Diamond chemical vapour deposition on seeded cemented tungsten carbide substrates

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Abstract

Diamond particles were deposited onto seeded cemented tungsten carbide (WC–Co) substrates using conventional hot-filament chemical vapour deposition (HFCVD) and time-modulated CVD (TMCVD) processes. The substrates were pre-seeded ultrasonically with diamond particles of different grit sizes. In this investigation, we employ timed methane (CH$_4$) gas modulations, which are an integral part of our TMCVD process in order to enhance diamond nucleation density. During diamond deposition using the conventional HFCVD process, methane gas flow was maintained constant. The total hydrogen flow into the reactor during TMCVD process was higher than in the HFCVD process. Hydrogen etching can be expectedly more prominent in the TMCVD process than in HFCVD of diamond particles. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) results showed that a proper selection of the diamond grit size for seeding using ultrasound can lead to enhancement in the nucleation density values of about two orders of magnitude ($10^7$ to $10^9$ cm$^{-2}$). The TMCVD process using the different seeded substrates can result in high nucleation density values of up to $10^{10}$ cm$^{-2}$.

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1. Introduction

One of the continuing challenges facing CVD diamond films on WC–Co substrates is to obtain smooth and adherent diamond coatings. There is on-going research and development in attempting to improve the coating performance. It is well known that, in CVD process, discrete particles of diamond crystals sparsely appear on the substrate during the early stages of CVD diamond deposition and coalesce subsequently to form a continuous film. The nucleation density of diamond particles plays an important role in defining the adhesive properties of the resulting films [1,2]. The presence of cobalt binder in WC–Co is problematic in diamond deposition since it solubilise carbon at high temperatures and catalyses the formation of graphite in the conditions typical for diamond growth. The high carbon solubility and diffusivity in cobalt retard diamond nucleation. This induces nucleation from graphite instead of tungsten carbide and results in a poor adherence. Thus, the success in obtaining good adherence and high diamond nucleation depends on the ability to suppress carbon–cobalt interactions. A number of surface treatments can be used to overcome these interactions including chemical etching, ion implantation, interface coating and bias treatment. Among these the widely used method is chemical etching [2–4]. Peters and Cummings [5] introduced a widely recognized two step etching procedure with effectiveness in improving the overall coating adhesion.

The most commonly used method to enhance nucleation on non-diamond substrates is by damaging the surface of the substrate either mechanically (polishing) or by ultrasound abrasion using diamond or other abrasives [6–8]. Ihara et al. [9] correlated the diamond nucleation density to the amount of diamond dust (seed) left on the substrate surface after prolonged ultrasonication in a diamond powder suspension. They noticed changes in the nucleation density values from $10^6$ to $10^{10}$ nuclei cm$^{-2}$ on mirror polished silicon substrates treated in various suspensions consisting of different sized diamond abrasive particles.

In this paper, we ultrasonically seed WC–Co substrates with different sized diamond particles and subsequently use TMCVD and HFCVD processes to deposit diamond particles onto their surfaces. The current investigation will correlate the as-obtained nucleation densities, using TMCVD and HFCVD processes, with the size of the diamond particles used for
seeded. The quality of the diamond particles deposited will be assessed using Raman spectroscopy. Finally, we discuss our findings in relation to the type of CVD process used to produce the diamond deposits.

2. Experimental

2.1. Substrate pre-treatment

The WC–Co samples used in this investigation were of commercial grade, as supplied by Palbit (Portugal) and consisted of 6-wt.% cobalt content with an average WC grain size of 6 μm. The samples were cylindrically shaped and were ground using D126/C75 and D20/C75 diamond wheels in order to obtain final dimensions of 6 ± 0.05 mm diameter and 0.4 ± 0.05 mm height. To remove the defects induced during grinding, the sample heights were reduced 0.03 ± 0.01 mm by mechanical polishing using diamond paste of 7 and 3 μm. After polishing, the samples were ultrasonically cleaned in pure acetone for 5 min. The substrates were chemically etched with Murakami’s solution (10 g K3(Fe(CN)6) + 10 g KOH + 100 ml H2O) for 6 min at room temperature in ultrasounds followed by a rinse in de-ionised water. Subsequently, the surface cobalt was removed by acid treatment (1 ml 46-wt.% HNO3 + 9 ml 30% m/v H2O2) for 10 s, followed by a rinse in de-ionised water.

Prior to diamond deposition, the samples were ultrasonically abraded for 20 min in diamond suspension. The suspensions were prepared using three different grit sizes, of commercial diamond; (i) <0.25 μm, (ii) 3–5 μm and (iii) 30–50 μm. In all cases, 1 carat of diamond powder was mixed with 20 ml of pure methanol. Table 1 gives details of the substrates, surface pre-treatment, and the CVD process employed to produce the diamond deposits.

