Enhanced Growth Rate of Chemical Vapor Deposition Diamond Coating Motivated by Graphene Oxide

Fan Zhou 1, Naichao Chen 1,2,* and Fasong Ju 1

1 School Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, China; ZhouFan@mail.shiep.edu.cn (F.Z.); jusong9527@mail.shiep.edu.cn (F.J.)
2 Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai 200090, China
* Correspondence: chennaichao@shiep.edu.cn

Abstract: To improve the growth rate of chemical vapor deposition (CVD) diamond coating, increasing the chemical reaction rate is essential. A novel method of dispersing graphene oxide (GO) particles as adsorbent on the substrate prior to deposition was proposed, with which the diamond coating with large grain size and high thickness was deposited on the silicon nitride under the normal CVD environment. The as-deposited diamond coating was characterized by scanning electron microscopy (SEM), surface profilometer, atomic force microscope (AFM), Raman spectrum, and indentation. The surface morphologies showed that the GO particles were covered by a layer of diamond coating. The diamond coating without and with GO particles had growth rates of 1.10–1.38 and 1.50–2.94 \( \mu \text{m h}^{-1} \), respectively. No differences in the Raman spectra of the microcrystalline diamond (MCD) coatings without and with GO particles were found. Indentation tests suggested that GO particles could enhance the adhesive strength and the crack resistance of diamond coating, which may result from the large thickness and the strong adsorbed capacity of destructive energy. Hence, dispersing particles on the substrate can be regarded as a potential and alternative technique by accelerating the CVD chemical reaction to obtain desired diamond coating.

Keywords: diamond; graphene oxide; chemical vapor deposition; growth rate

1. Introduction

Chemical vapor deposition (CVD) diamond coatings have attracted intensive interest from scholars and engineers due to their remarkable properties, such as high hardness, great wear resistance and high thermal conductivity [1–3]. In the past decade, numerous experimental and theoretical studies were conducted to improve the properties of CVD diamond coating [4,5]. Among them, the growth rate has been considered as a greatly important deposition parameter because it plays a significant role in determining the production efficiency and the cost of CVD diamond coating [6,7].

It is well known that the mixture of carbon source and hydrogen gas is the main reactant gas of CVD diamond coating deposition [8,9]. Hence, the substrate must possess the hydrocarbon adsorption capability, which can be regarded as the first step of generating diamond grains [10]. Meanwhile, the surface area of substrate is closely associated with the total number of adsorbed hydrocarbon functional groups that considerably influences the chemical growth rate of diamond coating. In this way, rough pretreatments for substrate becomes a convenient and effective approach to accelerate the diamond nucleation [11]. On the other hand, plasma pretreatment, which can form some active sites on the substrate, has been demonstrated as an effective approach for the diamond nucleation [9,12]. Apparently, the above-reported methods changed the adsorption process between the substrate and hydrocarbon radicals, which affects the growth rate of CVD diamond coating [13]. However, the adsorption capacity is the intrinsic property of the substrate, which is hard to be modified by physical pretreatments. For the chemical point of view, increasing the active
sites by distributing a suitable adsorbent on the substrate might be feasible to improve diamond growth rate owing to easily capturing the more hydrocarbon radicals [14].

Recently, Wang et al. [15] reported that graphene oxide (GO) exhibited a strong adsorption capacity for hydrocarbon radicals. GO had rich surface chemistry activity and large aspect ratio which are favorable for adsorbing organic matters [16]. In this work, GO particles were selected as the examined adsorbent to study the effect on the growth rate of the diamond coating. The as-deposited diamond coating was characterized by scanning electron microscopy (SEM), surface profilometer, atomic force microscope (AFM), Raman spectrum and indentation. Meanwhile, the pure diamond coating was also fabricated for comparison.

2. Materials and Methods

In this work, silicon nitride flat square plane with $10 \times 10 \text{mm}^2$ was selected as the substrate to fabricate diamond coating, which was the same as our previous work [17–19]. Prior to distributing the GO particles, all the substrates were submitted to a three-step pretreatment: (i) polishing by abrasive paper combining with diamond particles slurry for 20 min to roughen the surface; (ii) rinsing with deionized water in the ultrasonic vessel for 10 min; (iii) immersing into high-purity acetone ultrasonically cleaned for 20 min to remove the native impurities on the surface.

