucleation surface
Indentation	5.3	2	CVD growth surface
Indentation	5	11	single crystal
Indentation	4	12	single crystal
Compact-tension	6.3	present work	CVD
Fracture mirror	7	3	CVD

B. Fracture-mechanics testing

Disk-shaped compact-tension DC(T) specimens were used for the toughness measurements; such samples are routinely utilized for K_c measurements[7] in metals and intermetallics, and more recently in ceramics (see Refs. 8 and 9 for stress intensity and compliance solutions for this geometry). Specimens were prepared for mechanical testing by laser cutting the center of a free-standing slab to a 25 mm diameter. Additional features were produced to accommodate mechanical gripping, along with a slit centered between the gripping holes; the latter defines the plane for extension of the crack under load from the local concentration of stress at the tip of the slot. A sharp notch was further defined at this location by laser cutting to half of the specimen depth, in order to promote notch acuity and crack stability, which increases with initial crack length. Crack lengths in these specimens were continuously monitored *in situ* by electrical-potential measurements across a thin metallized (NiCr) gauge (~1000 Å thick) sputtered on the substrate side of the disk; this surface had a specular surface finish of better than 0.25 μm roughness. With this electrical-potential technique, (surface) crack lengths can be determined to a resolution of

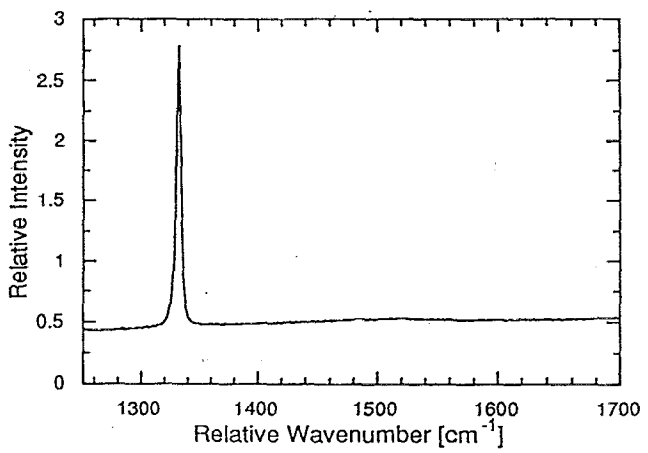

FIG. 3. Raman spectrum of a CVD sample, showing a fully diamond (sp^3 bonding) structure.

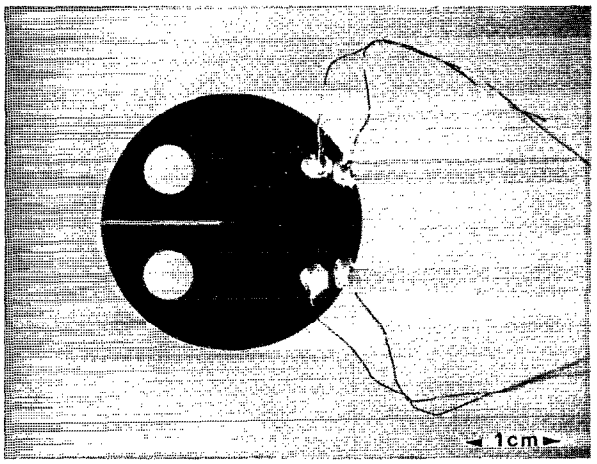

FIG. 4. Low magnification photograph of a diamond disk-shaped compact-tension DC(T) specimen used to measure fracture toughness K_c values, showing the pre-notch, loading-pin holes, and the evaporated metal-film gauge for monitoring crack length.

typically ± 2 μm. A macrograph of a diamond DC(T) specimen, with a deposited crack-monitoring gauge, is shown in Fig. 4.

In order to determine the toughness under "worst case" conditions, it is preferable to sharpen the notch in the test specimen, e.g., by cyclic fatigue, such that fracture is initiated at a nominally atomically-sharp crack. However, attempts to precrack the DC(T) samples by cyclic fatigue were unsuccessful; correspondingly, the as-notched samples were loaded monotonically under displacement control in order to determine resistance curve, $K_R(\Delta a)$, behavior, representing how the stress intensity for cracking varies with crack extension, Δa. Since initial cracking was immediately unstable, the fracture toughness, K_c, was defined as the critical stress intensity at the point of instability, in accordance with ASTM Standard E-399,[7] an established procedure followed by the "mechanics of materials" community. Stress intensities were computed in terms of the applied load P, crack length a, test-piece thickness B, and width W:[7,8]

$$K=\frac{P}{BW^{1/2}}f(a/W),$$

where

$$f(a/W)=\frac{2+a/W}{(1-a/W)^{3/2}}\times[0.76+4.8(a/W)-11.58(a/W)^2+11.43(a/W)^3-4.08(a/W)^4]. \quad (1)$$

Note that Eq. (1) pertains to conditions ahead of a sharp crack in the tensile opening mode (mode I), and is accurate to within $\pm 0.3\%$ for $0.2 \leqslant a/W \leqslant 1$.