2.2. HFCVD and TMCVD processes

Diamond deposition was carried out in a custom built stainless steel HFCVD system. Deposition pressure and filament power values were set to 5 kPa and 200 W per filament, respectively. The substrate surface temperature was measured using a K-type thermocouple, which was located directly underneath and touching the bottom of the substrate during deposition. In the HFCVD process, the substrate temperature was 700 ± 8 °C whereas in TMCVD, the substrate temperature was in the range 680 ± 5 to 700 ± 8 °C. The temperature fluctuation in TMCVD was due to the timed CH4 modulations with respect to deposition time. In HFCVD process, the total gas flow was kept constant at 200 sccm. The CH4/H2 volume ratio was fixed at 1% as per calculation from Eq. (1), where \( t, n \) and \( A \) represents the time of the modulation, the number of modulation in deposition cycle and the total amount of CH4 in each modulation, respectively. The indices 1 and 2 refer to the high and low volume of CH4 in the cycle in accordance with the graphical representation shown in Fig. 1. In both cases, the deposition time was set to 32 min. For each condition, the tests were carried out twice in order to check the reproducibility and repeatability of the results.

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CH_4 = \frac{t_1 n_1 A_1 + t_2 n_1 A_1}{n_1 t_1 + n_2 t_2}
\]

2.3. Characterization techniques

Surface morphology of the as-grown diamond deposits was characterized by scanning electron microscopy (SEM/EDS, Hitachi 4100) and atomic force microscope (AFM: Nanoscope03-Digital Instrument). The nucleation density values were determined by digitalizing SEM images (total area of 46 μm² each at three different locations) using AUTOCAD software. The quality of diamond nuclei was assessed by Raman spectroscopy at room temperature using a ISA JOBIN YVON-SPEX T6400 spectrometer equipped with an argon ion laser (λ = 514.5 nm). The data was smoothened and then fitted

![Fig. 1. The flow of CH4/H2 gas used during diamond deposition using the HFCVD and TMCVD processes.](image-url)

3. Results and discussion

3.1. Chemical pre-treatments

The average substrate surface roughness ($R_a$) was measured using a surface profilometer (Hommel Tester T1000 profilometer). After Murakami’s and acid etching pre-treatments the surface roughness was found to be $0.07 \pm 0.01 \mu m$. Fig. 2a) shows the SEM image of the roughened surface after etching the sample by Murakami’s reagent for 6 min. The presence of intergranular cobalt is apparent from the SEM image. The presence of cobalt was evident in EDS microanalysis since it was not attacked by the alkaline solution of potassium ferricyanide. Fig. 2b) shows the surface morphology of the same sample after 10 s etching with acid, $HNO_3 + H_2O_2$ solution. This extended acid treatment dissolves any binder residues remaining behind after Murakami’s etching.

3.2. Diamond seeding

SEM results showed very good seeding uniformity in the substrates and high reproducibility. From Fig. 3a) it is evident that residual diamond particles with sizes between 8 and 40 nm cover the WC grains. The decrease in the number of seeding sites with larger sized diamond particles was apparent from SEM examinations (see Fig. 3b). It is expected that smaller sized diamond particles are likely to get trapped and become embedded in the WC–Co substrate cavities, whereas, for larger sized particles the process of particle entrapment in the cavities is more difficult. Therefore, by using smaller sized powders, this will result in the seeding of greater number small sized particles compared to larger powder sizes, which are the active sites for subsequent diamond nucleation using CVD.

The correlation between the as-obtained diamond nucleation densities and the diamond grit size used during ultrasonic seeding is shown in Fig. 4. Under our standard experimental conditions, the diamond nucleation density for $0.25 \mu m$ was more than two orders of magnitude higher than for $30 – 50 \mu m$ size diamond powder. The comparison of nucleation density values attained by the two CVD processes are shown in Fig. 5a and b. Using $0.25 \mu m$ size diamond powder in seeding the WC–Co substrates, we observed an increase in the nucleation density from $\sim 4 \times 10^6$ to $1.5 \times 10^{10}$ which is approximately an order of magnitude. Detailed SEM studies showed that with TMCVD the grain size distribution of the diamond nuclei was more homogeneous, the grains were in the nano-range and the deposits displayed better substrate surface area coverage. This is in agreement with our earlier reports [11,13,14], which demonstrated that the TMCVD process promoted secondary diamond nucleation during the timed methane modulations. It is remarkable, the high uniformity and reproducibility is obtained in all the samples, as can be seen at low magnification micrographs, Fig. 5c and d. Both SEM (Fig. 5a) and AFM (Fig. 6a and b) micrographs show the formation of diamond grains of size ranging from 50 to 110 nm. The size distribution of the particles produced by the TMCVD process, as shown in Fig. 7 suggests a Gaussian distribution with an average crystal size of 82.5 nm. Similar distribution was found for the HFCVD process, which produced diamond particles with an average...
size of 110.5 nm. From these observations, it is indicative that the rate of crystal growth on the diamond seeds is practically almost the same, which is in some agreement with the kinetic model proposed by Molinari et al. [15].