A very important pretreatment was to distribute GO (5 $\mu$m, JiangNan Graphene Inst., Changzhou, China) on the cleaned substrate surface. Nanoparticles were easily aggregated because of small grain size and large specific surface area [20]. Here, wet dispersion, as a useful way to eliminate particle aggregation, was conducted to distribute GO particles on the substrate surface. Firstly, GO particles (weight 0.1 g) were dispersed in ethyl alcohol (100 mL) by ultrasonication to prepare a homogeneous suspension. Then, this mixture solution was dripped on the substrate surface to cover the whole surface. Finally, the sample was placed into a drying oven to remove the ethyl alcohol. In this way, the GO particles would uniformly settle down on the substrate surface in the desired proportionate manner achieved by controlling the concentration of GO particles, which was also favorable for the mass production because of the operability and the uniformity.

The diamond deposition was fabricated by conventional hot filament CVD technology. An acetone–$\text{H}_2$ gas mixture was used as the reactant gas to deposit the diamond coating. Four parallel tantalum wires as hot filaments were tightened by springs to provide a constant distance of 20 mm between filaments and substrate. The filament temperature during deposition was 2000–2200 $^\circ\text{C}$, and the substrate surface was maintained at about 800–900 $^\circ\text{C}$. The concentrations of acetone and $\text{H}_2$ were set as 90 and 240 sccm, respectively. The deposition process was divided into nucleation and growth stages. The nucleation time was set to 40 min, and the growth time was 4 h. Their reaction pressures was 1.5–2.0 kPa and 4.0–5.0 kPa respectively. In order to verify the effect of GO particles on the diamond coating, the pure diamond coatings without GO particles were deposited for comparison.

The surface morphologies of diamond coatings at different nucleation time were characterized by SEM (Hitachi Ltd., Tokyo, Japan) to explore the influence of GO particles on the diamond growth. The diamond quality was analyzed by Raman spectra (Horiba Jobin Yvon Ltd., Paris, France), using an $\text{Ar}^+$ laser with an excitation wavelength of 532 nm.

A Rockwell indentation test was conducted to evaluate the adhesive strength of as-deposited diamond coating by analyzing the indentation scars. A standard diamond indenter with a cone angle of 120 degrees was used to penetrate the diamond coating. Here, two indentation loads of 200 and 300 N were applied to obtain the indenting behaviors of the diamond coating. The morphologies of indentation were characterized by SEM image to evaluate the level of fracture.
3. Results and Discussion

3.1. Characterization of Diamond Coating

Prior to the deposition, GO particles underwent the heating treatment to verify whether they would decompose themselves at the temperate of 800–900 °C for 4 h in the CVD deposition process or not. Figure 1 shows that the GO particles can survive under the CVD deposition environment. Hence, GO particles can be used as the examined adsorbent that will be distributed on the substrate to deposit the CVD diamond coating.

Figure 1. SEM image of GO particles after 800–900 °C for 4 h under CVD deposition environment.

Figure 2 shows the surface morphology of substrate with GO particles after wet dispersion. As can be seen, the GO particles were distributed on the surface. Although a few particles aggregated together or were closed to each other, many particles had been separated with different intervals. This would be useful to obtain the uniform material properties of the as-deposited diamond coating.

Figure 2. SEM surface morphology of the substrate with GO particles.

With the purpose of exploring the effect of GO particles on the nucleation of diamond grain, the surface morphologies of substrate at the different nucleation time (10, 20, 40 min) were observed, as shown in Figure 3. The substrates with and without GO particles were partially covered by many tiny granular diamond crystallites after 10 min, which was
also reported previously [14]. The nucleation density of diamond nuclei was estimated by calculating the total number of particles in the known substrate area. The average nucleation density of diamond coating with GO particles was $6.82 \times 10^8$ /cm$^2$, while the nucleation density of pure diamond coating was $4.41 \times 10^8$ /cm$^2$. The substrate with GO particles had the more number and larger size of diamond grains than the pure substrate, indicating that the GO particles facilitated the diamond growth. After 20 min, a layer of diamond coating was covered on the substrate. Since the short nucleation time cannot offer the enough time to form an integrated diamond coating, some holes presented inside the diamond coatings with and without GO particles. In addition, many branch-shape grains generated on the diamond coating with GO particles, which was not observed on that with GO particles. With the increase of the nucleation time, both substrates with and without GO particles were covered by the diamond coating after 40 min, and the GO particles were fully embedded inside the diamond coating. Hence, the conclusion can be drawn that the certain number of GO particles on the substrate did not restrain the CVD diamond growth; and the diamond coating was capable to cover these GO particles. Thus, these particles will be embedded at the interface between diamond coating and substrate, which can be regarded as a discontinuous interlayer.

