Mechanical properties of micro- and nanocrystalline diamond foils

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Diamond coating of suitable template materials and subsequent delamination allows for the manufacturing of free-standing diamond foil. The evolution of the microstructure can be influenced by secondary nucleation via control of process conditions in the hot-filament chemical vapour deposition process. Bending tests show extraordinarily high strength (more than 8 GPa), especially for diamond foils with nanocrystalline structure. A detailed fractographic analysis is conducted in order to correlate measured strength values with crack-initiating defects. The size of the failure causing flaw can vary from tens of micrometres to tens of nanometres, depending on the diamond foil microstructure as well as the loading conditions.

1. Introduction

For all crystalline materials, the medium binding strength of the atoms correlates directly with the mechanical strength. Because of this, crystalline diamond is the material with the highest theoretical strength. But, as for all brittle materials, the mechanical strength, especially under tension, is defined by the largest flaw in the body. The stress concentration at inner defects leads to local decohesion and initiates a crack with catastrophic failure at load magnitudes far below the theoretical strength. In many brittle (ceramic) materials, pores define the strength as, often, standard manufacturing processes via powder routes including densification techniques (e.g. cold pressing and sintering) are used. Also, the largest flaws originate from inclusions or scratches from surface preparation. In an ideally dense material, the grain size defines the largest flaw. To build up brittle materials with maximum mechanical strength a
preparation method on the atomic scale is necessary, allowing for careful bottom-up manufacturing of ‘atom on atom’. Hence, crystal growth at ideal lattice sites forms undisturbed crystals. Chemical vapour deposition (CVD) of diamond allows this step-wise formation of diamond crystal planes from gaseous carbon precursors (e.g. methane) without pores. By enhancing secondary nucleation during growth of the diamond crystals, it is possible to keep the grain size in the range of nanometres. In contrast to atomic layer deposition, diamond CVD allows growth rates faster than 0.1 \( \mu \text{m h}^{-1} \). In this way free-standing, stable foils with a surface of several thousand square centimetres are achievable in few days [1]. This article presents the exceptional mechanical properties of this novel diamond material under bending and tensile load. The correlation of flaw size and mechanical strength is described through fractographic analysis of fractured material. By varying CVD process parameters, such as methane content, gas and surface temperature and gas pressure, the shape of the grains, the ratio of sp\(^3\)- and sp\(^2\)-hybridized species at the grain boundary and the intrinsic stresses related to growth can be influenced. Further improvement of microstructure evolution control during growth of nanocrystalline diamond foils (NCDFs), therefore, poses the possibility for future increase of strength in the region of theoretical strength.

2. Manufacturing of diamond foil

Synthetic diamond can be produced in a low-pressure hydrogen/methane atmosphere by hot-filament CVD (HFCVD) [2–5]. Hydrogen molecules are split into H-radicals at resistively heated tungsten carbide filaments with temperatures of up to 2300°C. The reaction of these H-radicals with methane creates methane radicals in the gas phase. At the same time, surface bonds are activated by the reaction of H-radicals with H-saturated carbon of diamond nano seeds deposited prior to the coating process. Through attachment of methane radicals to the free bonds and removal of bonded hydrogen by H-radicals, diamond grows on the surface. It has to be noted that, under the conditions used, sp\(^3\)-hybridized carbon (i.e. diamond) is thermodynamically unstable and sp\(^2\)-hybridized phases (e.g. graphite) should be favoured. Nevertheless, the kinetic conditions stabilize sp\(^3\)-carbon and sp\(^2\)-carbon is etched by H-radicals preferably. As a result, a dense sp\(^3\)-diamond layer grows on the substrate.

