Investigation of thick CVD diamond film with SiC interlayer on tungsten carbide for possible usage in geologic explorations

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Abstract

Diamond film on high-Co containing tungsten carbide is explored for specific geologic explorations. A 153 μm thick diamond film was synthesized using a SiC interlayer, and its micro-structural and frictional properties were investigated accordingly. The results show that: (i) the film exhibits a well-grown and dense columnar structure in the depth direction, and its preferred crystallographic orientation lies at 2θ = 75.2° for the diamond plane (220); (ii) an approximately 7-μm-thick intermediate SiC layer between the film and substrate buffers Cobalt diffusion is evidently favorable for depositing diamond film; (iii) a sharp peak around 1332.7 cm⁻¹ in Raman spectra indicates that the film possesses the distinct diamond nature, and it is mainly composed of diamond crystallites in quality; and (iv) the average friction coefficients in three environments are 0.134 in dry friction, 0.0413 in oil lubrication, and 0.184 in mortar.

Equipment for explorations is a complex system which is usually interacting with geologic elements like slurry and rock. The failure of drilling mechanisms is mainly attributed to the mode of rigid abrasive wear [1]. Such abrasive wear problems under rough working conditions may suitably coped by combining the hardest and super wear-resistant diamond (Tungsten Carbide:Cobalt (WC:Co)) substrate, which is so far proved to be one of the few applicable surface modifications [2,3]. This methodology will be a directional strategy for deploying the resources in exploring natural resources buried deeply underground. The Co content in such devices is usually above 10% and the carbide mechanism in such manner is therefore classified as high Co-containing or high Co. It is recognized that the employment of carbide components with high Co contents for such special devices used for geologic exploration effectively enhances the exploration and construction.

Hot-filament Chemical Vapor Deposition (HFCVD) can grow diamond film directly on the special exploration components of complex-shapes like inserts with chip breakers, drills and end mill cutters, whereas the commonly used commercial sintered and brazed Polycrystalline Diamond (PCD) tools with thickness beyond 50 μm cannot [4,5]. Depositing oriented diamond film on such high-Co carbide is rather lacking in literature. The two basic reasons are mainly due to: (i) the double-edged effect of Cobalt — Usually (a) Cobalt plays a role to bind WC particles together in the carbide structure and hence higher Co content brings a better toughness of the carbide, and (b) the strong tendency of graphitization of cobalt during diamond deposition tends to restrict the nucleation of diamond in the initial growth period [6]; and (ii) the rigorous geologic conditions bring along the requirement for synthesizing diamond film beyond 100-μm-thick so as to accomplish its serving purpose.

Two available approaches, (i) chemical pretreatment and (ii) interlayer [3], have been adopted specifically for dealing the Co diffusion during the deposition. There are two drawbacks in the first approach. These two drawbacks are typically: (a) the reduction of breaking strength of the substrate as a result of removing cobalt and appearing of substrate scratching, which limits the use of the approach for high Co substrate; and (b) the requirement of specialized staff to complete about 20 pretreatment steps ranging from cleaning to drying, which may greatly increase its processing cost. It is noteworthy to point out that these pretreatments may not be allowed or employed for some special mechanical parts with complex shapes that usually involve with intricate pretreatment processes [7].

The work in this paper was initiated to search for an HFCVD technique to fabricate an oriented diamond film on high Co substrate for special geologic explorations. Such technique will provide two special characters like: (i) no chemical pretreatment to deteriorate the substrate performance that makes the technique applicable for complex-shaped components; and (ii) film thickness over 100-μm to minimize the SiC interfacial layer for roping negative Co effect from the substrate. The influence of synthesizing
method on film microstructure and frictional properties is also explored so as to provide insight of how to let diamond be coated on to carbide parts for the geologic explorations.

Diamond film was deposited using an HFCVD system, and the details of coating system has been reported previously [8]. Cemented carbide inserts (WC-1.5 μm: Co-12%, sintered, 10 mm × 10 mm × 2 mm) were used as substrates. The main deposition parameters were listed in Table 1. The deposition was performed by using tetramethylsilane and hydrogen as precursor for depositing SiC interlayer, following with the use of gas mixture of CH4/H2 for diamond layer. Prior to diamond deposition, the samples were ultrasonically seeded for 20 min with 0.25 μm diamond powder suspension (concentration: 50 ct/l).