C. Indentation tests

The fracture toughness was also measured by a Vickers indentation method; results were compared to the previous measurements on free-standing films of CVD diamond[2] in order to examine any influence of microstructure, e.g., grain

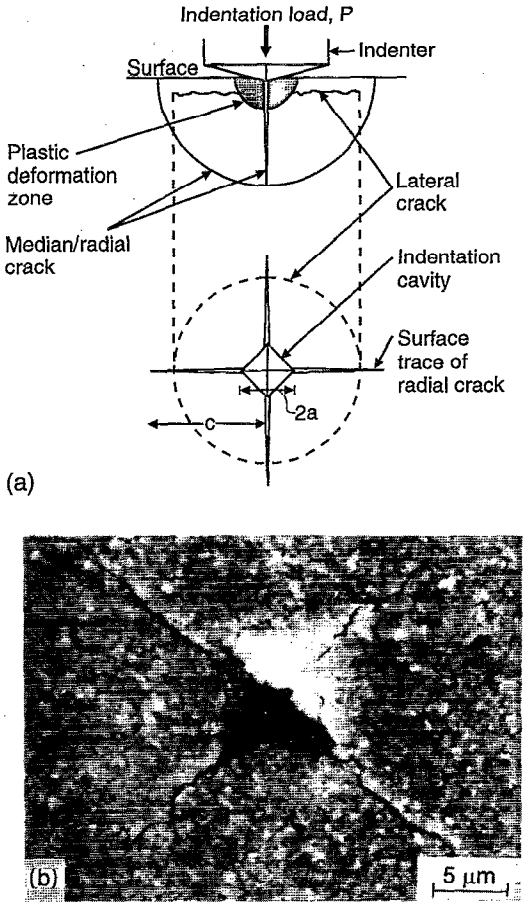

FIG. 5. (a) Schematic illustration of the radial and lateral cracks produced in a brittle material by Vickers hardness indentation, and (b) backscattered electron SEM image of the radial cracks emanating from the corners of an indentation in CVD diamond; the length of such cracks, together with the magnitude of the indentation load, is used to determine an approximate value of the fracture toughness, K_c.

size. In the present study, the fracture toughness of the *nucleation* side of the sample was examined by indenting under a small load (500–700 g). The value of K_c can be determined in terms of the indentation load P, the mean length (surface tip-to-tip length $2c$) of the radial cracks emanating from the corners of the pyramidal hardness impression [Fig. 5(a)]:[5]

$$K_c=\xi(E/H)^{1/2}(P/c^{3/2}), \quad (2)$$

where E is the Young's modulus, and H is the hardness. The parameter $\xi(=0.016\pm0.004)$ is an empirically derived constant that provides agreement between indentation fracture toughness data for a broad range of ceramic materials to fracture toughness measurements made by other methods.[6] Uncertainties in ξ have led previous researchers to conclude that up to 20% error may be expected in K_c measurements for ceramic materials using this method.[5]

Radial crack measurements were made using scanning electron microscopy (SEM) in the backscattered electron mode. In the past, such measurements have been invariably performed using optical microscopy or SEM in the secondary electron mode; the difficulty in resolving precise crack lengths with these techniques has led to uncertainties in the toughness and a large variance in reported K_c values

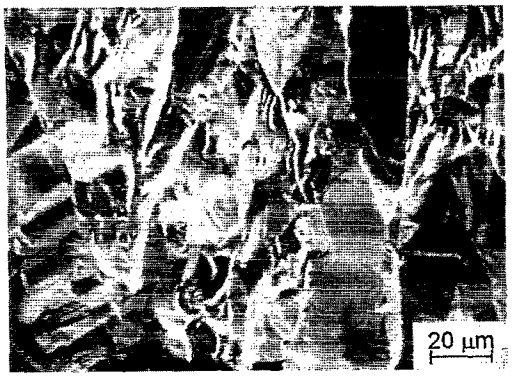

FIG. 6. SEM micrograph of the fracture surface of a failed CVD diamond DC(T) sample, showing primarily intergranular failure.