Typical substrates for diamond coating are titanium, silicon, silicon carbide, tungsten or molybdenum. We could also show that diamond coating of steel is possible [6]. In all these systems, a good adherence of diamond coating to the substrate is crucial. For the production of self-supporting diamond foil, the opposite is the case, i.e. the deposited diamond layer is to be delaminated easily from a chosen template. The latter can be copper, as there is no stable copper carbide which could act as an adhesive interlayer, or silicon, which shows only slight adhesion. The process of producing diamond foil can be subdivided into four steps [7]. First, seeding of a template with diamond crystals in the range of nanometres suspended in ethanol by ultrasonication or dip-coating. Second, diamond coating by HFCVD. High methane content and low pressure lead to a high ratio of secondary nucleation and consequently to nanocrystalline diamond (NCD) growth [8] (figure 1a, showing the growth side (GS)). Low methane content and higher pressure lead to the growth of favourably orientated crystals resulting in microcrystalline diamond (figure 1b).

The third step is the delamination of the grown diamond layer from the substrate. This can be accomplished by a combined laser-cutting/ultrasonication process. As a result, a disc-shaped diamond foil with a diameter of up to 140 mm is obtained. The thickness depends on the coating time, e.g. in a 100 h process, a thickness of 40 \( \mu \text{m} \) is achieved. After delamination, the former nucleation side (i.e. substrate-facing surface; NS) can easily be accessed. Figure 2 shows the NS at two different magnifications. So-called supergrains can be seen, each being the result of the growth of a colony of crystals on a nanodiamond seed. Thus, supergrain size depends directly on seeding density. It has to be noted that no silicon carbide interlayer can be detected (e.g. by Raman spectroscopy) on the NS of the diamond foils.
Figure 1. Growth side (GS) of diamond foil produced under different process conditions. A high rate of secondary nucleation leads to a grain size in the range of nanometres (a). ‘Standard’ microcrystalline diamond with facet lengths in the range of micrometres (b).

Figure 2. (a,b) Nucleation side (NS) of diamond foil at two different magnifications. Colonies of crystals around the pre-treatment nanoseeds form so-called supergrains which are bordered by small trenches, the supergrain boundaries.

3. Experimental set-up

(a) Sample preparation

Prior to the deposition of diamond, smooth silicon templates were seeded in an ultrasonic bath containing a dispersion of ethanol and nanoscale diamond particles. The growth of NCD on the seeded templates took place in a commercial Cemecon CC800/9 hot-filament CVD plant. At a chamber pressure of 6 mbar, the gas flow of methane and hydrogen was set to 72 ml min$^{-1}$ and 2000 ml min$^{-1}$, respectively. The diamond coating was detached from the template by ultrasonic treatment. To cut samples for mechanical characterization, a Rofin SMP065 Nd:YAG solid-state laser was used. This method provides for precise cuts and smooth edges. Samples were shaped as shown in figure 3, and are described more precisely later. A detailed description of the sample preparation is also given in [9,10].

(b) Tensile test

For the determination of tensile strength and Young’s modulus (YM), dog-bone-shaped samples were used (figure 3a). They feature a special design of the region between the gauge length and shoulders of the sample. Instead of a radius, a Bézier curve was used to describe it. In this way, the stress concentration in such an area can be reduced, which leads to less fracture outside the gauge length [11]. The thickness of the samples was $87 \pm 2 \mu$m.
Figure 3. Geometry of samples with dimensions in millimetres. (a) Dog-bone-shaped samples for tensile testing; black squares on the sample’s contour are the control points of the Bézier curve. (b) Double-edge notched samples to measure fracture toughness and (c) round samples for B3B bending.

The tensile load was applied with a Kammrath & Weiss tensile/compression stage, using a 500 N load cell and a displacement speed of 0.1 \( \mu \text{m} \text{s}^{-1} \). The sample was attached in a specially designed specimen holder with cyanoacrylate adhesive (figure 4). A slot in the specimen holder provides for correct alignment. Friction between gauge length and slot was avoided by milling the respective areas. Strain measurement was realized by digital image correlation (DIC). This is a contactless method based on tracking the changes in appearance of a randomly structured sample surface during deformation [12]. For this purpose, 8-bit grey tone images of the naturally structured GS of the sample were taken with an imaging system. The latter consists of a Wild 420 macroscope with a magnification of 32 and a Leica camera with a resolution of 1944 \( \times \) 2592 pixels. Subsequently, the displacement was calculated by employing cross-correlation and a sub-pixel algorithm provided by the software VEDDAC.