Morphology and elemental composition of diamond film were observed using three-dimensional white-light interfering profiler, Field Emission Scanning Electron Microscopy (FE-SEM) equipped with Energy Dispersive X-Ray Spectroscopy (EDS), respectively. Structural composition was characterized using X-Ray Diffraction (XRD), and bonding structure was detected using Raman spectrometer. Frictional property was evaluated using a ball-on-disk tester according to the procedures as specified in our patented technique [9] in atmosphere. The testing conditions were basically involved with: (i) using Si3N4 ball (3 mm diameter) as counterpart; (ii) the three frictional modes of dry friction, oil lubrication (PAO, Poly Alpha Olefin), and mortar (75% SiO2 and 15% Al2O3, sand size ranging 20–40 μm, and content of 400 mg/L); (iii) rotary speed at 400 rpm; (iv) sliding radius of 3 mm; (v) sliding velocity of 0.125 m/s; (vi) duration of 4 h; (vii) sliding distance of 1800 m; (viii) loads 4.9 N; (ix) humidity at 43 ± 2%; and (x) temperature at 25 ± 2 °C.

Fig. 1 shows the surface morphology of diamond film deposited on WC substrate. Three-dimensional profiler image in Fig. 1a exhibits that (i) the film surface is evidently composed of continuously well-grown polycrystalline grains with sizes ranging from 20 to 35 μm; (ii) the film surface is coarse with Sa = 1.53 μm and Sz = 12.7 μm. SEM image in Fig. 1b shows that (i) the various notched grains are uniformly distributed on the film surface, and the phenomenon of carbon element (as detected by the EDX results) appearing only at both bottom and top of the grains seems to indicate a typical diamond nature of the film; and (ii) the formation of some tiny grains in notches, as indicated by red arrow, is mainly derived from the second nucleation during deposition [3].

Fig. 2 shows the cross-sectional SEM micrograph of the diamond film. It can be observed in Fig. 2 that the film is consisted of a dense columnar structure in the depth direction from substrate to film surface and the film thickness can be as thick as 153 μm. The inset image in Fig. 2 exhibits an approximately 7-μm-thick SiC interlayer lying at boundary between the film and the substrate. The existence of such interlayer improves effectively the interfacial property and subsequently the film adhesion, which is favorable for the growth of this thick film during deposition [10,11].

Table 1

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>SiC interlayer</th>
<th>Diamond layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4/H2 ratio</td>
<td>–</td>
<td>1.0 Vol%</td>
</tr>
<tr>
<td>Si(CH3)4/H2 ratio</td>
<td>5 Vol%</td>
<td>–</td>
</tr>
<tr>
<td>Total gas flow (sccm)</td>
<td>200 sccm</td>
<td>400 sccm</td>
</tr>
<tr>
<td>Reaction pressure (kPa)</td>
<td>0.5 kPa</td>
<td>4.0 kPa</td>
</tr>
<tr>
<td>Filament temperature (K)</td>
<td>1900 ºC</td>
<td>2000 ºC</td>
</tr>
<tr>
<td>Deposition temperature (K)</td>
<td>780 ºC</td>
<td>800 ºC</td>
</tr>
<tr>
<td>Bias current (A)</td>
<td>3.6 A</td>
<td>3.6 A</td>
</tr>
<tr>
<td>Duration (h)</td>
<td>3.25 h</td>
<td>74 h</td>
</tr>
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Note: A bias DC power was employed. The substrate was connected to a negative voltage in respect to the filaments. The substrate was biased for 30 min at its initial interlayer deposition so as to enhance diamond nucleation.
Fig. 3a shows the XRD spectrum of SiC interlayer on the substrate before diamond deposition. The (200), (220) and (311) diffraction peaks of cubic SiC [12] can be seen vividly around 2θ = 41.5°, 60.15° and 71.9°, respectively (Fig. 3a). The SiC (111) peak is overlapped with the most intense peak of WC at 2θ = 35.7°. Furthermore, the absence of cobalt signal indicates a good buffer effect of the layer. After the diamond deposition, as depicted in Fig. 3b, two intense diamond peaks are detected around 2θ = 43.9° and 75.3°, corresponding to diamond plane (111) and (220), respectively, with stronger intensity peak at the plane (220). Such XRD results confirm that the film possesses a typical diamond nature, and suggest that the crystal diamond grains have been well grown in HFCVD plasma and the preferred crystallographic orientation of the diamond film lies at 2θ = 75.3° for the diamond plane (220).

