Adhesion enhancement of diamond coatings on WC tools by high energy ion irradiation

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Abstract

Microcrystalline diamond thin films were deposited on cemented tungsten carbide cutting tools by hot-filament chemical vapour deposition process. The coatings deposited were irradiated with 50 MeV Si 7+ ions upto a dose of \( < 10^{13} \) ions cm\(^{-2}\). The adhesion and wear characteristics of as-deposited and irradiated coatings were studied and it was found that irradiation induced increased adhesion of the coatings to the substrate resulting in reduced coating failure during wear tests.

Keywords: Diamond, Coating, Irradiation

1. Introduction

Hard wear resistant coatings are commonly used for tool applications where the lifetimes of the bare tools could be improved by a factor of 10 or more [1,2]. The advent of various CVD techniques has made the use of diamond as a hard coating possible for many mechanical applications. Diamond coatings offer the possibility of superior wear resistant, low friction and chemically protective coatings [3]. Extensive research efforts are now being focused on the development of diamond coated tools such as cutting inserts or metal forming tools [4]. The diamond coatings for mechanical properties have been studied on tungsten carbide cutting tools [5,6], Si [7,8], SiN [9], Si-Al-O-N [10] and SiC [11] substrates.

At present, the fundamental barrier that has not been overcome in respect of the diamond coatings as applied to tools is their adhesion to various substrates. The cutting performance of the diamond coated inserts is strongly related to the adhesion strength. Kuo et al. [12] argued that an improvement in adhesion dramatically increases the cutting performance. Adhesion is affected not only by deposition parameters but also by the type of the substrate. To improve the adhesion, many methods such as proper selection of the interface, fine scratch marks by powders, introduction of buffer layers, etc. have been tried [13–15]. Improvement in adhesion due to ion irradiation has also been demonstrated by many workers [16–19] and is often associated with ion beam mixing at the interface. However, the degree of mixing required to improve the interfacial adhesion is not very high [20].

Considering the above, we have carried out some preliminary studies on the effect of high energy ion irradiation on the adhesion and wear behaviour of diamond coatings on WC cutting tool material without any pretreatment being given to the substrate. High energy ions (50 MeV Si 7+) were used to irradiate the films and the resulting changes in adhesion and wear were correlated with those of the as-deposited samples.

2. Experimental details

Hot-filament chemical vapour deposition technique was employed to deposit diamond coatings on tungsten carbide cutting tools. The details of the deposition set up are described elsewhere [21]. A mixture of 10% CH\(_3\) + 90% Ar and H\(_2\) were used as the source gases.
Table 1
Details of deposition parameters employed to deposit diamond thin coatings on WC cutting tools.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>CH(_4) vol.% (8(CH(_4)/H(_2)))</th>
<th>Working pressure (Torr)</th>
<th>Substrate temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.15</td>
<td>30</td>
<td>760</td>
</tr>
<tr>
<td>2</td>
<td>1.54</td>
<td>30</td>
<td>760</td>
</tr>
<tr>
<td>3</td>
<td>1.89</td>
<td>30</td>
<td>720</td>
</tr>
</tbody>
</table>

A set of three samples deposited at various CH\(_4\) vol.% (8(CH\(_4\)/H\(_2\))) in the feed gas were used for the present study. Prior to loading in the chamber, the tool inserts were thoroughly degreased and cleaned. Before commencement of deposition, all the samples were exposed to hydrogen treatment at \(\approx 760^\circ\)C. This treatment is expected to decarburize the WC grains and produce a rough surface to facilitate diamond nucleation [22]. The volume fraction of CH\(_4\) in carrier gases varied from 1.15 to 1.89 vol.%. The detailed deposition parameters are listed in Table 1.

In order to study the effect of irradiation on the adhesion and wear characteristics of the coatings, half of the surface area of each tool was masked with aluminum foil. The rest was subjected to 50 MeV Si\(^{+}\) ions from a 16 MV Tandem Pelletron accelerator at an angle of 30°. The beam current was maintained at 1 pA and the samples were subjected to a dose of \(< 10^{13}\) ions cm\(^{-2}\).

