Interfacial structure, residual stress and adhesion of diamond coatings deposited on titanium

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Abstract

The interfacial structures of diamond coatings deposited on pure titanium substrate were analyzed using scanning electron microscopy and grazing incidence X-ray diffraction. Results showed that beneath the diamond coating, there was one titanium carbide and hydride interlayer, followed by a heat-affected and carbon/hydrogen diffused Ti layer. Residual stress in the diamond coating and TiC interlayer under different process parameters were measured using Raman and X-ray diffraction (XRD) methods. Diamond coatings showed large compressive stress on the order of a few giga Pascal. XRD analysis also showed the presence of compressive stress in the TiC interlayer and tensile stress in the Ti substrate. With increasing deposition duration, or decreasing plasma power and concentration of CH in gas mixture, the compressive residual stress in the diamond coating decreased. The large residual stress in the diamond coating resulted in poor adhesion of the coatings to substrate, but adhesion was also related to other factors, such as the thickness and nature of the TiC interlayer, etc. A graded interlayer design was proposed to lower the thermal stress, modify the interfacial structure and improve the adhesion strength.

Keywords: Diamond; Residual stress; Adhesion; Titanium; Interlayer; PECVD

1. Introduction

Residual stress is an important aspect for diamond coating as it may influence not only the adhesion between coating and substrate, but also the maximum thickness to which coatings can be grown, the roughness of the coating as well as the tribological, fracture and fatigue properties [1–4]. The thermal gradient during deposition, coefficient of thermal expansion of the substrate, and microstructure of the coating could all have significant effects on the residual stress in a diamond coating [5,6]. For diamond coatings, the residual stress is mainly a combination of two sources: thermal and intrinsic [7]. Thermal stress forms during the cooling step after deposition, and is due to the difference in thermal expansion coefficient between the coating and substrate. The intrinsic stresses are mainly caused by the presence of non-diamond components, structural mismatch between coating and substrate, as well as the presence of impurities and structural defects in the diamond coating. Thermal stresses can be removed by an annealing process, but the intrinsic stress cannot. Thermal stresses can be calculated using some simple equations, while the intrinsic residual stresses are difficult to analyze.

There are many techniques which can be employed for the measurement of residual strain or stress in diamond coatings, for example, the curvature method [8], Raman spectroscopy [9,10], X-ray diffraction (XRD) [11–13], etc. Each method has its advantages and disadvantages, and there is a substantial disparity in the magnitude of residual stresses for the data obtained using different methods [14,15]. Raman spectroscopy is one of the most important tools for characterizing diamond [16]. Stress-free diamond is known to have a peak located at 1332 cm\(^{-1}\) in its Raman spectrum. The internal stresses in diamond coatings can be estimated from the quantity of Raman line shift, \(\Delta v\), with the following expression [17]:

\[ \sigma = -A\Delta v \]
where $A$ is a constant, the stress gauge factor. However, there are some questions remaining for this method. Firstly, the value of $A$ is quite different in different papers since the shift of Raman peak is caused not only by residual stress in the lattice of the diamond crystals, but also other parameters, such as crystallinity, temperature, defect density, etc. [18]. Secondly, in the highly stressed region of the adhered film, the Raman spectra show splitting, which brings some difficulty in determining the Raman peak shift and calculating the real stress value [9]. Thirdly, Raman analysis measures the relatively localized stresses compared with X-ray and curvature methods. The XRD method offers a unique opportunity to measure the crystalline structure and orientation distribution in the coating and the residual stress in both the coating and the substrate. This is important for diamond deposition on titanium based materials, in which there are different interlayers formed [19].

The major impediment for the wide application of diamond coatings is associated with the poor adhesion strength of CVD diamond films with the substrate. There is a need to study the factors which control adhesion of diamond films to the substrate and develop methods which can improve significantly the adhesion, thus allowing for the production of consistently well-adherent diamond coatings [20,21]. One solution is to deposit an interlayer or buffer layer on the substrate [22–24]. The functions of an interlayer to improve adhesion include (1) to enhance diamond nucleation rate; (2) to minimize thermal and interfacial stresses; (3) to provide an intermediate layer for bonding.

In this study, the diamond coating was deposited on pure titanium. The interfacial structures of diamond coatings deposited on the pure titanium substrate were characterized. The effects of deposition duration, CH$_4$/H$_2$ ratio, and plasma power on film stress and adhesion were investigated. A graded interlayer was proposed to lower the thermal stress and improve the adhesion strength.