A typical Raman spectrum for the thick diamond film was shown in Fig. 4. It shows that the film possesses a sharp and intense diamond peak at 1332.7 cm⁻¹ and a noticeably broad non-diamond peak consisting of sp² carbon bond around 1562.7 cm⁻¹. The diamond film possesses a distinct diamond nature, and it is mainly composed of quality diamond crystallites in that the detection sensitivity for sp²-carbon band is much higher than that of the sp³-carbon band in Raman testing [13]. From the frequency ν of the diamond band, its residual compressive stress has been determined and given value as low as 0.397 GPa by using the equation σ (GPa) = −0.567(ν – ν₀), where ν₀ = 1332 cm⁻¹ is the frequency of unstressed diamond crystal [14].

Fig. 5 compares three friction coefficient curves in ball-on-disc testing conditions of dry friction, PAO oil lubrication and mortar. As shown in Fig. 5, the COF of the dry friction is initially at approximately 0.55 and then decreases to about a value of 0.14 in a slid distance of about 150 m. It then fluctuates around this value so as to give the average dry COF as about 0.134. The initial high COF in running-in stage may due to the coarse surface of this thick diamond film, and the fluctuation of COF value in the subsequent period may mainly be caused by the fragmentation and deformation of contacting asperities [15]. The gradual decrease in COF is mainly because of the gradual blunting of asperities in the subsequent transition process.

As for the curve of PAO oil lubrication in Fig. 5, its COF exhibits a tendency of steady change as compared with its counterpart in dry friction, whereas its average COF decreases to 0.0632, which is evidently much lower than that in dry friction. During the boundary friction, the COF is approximately 0.35 and decreases to about 0.05, and then fluctuates around this value after covering about 200 m sliding distance.

As for the curve for mortar in Fig. 5, the COF exhibits an increasing tendency in running-in stage and reaches a maximum value at 0.210 approximately. The COF then gradually decreases and finally fluctuates near 0.184. Its initially high value in running-in stage may mainly be due to the sliding mode to wear the grains (SiO₂, Al₂O₃) in mortar between mating pair. The subsequent sliding of irregular hard grains with diamond film leads to an increasing and fluctuating COF. The worn grains are then
smoothened by grinding, and hence the COF value is reduced. In the study, all diamond films showed neither any spontaneous flaking after deposition nor any film delamination during the tribo-tests.

In summary, HFCVD diamond film on high-Co WC substrate has been successfully synthesized and investigated for its possible usage in geologic explorations. The film has exhibited a well-grown and dense columnar structure through its depth direction. The existence of an approximately 7-μm-thick intermediate SiC layer between the film and the substrate improves the film adhesion effectively, and is favorable for depositing diamond film. Raman spectrum has indicated that the film possesses a distinct diamond nature and it is mainly composed of quality diamond crystallites, and it gives residual stress as low as 0.397 GPa. The average COF in dry friction has been found at about 0.134, whereas extremely low COF (≈0.0413) has been found in oil lubrication and relatively high COF (≈0.184) has been found in mortar.

It is supposed that the thick diamond film on the carbide has been contributed by: (i) the 7-μm-thick SiC interlayer offerings (a) a preferred interfacial transition from the carbide substrate to the film, (b) an excellent buffer for the Co diffusion so as to make the substrate pretreatment ignorable, and (c) a crystalline state of cubic SiC to provide favorable morphology for the growth of diamond crystalline; and (ii) the thick diamond layer on which it grows film with low residual stress.

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References