(e.g., Ref. 2). Secondary electron SEM, for example, has the inherent problem that to maximize secondary electron emission, reabsorption must be minimized by shallower penetration, which leads to lower accelerating voltages, longer wavelengths and hence lower resolution. These problems were avoided with the use of backscattered electrons; in fact, the resulting higher resolution led to a smaller standard deviation in indentation K_c values than has been reported[2] previously.

III. RESULTS AND DISCUSSION

The fracture toughness of the free-standing CVD diamond films was measured on two DC(T) specimens; values of K_c=5.3 and 7.3 MPa$\sqrt{m}$ were obtained. Scanning electron microscopy of the fracture surfaces revealed predominantly intergranular failure (Fig. 6), with an expected coarsening of the facet size from the nucleation to growth side of the film. It is important to note that in the computation of these values using Eq. (1), allowance was made for the fact that crack initiation occurred ahead of a blunted notch; in addition, in one sample a correction was made for a deflected crack path off the plane defined by the laser-machined notch. The analyses associated with these corrections are described below and in the Appendix; a summary of values is given in Table II.

Using the analysis described in Appendix, allowance for the deviation from the sharp crack assumption of Eq. (1) yields an expression for fracture toughness K_c in terms of the measured value K_Q:

$$K_c = \frac{K_Q}{1+\rho/2r}, \tag{3}$$

TABLE II. Summary of present DC(T) measurements of the fracture toughness of diamond

Sample	Measured K_c (MPa$\sqrt{m}$)	With deflection correction (MPa$\sqrt{m}$)	With blunt notch correction (MPa$\sqrt{m}$)
1	10.6	–	5.3
2	15.7	14.6	7.3

TABLE III. Indentation toughness measurements — present work.

Sample Number	Impression size $2a$, (μm)	Crack length c (μm)	Hardness H (GPa)	Fracture toughness K_c, (MPa$\sqrt{m}$)
1	11.9	15.3	97.0	5.9
2	11.7	16.0	100.3	5.4
3	11.8	16.2	97.0	5.4
4	11.8	14.8	98.6	6.2
5	12.1	15.9	93.8	5.7
6	11.9	16.3	97.0	5.4
7	12.2	16.1	92.3	4.9
8	12.2	16.0	96.0	5.6
Average	12.0	16.0	96.0	5.6
	±0.2	±0.8	±3.0	±0.4

where ρ is the radius of curvature of the notch root. An upper bound value of K_c can then be obtained by setting $\rho/2r=1$, which gives an estimate of the fracture toughness for the first sample as 5.3 MPa$\sqrt{m}$ (Table II). A similar analysis was required for the presence of the notch in the second sample, following an additional correction to account for the off-axis deflection of the crack, in this case by φ=31.7°, from the plane of maximum tensile stress. Using the notch correction and the crack deflection mechanics outlined in the Appendix, the fracture toughness of the second sample was found to be 7.3 MPa$\sqrt{m}$ (Table II).

These data represent the first measurements of fracture toughness of diamond using full-scale fracture-mechanics testing techniques; such techniques have become standard for the vast majority of structural materials,[7] but have remained hitherto unperformed on diamond materials because of the fabrication difficulties and high cost of obtaining appropriately large samples. The results, however, are consistent with measurements of the fracture toughness of diamond using more approximate methods. In the present study, Vickers indentation measurements of K_c were made on the nucleation surface of the broken compact-tension samples under 700 g load. Several indentation were made across the film, with crack measurements being performed with the backscattering mode by scanning electron microscopy; an example is shown in Fig. 5(b). As summarized in Table III, an average K_c of 5.6 MPa$\sqrt{m}$ was found.

Both the compact-tension and indentation results are similar to previous estimates of the K_c value for this CVD diamond determined by indentation methods, where an average value of 5.3 MPa$\sqrt{m}$ was found by testing a polished section of the growth surface.[2] The results are also consistent with the indentation values of K_c performed on single crystal (natural-type Ia and high-pressure synthetic) diamonds.[11–13] A listing of fracture toughness values for diamond is given in Table I.