The scratch adhesion test of the coatings was carried out using a scratch adhesion tester (Revetest). The scratch adhesion test was chosen because it is a relatively surface specific as compared with other material testing techniques [23,24]. The stylus in the tester was made to scratch the coating under a progressively increasing load of 0–50 N. Sufficient number of scratches were made on the samples to arrive at a statistically reliable value. The wear measurements were carried out by replacing the diamond stylus with a 10-mm diameter AISI52100 bearing steel ball and scratching the same wear track at constant loads of 20 N and 50 N.

Before and after each measurement the sample and the steel ball were ultrasonically cleaned in acetone and weighed in an electronic balance for loss in weight due to wear. The electronic balance could measure weight loss up to \(10^{-5}\) g.

3. Results and discussion

3.1. Microstructure of the coatings

Fig. 1a,b and c show the SEM micrographs for samples 1, 2 and 3 respectively. The variations in parameters used for the deposition of the coatings are seen to reflect in the crystalline quality of the coatings. All the coatings are found to be dense and possessed a rough surface topography. Sample 1 shows highly faceted particles. The surface morphology for sample 2 depicts a lower degree of faceting. Sample 3 shows large sized cauliflower-shaped particles indicating considerable presence of nondiamond phases in the coating.

Fig. 2a,b and c show the SEM micrographs of the coatings after being subjected to a dose of \(< 10^{13}\) ions cm\(^{-2}\) with 50-MeV Si\(^{+}\) ions at an angle of 30° with respect to the target. The samples do not show major changes in the surface structure. This is so because all the three samples were irradiated with a dose that is lower than the threshold dose causing amorphization of the coating at the expense of diamond phase [25,26]. This threshold dose corresponds to that at which major changes in the film microstructure are observed [25,26].
Fig. 3 shows the typical XRD pattern for sample 2. The diffractogram shows prominent peaks at $2\theta = 43.9^\circ$ and $75.5^\circ$ corresponding to diffraction from (111) and (220) planes of the diamond lattice. Other peaks occur due to the WC substrate and tungsten. The XRD patterns for other samples were found to be similar and, therefore, they are not presented.

The Micro-Raman spectrum for sample 2 is shown in Fig. 4a. The spectrum shows a sharp peak at 1335.2 cm$^{-1}$ having a narrow line width of 10.9 cm$^{-1}$ corresponding to the predominant presence of crystalline diamond phase in the film. The Raman bands corresponding to nanocrystalline diamond phase are also seen at 1130.9 cm$^{-1}$ and 1463.8 cm$^{-1}$ [27,28]. The ‘D’ and ‘G’ bands, due to amorphous carbon phase, are found at 1356.3 cm$^{-1}$ and 1567.6 cm$^{-1}$, respectively. The spectrum, thus, indicates that the coating is a composite of crystalline diamond, nanocrystalline diamond and amorphous carbon phases. This amorphous carbon phase is expected to occur at the interface and in the intergranular regions of the diamond crystals.

The Micro-Raman spectrum for the irradiated sample 2 is shown in Fig. 4b. The spectrum again shows a sharp peak corresponding to crystalline diamond at 1335.6 cm$^{-1}$ with a line width of 11.8. This increase reflects the introduction of defects in the diamond crystallites as a result of irradiation [25,26]. The Raman peaks corresponding to nanocrystalline diamond phase are found at 1138 and
1453.8 cm$^{-1}$. The ‘D’ and ‘G’ bands due to amorphous carbon phase occur at 1345 and 1554.8 cm$^{-1}$, respectively. As compared to the as-deposited sample, the irradiated sample shows a small increase in the relative abundance of the amorphous carbon phase although the film is again a composite of crystalline diamond, nanocrystalline and amorphous carbon phases. Thus, the Raman spectrum shows that the irradiated film does not suffer appreciable damage.