From the slope of the linear relationship between displacement and the position of the details on the sample’s surface, the strain can be derived. A set of 30 samples was tested in order to interpret the strength according to Weibull statistics (DIN EN 843-5). In this way, the statistical distribution of strength in ceramic material depending on the flaw size in the tested volume can be captured. The probability of failure \( P \) is a function of the fracture strength \( \sigma_f \), the characteristic strength \( \sigma_0 \) and the Weibull modulus \( m \) (equation (3.1)). To accurately determine \( \sigma_0 \) and \( m \), the maximum-likelihood method was used. To plot the data in a Weibull diagram, a rank estimation function \( P_{Fi} = (i - 0.5)/N \) was used. There the total number of \( N \) samples in the set is arranged in ascending order and given a rank \( i \).

\[
P(\sigma_f) = 1 - \exp \left[ - \left( \frac{\sigma_f}{\sigma_0} \right)^m \right]. \quad (3.1)
\]

(c) Fracture toughness

According to Griffith [13], the fracture toughness \( K_{lc} \) of a material can be determined by breaking a sample on a defined sharp notch. Then \( K_{lc} \) is a function of the fracture strength \( \sigma_F \), the notch length \( a \) and a geometric term \( Y \):

\[
K_{lc} = \sigma_F \sqrt{\pi a} \cdot Y. \quad (3.2)
\]

Here rectangular double-edge notched samples with a thickness of 86 ± 4 \( \mu \text{m} \) were used (figure 3b). The laser-cut notches were 160 \( \mu \text{m} \) in length and had radius between 14 and 35 \( \mu \text{m} \). Therefore, \( Y \) is 1.0084 ± 0.0078. It has to be noted that the NCDF used for the fracture toughness
test originated from a silicon template with a slightly rougher surface than the NCDF for the tensile and bending tests. This is not assumed to influence the result because the notches (and the stress concentration accordingly) are much larger than the surface roughness. For the determination of the fracture toughness, the same test stage and parameters as for the tensile tests were used.

(d) Ball-on-three-balls bending strength

The ball-on-three-balls (B3B) bending test [14,15] was conducted in an Instron 5565 testing machine using a 500 N load cell and feed rate of 0.05 mm min\(^{-1}\). The disc-shaped sample with radius \(R_D = 4.8\) mm (figure 3c) is supported by three touching 100Cr6 balls while the load \(F\) is transferred via a single ball, which pushes onto the sample from the other side. To hold the samples in place a preload was applied prior to testing. After failure, the thickness \(t\) of each sample was determined with an accuracy of \(\pm 1\) \(\mu\)m. The maximum stress occurs in the centre of the sample surface on the opposite side of the loading ball. The stress \(\sigma_f\) can be calculated by equation (3.3). The stress also depends on a geometric parameter \(\alpha\) and Poisson’s ratio \(\nu\). Values of \(\alpha = 0.2\) [16] and \(\nu = 0.0691\) [17] were reported by other authors.

\[
\sigma_f \equiv \frac{3F(1+\nu)}{4\pi t^2} \left\{ 2\ln \left( \frac{R}{\alpha t} \right) + \frac{1 - \nu}{1 + \nu} \left( \frac{R}{R_D} \right)^2 \right\}. \tag{3.3}
\]

4. Results

(a) Tensile test

Figure 5 illustrates the displacement of the sample surface for two different stress states. For higher stresses, the curve is steeper, corresponding to a higher strain. The sample is stressed evenly, as can be seen from the linear curve and the displacement occurring parallel to the direction of load.
Figure 5. Diagram showing that the displacement of surface details in NCDF, detected by DIC, is a linear function of their position on the sample. At higher loads the slope (i.e. the strain) increases. (Online version in colour.)