In this work, the reproducible CVD diamond fabrication experiments were conducted to avoid the occasional case that would mislead the evaluation of the intrinsic material properties of the diamond coating with GO particles. The corresponding diamond coatings were produced three times using the same deposition parameters. Meanwhile, the substrate with and without GO particles were put together in the chemical reaction chamber to deposit the diamond coatings for each time with aims of maintaining the absolutely same CVD conditions. Figure 4 shows the surface morphologies of the as-deposited diamond coatings with and without GO particles after the growth time of 4 h. Both substrates were covered by well-faceted and columnar diamond crystalline grains at microsized level, which was a typical feature of MCD coating. It can be seen from the figures that the MCD coating with GO particles had the similar topographic properties as the pure MCD coating. All the surface morphologies demonstrated the good reproducibility for depositing the diamond coating with GO particles. In addition, all the MCD coatings with GO particles exhibited the larger diamond grains than the pure MCD coatings, which may attribute the strong chemical activity of GO surface for the hydrocarbon functional groups to the increase of the CVD diamond growth. Furthermore, the cross-sectional images, as shown in Figure 5, were also obtained to explore the growth rate of diamond coating by the thickness of coating. It can be found that the thicknesses were about 5.50, 4.5 and 4.4 µm for the three pure MCD coatings, respectively. For the MCD coatings with GO particles, the corresponding thicknesses were about 11.75, 6.4 and 6 µm. Although the growth conditions were supposed to remain constant, the variation of thicknesses for the diamond coatings with and without GO particles implied the complex influence of GO particles on the diamond growth, since the thickness also might depend mostly on process parameters. In this work, we did not focus on the further investigation of the effect of the coupling relationship between GO particles and process parameters on the diamond growth. This task will carry out in the future. It was noted that all the diamond coatings with GO particles exhibited the larger thickness than the pure diamond coatings. The growth rates of MCD coating without and with GO particles were 1.10–1.38 and 1.50–2.94 µm h$^{-1}$, respectively. These results indicated that GO particles can enhance the diamond growth rate.
Surface roughnesses of MCD coatings with and without GO particles were carried out by stylus-type surface profilometer and AFM. Figure 6 showed all the surface profiles of the as-deposited diamond coatings. The profile roughness parameter (Ra) was obtained to evaluate the surface roughness of the diamond coating. The Ra of three MCD coatings without GO particles were 141, 136 and 168 nm, respectively. Since the grain size increased, the corresponding Ra of three MCD coatings with GO particles were 216, 223 and 226 nm. Hence, GO particles were not favorable for the smooth surface of the coating, and a high growth rate possibly roughened the surface of the diamond coating.
Figure 4. SEM surfaces morphologies of three reproducible CVD diamond coatings: (a,c,e), pure MCD coating and (b,d,f) MCD with GO particles, respectively.

The surface morphologies of the as-deposited diamond coatings without and with particles imaged by AFM are shown in Figure 7. Their surface roughness values of Ra were measured as ~43.3 and 62.5 nm over a 10 × 10 μm² scanning region, respectively. Obviously, the large grain size roughened the surface of diamond coating with GO particles.

Raman analysis was employed to evaluate the quality of the as-deposited diamond coatings. Figure 8 shows the Raman spectra of the MCD coatings with and without GO particles. Only one peak (1332 cm⁻¹), which was assigned to diamond phase [21], was found in all the Raman curves of MCD coatings with and without GO particles. Raman spectra indicated the little residual compressive stress in the MCD coating with GO particles, since its main Raman band located at ~1332 cm⁻¹ [22]. There were not any amorphous carbons on the surface of the diamond coating with GO particles. The influence
of GO particles on the quality of diamond coating seemed to be very limited, since the GO particles were covered by the diamond coating with a certain thickness. Hence, with the increase of thickness, the surface of the diamond coating with GO particles would have an increasing quality of diamond phases. This also implied that additional GO particles will not deteriorate the diamond crystal quality.