3.2. Adhesion and wear of the coatings

Fig. 5 shows the acoustic emission curves of the scratch adhesion tests performed on the as-deposited as well as irradiated samples 1, 2 and 3. The curves shown here present a statistical average of many tracks made parallel to each other.

Sample 1 in as-deposited state does not peel off up to a load of 50 N. The irradiated coating also did not indicate any failure and thus indicates good adhesion. These results are further confirmed by the SEM micrographs of the adhesion track as shown in Fig. 6.

Sample 2 in as-deposited condition shows complete failure at a load of 27 N. However, an increase in adhesion is clearly seen in the irradiated sample which delaminates at 34 N, an increase of $\approx 7$ N over that for the as-deposited sample. The adhesion tracks for as-deposited and irradiated sample 2 are shown in Fig. 7 and show the area at which coating failure has occurred.

In contrast to samples 1 and 2, sample 3 which showed considerable nondiamond phase with large grains showed very poor adhesion to the substrate and the as-deposited sample completely got detached at a load of 6 N only. Presence of nondiamond contents has been found to be one of the main reasons for low adhesion [29]. The irradiated sample, however, showed slight improvement and the failure occurred at a load of 8 N. This value is not appreciable as compared to the results for the previous two samples. The same behaviour can be seen from the SEM micrographs given in Fig. 8 which depict film failure near the beginning of the track. The adhesion results described above are summarized in Table 2.

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Fig. 5. Acoustic emission curves for as-deposited and irradiated diamond coatings on WC tools. (a) Sample 1, (b) Sample 2, and (c) Sample 3.

Fig. 6. Scanning electron micrographs of adhesion tracks on (a) as-deposited sample 1 and (b) irradiated sample 1.
It has been observed that sample 1 with highest crystalline quality showed highest adhesion to the substrate in as-deposited state. This observation is in agreement with those of Bull et al. [30] Alam et al. [31] also reported that the processing parameters, which determine the coating quality, critically affect the coating adhesion. Non-diamond content of the coating has been found to govern the adhesion of the coatings in as-deposited state.

Adhesion of the coatings to the substrates is also strongly influenced by the substrate surface roughness, its reactivity and the stresses developed at the interface. However, many workers [32–34] found good quality deposition as well as adhesion when the coatings were deposited following a decarburization treatment. In the present studies also, decarburization prior to deposition was carried out. Surface decarburization is expected to produce a surface with fine grains of WC. Improvement in adhesion occurs essentially due to increased surface contact area between the substrate and the coating.

As a result of high energy irradiation by 50 MeV Si⁺ ions below doses of $< 10^{13}$ ions cm⁻², we have found a clear improvement in the adhesion behaviour of the coatings. It has been found that large changes in the microstructure of our diamond thin coatings commence only above doses of $> 10^{13}$ ions cm⁻² for 50 MeV Si⁺ ions [26]. Therefore, the irradiation process is not expected to alter the microstructure and hence the hardness and diamond content of the coatings to a considerable extent.

Fig. 7. Scanning electron micrographs of adhesion tracks on (a) as-deposited sample 2 and (b) irradiated sample 2.

Adhesion of thin coatings can be improved by ion irradiation induced interface chemical bonding. An adhering interface ideally would consist of both coating and the substrate mixed to an extent of a few monolayers [35]. It has been suggested that irradiation leads to a short range redistribution of chemical bonds between the atoms of the coating and the substrate producing an interface region which is one or two monolayers deep whose low energy represents enhanced adhesion. In addition, the hydrogen evolution from the coatings further contributes to disruption of bonds and resulting adhesion enhancement by redistribution of bonds at the coating–substrate interface. Adhesion enhancement by ions (with energy of the order of a few hundred keV) which provide significant collisional energy loss in various materials [16–19] has been reported but in the case of diamond coatings, such irradiations are known to lead to graphitization with increasing dose. This graphitization is a manifestation of the meta-

Fig. 8. Scanning electron micrographs of adhesion tracks on (a) as-deposited sample 3 and (b) irradiated sample 3.