Figure 6. Typical stress–strain diagram for NCDF: YM corresponds to the slope of the linear data.

For linear elastic materials, such as diamond, YM equals the slope of the material's stress–strain curve. Figure 6 illustrates a typical stress–strain curve for NCDF. From the linear data, YM was found to be $621 \pm 88$ GPa. This unexpectedly low value for a diamond material (cf. [18]) could be confirmed by mechanical resonance testing using longitudinal oscillations ($560 \pm 5$ GPa).

The distribution of the fracture strength is shown in a Weibull plot in figure 7. The fracture probability of the data points was determined by a rank estimation function while the line was calculated by the maximum likelihood method. The latter was used to determine $\sigma_0 = 536$ MPa, the stress at which $63.2\%$ of the samples fail, and $m = 3.39$, the slope of the data. One-third of the samples (grey triangles) fractured within the gauge length due to the improved design of the samples. The rest of the samples broke just outside the gauge length. As their values do not deviate from the ones inside the gauge length, they were also considered for the statistical evaluation.
Fracture toughness

For NCDF, a fracture toughness of $5.2 \pm 1.0 \text{ MPa m}^{1/2}$ was measured. Since the laser-cut notches cannot be considered sharp on an atomic scale this value has to be adjusted by a factor of $2/3$ [19,20]. After this conservative correction, the fracture toughness for NCDF averages $3.5 \pm 0.7 \text{ MPa m}^{1/2}$. Other authors have found a value of $6.9 \text{ MPa m}^{1/2}$ for micro-scaled ultrananocrystalline diamond samples [21]. In figure 8, a crack that propagated between the two notches can be seen. This demonstrates that the notch geometry is capable of causing fracture between the notches.

(c) Ball-on-three-balls bending test

A very easy method to verify the B3B test is an optical analysis of the fracture pattern of the broken samples. As shown in figure 9, the number of fragments is supposed to rise with increasing fracture strength due to the higher amount of stored elastic energy. Furthermore, a valid test requires crack initiation right in the centre of the sample, where the highest load occurs.

Figure 10a shows a Weibull plot of the measured fracture strength of NCDF for both the NS as well as the GS. The GS is slightly stronger (approx. 5.5 GPa versus 5.2 GPa) than the seeding side. This is true also for the Weibull modulus (12.0 versus 7.4). This can be explained by the
Figure 9. Fractured NCDF samples, arranged in order of fracture strength. Higher fracture strength results in a higher number of fragments owing to the release of more elastically stored energy.

Figure 10. Weibull plots of B3B bending strength of nanocrystalline (a) and microcrystalline (b) diamond foil, both loaded on the GS (filled data points) as well as the NS (open data points). The NCDF shows quite similar strengths for both sides, whereas the microcrystalline diamond foil is much weaker on the GS but much stronger on the NS. The latter can be explained by the fact that optimization of pre-treatment in (b) leads to a higher seeding density than for the NCDF shown in (a) and fewer particle residues (cf. figure 13).

In figure 11, the outstanding strength of NCDF is shown in comparison with conventional ceramic foils of the same size. A Weibull modulus of 10 is depicted by a dashed line as it is usually the prerequisite for technical use. A strength of up to 8 GPa can be reached with NCDF, more than four times that of yttrium-stabilized zirconium oxide and more than eight times that of aluminium oxide. Based on those results, NCDF can be seen as the strongest ceramic foil material of the world.

5. Correlation of structure and properties

Figure 12 shows YM of different carbon materials versus density, according to [22]. The measured YM of NCDF follows the given trend nicely. This means that a carbon material with a density magnitude of the structure sizes, which is very similar on the NS and on the GS of NCDF. Larger microcrystalline crystals are therefore expected to show less strength, which is proven by figure 10b. The coarse GS of microcrystalline diamond foil only shows a strength of approximately 2.7 GPa with a Weibull modulus of 9.8. The very high strength of the seeding face, which even exceeds the strength of NCDF, is due to the improved seeding procedure used for the samples shown, leading to very small supergrains on the NS. The homogeneous distribution of the latter is also demonstrated by the high Weibull modulus of 14.7.