The present compact-tension measurements of K_c for CVD diamond provide a new source of toughness data, hitherto unreported in diamond yet well established for other materials. However, some degree of uncertainty still remains with respect to the difficulty of pre-cracking the test specimens, and in the assumption that the Young's modulus of the tested material is similar to published values.[14]

An important aspect of interpreting K_c data is to examine the influence of microstructure on fracture toughness, which as noted above is not well understood for polycrystalline diamond. This issue is addressed here by comparing the previous indentation toughness measurements on the growth surface of the free-standing films,[2] with the current indentation measurements on the nucleation surface and the "bulk" through-thickness measurements obtained with the compact-tension tests. A variation in K_c with grain size might be anticipated if appreciable non-diamond carbon (which has significantly lower Young's modulus[19]) is present in the grain boundary region, as the relative volume of this phase increases inversely with grain size. However, the indentation K_c measurements on the nucleation surface are found to be within one standard deviation (± 0.4 MPa$\sqrt{m}$) from those on the growth surface (Table I), indicating that within the resolution of the experimental methods, the toughness of CVD diamond is relatively insensitive to grain size.

IV. CONCLUSIONS

The fracture toughness properties of free-standing (~150–200 μm thick) CVD diamond films were examined using conventional fracture mechanics methods, involving pre-notched compact-tension DC(T) test geometries, and using approximate Vickers indentation methods. Respective average values of K_c for polycrystalline diamond of 6.3 MPa$\sqrt{m}$ and 5.6 MPa$\sqrt{m}$ were obtained with the two techniques, which compare closely with previous K_c measurements for synthetic and natural diamond. Microstructural variations did not reveal any discernible variation in fracture toughness with grain size, a surprising result given the inevitable presence of non-diamond carbon near the nucleation layer.

ACKNOWLEDGMENTS

The work was supported by the National Science Foundation under Grant No. III-9260860 (for MDD), and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 (for RHD, AK, and ROR). Thanks are due to Dr. Joel W. Ager for several helpful discussions.

APPENDIX

1. Crack deflection correction

The elastic solutions for a crack subjected to applied far-field mode I (tensile opening) and mode II (shear) stress intensities, K_I and K_{II}, respectively, which undergoes aninplane deflection of φ from the crack plane normal of the loading direction, gives values for the *local* mode I and II stress intensities, k_1 and k_2 respectively, at the crack tip, as:[15,16]

$$k_1 = \cos^3(\varphi/2)K_I - 3\sin(\varphi/2)\cos^2(\varphi/2)K_{II}$$
$$k_2 = \sin(\varphi/2)\cos^2(\varphi/2)K_I + \cos(\varphi/2) \times[1-3\sin^2(\varphi/2)]K_{II}. \quad \text{(A1)}$$

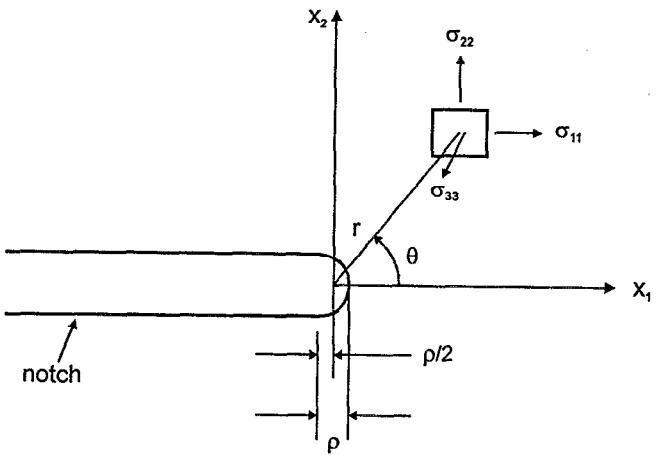

FIG. 7. Coordinates for the local stress distribution at distance r, θ ahead of a notch of length a and root radius ρ.

The driving force for such a deflected crack can be identified in terms of a maximum strain energy release rate, G. Interpreted in terms of stress intensity, this leads to a more precise computation for the stress intensity for a deflected crack in terms of an "effective K," given by:[15]

$$K_{eff} = \sqrt{k_1^2 + k_2^2}. \quad \text{(A2)}$$

In the present study where the crack path in sample #2 was deflected through an angle of $\varphi = 31.7°$, as there is no applied shear loading ($K_{II}=0$) with the DC(T) specimen, allowing for such deflection leads to a 7% reduction in the measured K value.