Table 2
Results of scratch adhesion tests carried out on as-deposited and irradiated diamond thin coatings on WC tools.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load (N)</th>
<th>Catastrophic failure load (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-deposited</td>
<td>Irradiated</td>
</tr>
<tr>
<td>1</td>
<td>0–50</td>
<td>No failure</td>
</tr>
<tr>
<td>2</td>
<td>0–50</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>0–50</td>
<td>6</td>
</tr>
</tbody>
</table>
bility of diamond under ambient conditions. However, high energy ions provide high electronic energy deposition with low nuclear losses. The 'TRIM' calculations show that 50 MeV Si\(^{17}\) ions used in the present study show high electronic losses of 546.3 eV Å\(^{-1}\) and low nuclear losses of only 0.52 eV Å\(^{-1}\). The projected range of these ions calculated by 'TRIM' Monte Carlo simulation, at 30° incidence is ≈ 5 μm which is more than the coating thickness of ≈ 3.0 μm. The 'TRIM' simulation of the defect ions on the diamond film/WC composite shows that the Si\(^{17}\) ions have a range of 4.43 μm which is again more than the thickness of the film. Thus, the ions are ultimately embedded into the substrate. As the end of the projected range is approached, the defect production density increases. As a result the atoms of the substrate and the coating are dislodged from their respective positions, and gain mobility due to electronic energy relaxations of the subsequent ions. The atoms of the substrate and the coating may, therefore, mix up to a few monolayers causing an increase in the adhesion as observed in the present studies. Thus, the use of high energy ions can preserve the coating characteristics along with adhesion enhancement by interface bonding.

The wear results obtained for different samples while rubbing against bearing steel balls are given in Table 3. Sample 1 was subjected to 100 strokes at a load of 50 N on the same wear track with a velocity of 1 mm s\(^{-1}\). Under these conditions, the as-deposited coating suffered a loss of 0.1 mg while the irradiated coating did not show any measurable wear loss. The steel balls used for the study were found to be considerably worn off.

Sample 3 at 50 N load showed removal of the coating in the as-deposited region after only 25 strokes. But at 20 N load, this failure was not observed even after 100 strokes. On the other hand, the irradiated counterpart of the sample 3 was able to withstand about 43 strokes at 50 N before failure showing slight improvement in adhesion due to irradiation. The loss in weight suffered by the steel balls complemented these results as shown in Table 3.

Sample 3 is expected to contain non-diamond carbon and the SEM micrograph shows blunted crystallites. These defective crystallites have lower hardness and may easily be scratched off. On the other hand, sample 1 which contained good quality diamond crystallites, shows higher hardness so that the grains did not wear off easily. The decrease in the wear suffered by the coatings after irradiation is a direct consequence of the increase in adhesion of the coatings leading to decrease in film loss by cracking and delamination. No major structural change associated with the irradiation has been observed in these samples.

Fig. 9 shows the EDAX profile of the coating and the wear track for sample 1. The EDAX profile of the coating shows the characteristic peaks due to carbon and tungsten. However, within the wear track, peaks due to iron from the bearing steel transferred during rubbing from the ball to the coating surface are also observed. These peaks are observed despite thorough ultrasonic cleaning in acetone immediately after the wear tests were carried out.

In short, the coatings have also been found to have high wear resistance. High wear resistance is desirable as detached diamond particles can be extremely detrimental for tribological applications.

### 4. Conclusions

Diamond coatings deposited on WC cutting tools using hot-filament chemical vapour deposition process were subjected to a dose of < 10\(^{13}\) ions cm\(^{-2}\) of 50 MeV silicon ions. It was found that the crystalline quality of the film is a major factor affecting the tribological behaviour of the coatings. However, when the coatings were subjected to irradiation up to doses less than the threshold dose, a marked improvement in the adhesion of the coatings was observed. Due to enhancement in adhesion the wear resistive properties of the films were also found to improve.
References