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Figure 11. Fracture strength of NCDF in comparison with conventional ceramic foils. Both Weibull modulus and strength of NCDF exceed the strength of conventional foils by far.

Figure 12. Comparison of YM versus density for different carbon materials. NCDF fits in nicely, which proves, that a dense diamond material with expected stiffness has been produced.

of NCDF is expected to have YM in the range of 600 GPa, proving that the manufactured NCDF does not inhibit porosity or any other kind of internal defects that could reduce the mechanical coherence.

Even more interesting is the correlation of the fracture properties with the internal structure. First of all, the tensile strength is much lower than the measured bending strength. This can be explained by the bigger loaded volume. The nucleating procedure, where nanodiamond seeds are set on the template surface, is conducted under technical conditions, i.e. not under a clean room atmosphere. Thus, contamination of the template surface with atmospheric particles cannot be avoided completely. Furthermore, some of the pre-treatment dispersions that were used contain silicon carbide particles for highly efficient seed adherence. Both of the mentioned particle types
can be incorporated into the diamond foils, as shown in figure 13. On the opposite side of the particle defect, a bump on the surface can be seen. Owing to the high loaded volume in tensile testing, fracture initiation at those defects is certain. Large samples therefore exhibit fracture at large particle defects and thus reduced strength. The striations in the cross section of the diamond foil result from a multi-layer diamond structure, generated by varying the CVD-process parameters.

In B3B testing, the loaded volume and thus the probability for a particle defect to be tested is lower. Fracture initiation has to occur at diamond growth structures. On the GS, fracture occurs along the grain boundaries between crystals, therefore the growth structures at which failure occurs are the grains themselves (figure 14a,b). This explains the higher strength of NCDF in comparison with microcrystalline diamond foil. By contrast, the strength of the NS is less dependent on the growth conditions and therefore it is similar for micro-crystalline diamond foil and NCDF. Here, the supergrain boundaries act as the crack origin (figure 14c).

In figure 15, the correlations discussed above have been combined. In this figure, measured strength values are used to estimate the necessary initial crack length required for failure by applying the Griffith criterion. The result supports the fractographic analysis. Particle defects show an initial crack length of 10–30 µm, which corresponds to the size of silicon carbide particles identified as crack initiating. The strength of microcrystalline diamond foil yields crack lengths in the range of a micrometre, which is in good accordance with micrometre-sized crystals. Finally, the fracture origin on both nano- and microcrystalline diamond foils’ NSs and on nanocrystalline
diamond foils’ GSs deliver the smallest initial crack length of some hundreds of nanometres, which is a typical magnitude of the respective surface structures.

6. Conclusion

We present the fabrication of free-standing crystalline diamond foils as novel diamond wrought material with, for example, 150 cm² and 50 µm thickness with an upscaled hot-filament CVD thin-film technology. The use of short pulsed laser ablation enables reproducible manufacturing of a large number of millimetre- to centimetre-sized samples, which is necessary for mechanical testing of this brittle material with statistical evidence. B3B bending testing and micro-tensile testing were evaluated as feasible methods for mechanical characterization of diamond foil. The YM equals the expected stiffness of a diamond material with this density. Bending tests show that, on the GS under tensile load, the nanocrystalline foils exhibit higher strength than the microcrystalline ones. On the seeding side, no difference in strength occurs, as grain size is similar for both types of diamond foil. Rather, the bending strength depends on the seeding density and particle residues. Owing to the higher tested volume in tensile tests, tensile strength is much lower than bending strength. By fractographic analyses, we could correlate the mechanical values with defects and grain size in this ideally brittle diamond material. A defect-free NCDF shows extreme strength. Owing to the high binding forces, diamond foils are the strongest ceramic material that is available in the world. We hope that by further improvement of the growth process the defects in the foils can be further minimized and the excellent mechanical properties of the diamond foils can find new industrial application, e.g. as ultimate erosion protection.

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