2. Notch correction

The effect of the blunt notch is to reduce the stress intensity relative to that ahead of a sharp crack; if this effect is not considered, resulting toughness values become erroneously high. This is taken into account in the present study by equating the stresses near the crack and notch at an arbitrary (r,θ) coordinate. For example, the linear elastic mode I fields for the distribution of local stress normal to the crack plane σ_{22}, is given for a sharp crack as $r \to 0$ by (Fig. 7):[17]

$$\sigma_{22} = \frac{K_I'}{\sqrt{2\pi r}}\cos(\theta/2)[1+\sin(\theta/2)\sin(3\theta/2)], \quad \text{(A3)}$$

while for the blunt notch, of root radius ρ, in mode I, the corresponding linear elastic stress distribution is given by:[18]

$$\sigma_{22} = \frac{K_I}{\sqrt{2\pi r}}\cos(\theta/2)[1+\sin(\theta/2)\sin(3\theta/2)] + \frac{K_I}{\sqrt{2\pi r}}\frac{\rho/2r}{\cos(3\theta/2)}. \quad \text{(A4)}$$

By equating the two local stress distributions, given in Eqs. (A3) and (A4), at some characteristic radial dimension ahead of each stress concentrator, an equivalency between the stress intensities at a sharp crack and a rounded notch, K_I' and K_I respectively, can be obtained:

$$K_I = \frac{K_I'}{1 + \rho/2r}. \quad \text{(A5)}$$

Although there is some uncertainty in the notch root radius (at fracture) and the appropriate radial distance for equating the normal stresses between the blunt notch and sharp crack, a reasonable assumption is to rely on the upper-bound estimate for K_c given by Eq. (A5) by setting $(\rho/2r) \rightarrow 1$. Using such a notch correction, measured K values for both specimens were reduced; results are given in Table II.

[1] J. C. Angus and C. C. Hayman, Science **241**, 913 (1988).
[2] M. D. Drory, C. F. Gardinier, and J. S. Speck, J. Am. Ceram. Soc. **74**, 3148 (1991).
[3] J. J. Mecholsky, *Proceedings of the 2nd International Conference on Diamond and Related Materials*, edited by M. Yoshikawa, M. Murakawa, Y. Tzeng, and W. A. Yarbrough (MYU, Tokyo, 1993), p. 199.
[4] J. F. Knott, *Fundamentals of Fracture Mechanics* (Butterworths, London, U.K., 1973).
[5] G. R. Anstis, P. Chantikul, B. R. Lawn, and D. B. Marshall, J. Am. Ceram. Soc. **64**, 533 (1981).
[6] C. B. Ponton and R. D. Rawlings, Mater. Sci. Technol. **5**, 865 (1989).
[7] ASTM Standard E-399 "Standard Test Method for Plane-Strain Fracture Toughness," *Annual Book of ASTM Standards* (American Society for Testing and Materials, Philadelphia, PA, 1993), Vol. 3.01, Sec. 3.
[8] J. C. Newman, Jr., "Stress Intensity Factors and Crack Opening Displacements for Round Compact Specimens," NASA Report TM 80174, NASA Langley Research Center (1979).
[9] C. J. Gilbert, J. M. McNaney, R. H. Dauskardt, and R. O. Ritchie, ASTM J. Test. Eval. **22**, 117 (1994).
[10] J. W. Ager and M. D. Drory, Phys. Rev. B **48**, 2601 (1993).
[11] *The Properties of Diamond*, edited by J. E. Field (Academic, New York, 1979).
[12] N. V. Novikov and S. N. Dub, J. Hard Mater. **2**, 3 (1991).
[13] *The Properties of Natural and Synthetic Diamond*, edited by J. E. Field (Academic, New York, 1992).
[14] D. M. Jassorwski, Aerojet TechSystems Final Report of Air Force Contract No. F04611-88-C-0074, August 1988, Aerojet TechSystems, Sacramento, CA.
[15] B. Cotterell and J. R. Rice, Int. J. Fract. **16**, 155 (1980).
[16] B. A. Bilby, G. E. Cardew, and I. C. Howard, in *Fracture 1977*, edited by D. M. R. Taplin (Pergamon, New York, 1977), Vol. 3, p. 197.
[17] M. L. Williams, J. Appl. Mech. **24**, 109 (1957).
[18] M. Creager and P. C. Paris, Int. J. Fract. Mech. **3**, 247 (1967).
[19] M. E. O'Hern, C. J. McHargue, R. E. Clausing, W. C. Oliver, and R. H. Parrish, in *Materials Research Society Extended Abstracts* (Materials Research Society, Pittsburgh, PA, 1989), EA-19, p. 131.