Several researchers [16–18] reported that in HFCVD reactors, an additional source of hydrogen due to the heterogeneous dissociations of H2 on the filament is also included along with the experimentally observed H-atom [19] concentration. When the level of carbon in the gas phase becomes greater than a critical value, depending on the filament temperature, deposition of carbon onto the filament occurs. This deposition is commonly referred to as filament “poisoning” or “sooting”. Filament poisoning results in a reduced ability to transform H2 to H-atom [17,21,22]. A subsequent decrease in the substrate temperature arising from the increased methane concentration is the result of the lower level of H-atom production in the HFCVD reactor [23].

It is known that atomic hydrogen etches both diamond and graphite; however, under typical CVD diamond deposition conditions, the rate of diamond growth exceeds the etch rate whilst for other forms of carbon, such as graphite the case is reverse. In our case, we explain our findings by giving two hypothesis. First, during the high timed methane modulations in TMCVD, the relative monohydrogen concentration in the reactor is relatively (to HFCVD) lower, therefore, less hydrogen etching of the diamond seeds can be expected. In our case, we propose that as the hydrogen etches the seeds, thus reducing the surface density of diamond growth centres. We hypothesise that less of the seeds will be etched out during TMCVD compared to HFCVD of diamond deposits. In HFCVD process, the hydrogen concentration in the reactor is constant and the overall H-concentration is higher than in the TMCVD process. Therefore, more of the seeds are expectedly etched out leaving behind inactive sites for any possible diamond growth by CVD. Our SEM results showed that after the HFCVD and TMCVD processes, the density of the diamond seeds on the WC grains, as was clearly observed after ultrasonic seeding and prior to diamond deposition (see Fig. 3), had decreased significantly. We postulate by attributing the disappearance of these seeds to the hydrogen etching effect during diamond CVD.

Second, we can also expect some heterogeneous nucleation taking place in correspondence of surface defects or sites produced by the impacts of diamond particles during the seeding treatment. The larger CH4 concentration pulse would favour a more abundant heterogeneous nucleation process [24]. Therefore, we expect the heterogeneous nucleation rate to be higher in TMCVD than in the HFCVD process, mainly due to

![Graph showing the relationship between diamond nucleation densities and the size of diamond particles used for seeding for both HFCVD and TMCVD processes.](image)

![SEM images showing the diamond deposits formed on the surfaces of the WC-Co substrates using HFCVD (panels a and c) and TMCVD (panels b and d) processes.](image)
the utilisation of high/low timed methane gas flow cycles during deposition.

Secondary nucleation could also take place on defects on the surface of growing diamond crystallites. Again, we speculate that in this case the high methane bursts in TMCVD could have potentially increased the overall surface density of growing diamond crystals.

3.3. Raman analysis

Fig. 8 shows the Raman spectra of diamond deposits produced on seeded WC–Co substrates with diamond powder using TMCVD (a) and HFCVD (b) processes. In this case, the diamond powder size used for pre-seeding the substrates was 0.25 μm in size. Besides the diamond peak (1334 cm⁻¹), five other main components contributed from the carbonaceous
Raman background were noticed. A band centred around 1140 cm$^{-1}$ assigned to transpolyacetylene lying at the grain boundaries [24], a band around 1490 m$^{-1}$ from diamond precursors [25], the band around 1250 cm$^{-1}$ is generally accepted as arising from scattering in diamond, due to relaxation of the wave vector selection rule [26] and two broad bands at 1350 and 1580 cm$^{-1}$, attributed to D- and G-bands of graphite [27]. The full width at half maximum (FWHM) values for the Raman diamond lines were 8.0 for both the samples shown in Fig. 8. The variation in the FWHM values reflects the amount of disorder and defect densities [28]. The constant FWHM shows the uniformity in the crystallite size of diamond particles found in the TMCVD and HFCVD deposits. The data also confirm our previous findings, i.e., that the Raman quality of the diamond grown by TMCVD is only slightly lower than that obtained by conventional HFCVD.

4. Conclusions

Substrate pre-treatments and deposition conditions strongly influence the nucleation behaviour of diamond deposited onto seeded cemented WC–Co substrates. The size of the diamond seeding powder proved to be an influential factor in governing the diamond nucleation density.

The diamond deposits produced using conventional HFCVD or TMCVD process were of similar Raman quality, in terms of both crystallite size and carbon phase purity.

However, the TMCVD process enabled the enhancement of diamond nucleation density by about one order of magnitude compared to the HFCVD process.

We explained our findings by proposing that the larger time-averaged CH$_4$ concentration in the TMCVD process could have reduced the H-etching of diamond seeds, and enhanced both the heterogeneous and secondary nucleation processes.

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