**Figure 5.** SEM cross-sectional morphologies of three reproducible CVD diamond coatings: (a,c,e) pure MCD coating and (b,d,f) MCD coating with GO particles, respectively.
3.2. Indentation Property of Diamond Coating with GO Particles

The above results implied that the GO particles were embedded inside diamond coating and located near the interface between diamond coating and substrate, which might affect the adhesive strength of diamond coating. Hence, the effect of GO particles on the adhesive strength of the diamond coating was studied here. After all, the adhesive strength was classified as one of the most important technique indices of coating quality. The diamond coating with weak adhesive strength was not meaningful for industrial applications.
In this work, the indentation test was conducted to evaluate the adhesive strength and the crack resistance of the diamond coating. In order to eliminate the effect of thickness on the indentation property, the diamond coating with GO particles was fabricated again to obtain the similar thickness as the diamond coating without GO particles. According to our above experimental results, the 3 h growth time was set to grow diamond coating with GO particles. The surface and cross-sectional morphologies of the as-deposited diamond coating with GO particles were shown in Figure 9. The 4.7 µm thickness, which was almost equal to that of the pure diamond coating under 4 h growth time, also demonstrated that dispersing GO particles on the substrate was favorable for the growth rate of diamond coating. Figure 10 shows the indentation scars of both MCD coatings under the indentation loads of 200 and 300 N, respectively. Here, the maximum crack diameter of the indentation scar was measured to quantify the level of adhesive strength of the diamond coating. Under 200 N, the maximum crack diameters of diamond coatings without and with GO particles was about 465 and 369 µm, respectively, indicating that the additional GO particles contributed to the crack resistance of the diamond coating. Such phenomenon was also observed for both MCD coatings under the indentation load of 300 N. The measured data showed that the MCD coatings without and with GO particles had the maximum crack diameters of 659 and 408 µm, respectively. Such an improvement in crack resistance may result from two possible reasons. The one was the effect of the thickness of the diamond coating. As above mentioned, the diamond coating with GO particles had the larger thickness than the diamond coating without GO particles, Hence, the former would have higher hardness and crack resistance than the latter. The other reason may be owing to
the GO particles embedded inside diamond coating, which can be observed in the cross-sectional morphology of the diamond coating with GO particles, as shown in Figure 11. Since GO particles were softer than the diamond grains, the internal stress and destructive energy would be adsorbed or relieved when they passed through the GO particles. Thus, the crack was inhibited to some extent and could not easily propagate in the diamond coating. Hence, the additional GO particles would modify the material properties of the diamond coating. Therein, the crack resistance could be improved.

![Figure 9](image1.png)

**Figure 9.** SEM (a) surface and (b) cross-sectional morphologies of the diamond coating with GO particles after 3 h growth time.

![Figure 10](image2.png)

**Figure 10.** Indentation scars of: (a,c) pure MCD coating and (b,d) MCD coating with GO particles under the indentation load of 200 and 300 N, respectively.
Figure 11. SEM cross-sectional morphologies of the CVD diamond coating with GO particles. The blue rectangle showed the GO particles embedded inside the diamond coating.

4. Conclusions

In this paper, a novel method combining the conventional CVD technique with distributing the particles on the substrate surface was proposed to enhance the growth rate of diamond coating. The GO particles were selected as the sample to deposit the diamond coating. The diamond coating deposition was repeated three times under the same CVD process parameters in order to study the reproducibility. The surface morphologies showed that the GO particles would be covered by the diamond coating. As compared with the pure diamond coating, the larger grain size was observed for the diamond coating with GO particles, which lead to higher surface roughness. The growth rates of the diamond coatings without and with GO particles can reach 1.10–1.38 and 1.50–2.94 µm h\(^{-1}\), respectively. No obvious difference in the Raman bands between the diamond coatings with and without GO particles was found, indicating that GO particles will not deteriorate the diamond quality as the increase of thickness. The indentation test was conducted to evaluate the adhesion of CVD diamond coating and the maximum crack diameters of the diamond coating with GO particles under loads of 200 and 300 N were estimated as 392 and 565 m from SEM images, respectively, which were smaller than those of the pure diamond coating (465 and 659 m). The results implied that the GO particles with the strong hydrocarbon adsorption capacity will speed up the CVD chemical reactors, and in turn may improve the growth rate of diamond coating. Thus, this new method was adequate for the substrate to fabricate the CVD diamond coating with optimum mechanical performances.

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