2. Experimental

Pure titanium plates with a thickness of 3 mm were mechanically ground with sandpaper, then ultrasonically cleaned in acetone and ethanol baths. Deposition of diamond coatings on the Ti substrate was carried out by a MPS4 microwave plasma assisted CVD (PACVD) system (Coaxial Power Systems Ltd, UK). The microwave powers were changed from 0.8 to 2 kW and the output frequency was 2.45 GHz. The gas ratio of methane and hydrogen was varied from 198:2 to 190:10 and the total gas pressure was 30 Torr. The specimens were deposited with diamond for different durations up to 21 h. A multi-step deposition method was studied to lower the residual stress and improve the adhesion between the diamond and the titanium substrate. Plasma nitriding was performed in a PECVD system with a microwave power of 1 kW and duration of 1 h using pure nitrogen gas. Then the CH$_4$ gas was gradually introduced into the gas mixture, while the N$_2$ gas was gradually reduced. Finally, hydrogen was introduced, and gradually increased to 98% in H$_2$/CH$_4$ gas mixture to deposit diamond coating.

The surface and cross-sectional morphology of the deposited diamond coatings was investigated by a JEOL scanning electron microscope. The in-depth distribution profiles of crystalline phases were obtained by grazing incidence X-ray diffraction (GIXD) with Cu Kα 40 kV/30 mA. The coating quality and residual stresses were evaluated by micro-Raman spectroscopy. For {111} crystals, the shift and splitting of the diamond signal can be converted into stress values using a stress gauge factor $A$ of $-1.08$ GPa cm$^{-1}$ for the singlet, and $-0.384$ GPa cm$^{-1}$ for the doublet photon. If no splitting, then the gauge factor is $-0.348$ GPa cm$^{-1}$ [25]. For the XRD method, the residual stresses were determined by the traditional sin$^2\psi$–2θ method with Cu Kα radiation at 40 kV/30 mA, and the diffraction peak chosen in the present study was the diamond (311), TiC (420) and Ti (210). The adhesion of diamond coatings on Ti substrate was evaluated using a Rockwell indentation tester (with a normal load of 150 kgf).

3. Calculation of thermal residual stress

In order to evaluate the thermal residual stress, the effect of differential thermal expansion between the coating and substrate with temperature must be taken into account (Fig. 1, from Refs. [26,27]). The misfit strain between the two constituents at temperature $T_2$ and a deposition temperature $T_1$ can be expressed as:

$$
\Delta \varepsilon = \int_{T_2}^{T_1} [\alpha_d(T) - \alpha_s(T)]dT
$$

Fig. 1. The thermal expansion coefficient of Ti and diamond as a function of temperature.
calculated using Eq. (43x262) diamond-coated titanium, the misfit strain values can be
will be given by the following equation
(biaxial stress state, then the thermal stress in the film
is entirely accommodated within the film with an equal
parameters. For the Ti substrate, 
coating, which is controlled by the different processing
dominating element. During the PACVD process, carbon and hydrogen
atoms/ions will easily react with Ti atoms to form
titanium carbide and titanium hydride. The cross-sectional
observation of this coating shown in Fig. 4 reveals the
existence of different layers. The diamond coating is approximately 5–7 μm thick and is dense and homogeneous. The TiC layer is a little porous which is easily etched by Keller’s solution, and the thickness of the TiC layer is about a few microns. Microhardness measurements reveal a 40 μm thick zone of changing hardness in the Ti substrate beneath the TiC layer, generated by the diffusion of carbon or hydrogen into the titanium substrate. Results also showed that with the increase of plasma power, the thickness of both the TiC interfacial layer and the diffusion layer increases. The interfacial structure of the TiC layer can also be seen from the spalled area shown in Fig. 5. The porous and rough layer beneath the diamond coating is actually a TiC layer, and there are even some cracks penetrating deep into the substrate. The interfaces between the diamond coating, the TiC layer and the Ti substrate are vulnerable areas where the spallation, cracking and delamination of diamond coatings easily occurs.

4. Experimental results and discussions

4.1. Interfacial structure

GIXD analysis of the diamond film (deposited under 1 kW, gas mixture of 196/4 for 12 h) with X-ray impinging angles of 1–9° are shown in Fig. 3. The XRD patterns confirm the formation of a polycrystalline diamond film on the surface layer. Beneath the diamond film, there is a layer of titanium carbide and titanium hydride. Titanium is an active hydride/carbide-forming element. During the PACVD process, carbon and hydrogen atoms/ions will easily react with Ti atoms to form titanium carbide and titanium hydride. The cross-sectional observation of this coating shown in Fig. 4 reveals the existence of different layers. The diamond coating is approximately 5–7 μm thick and is dense and homogeneous. The TiC layer is a little porous which is easily etched by Keller’s solution, and the thickness of the TiC layer is about a few microns. Microhardness measurements reveal a 40 μm thick zone of changing hardness in the Ti substrate beneath the TiC layer, generated by the diffusion of carbon or hydrogen into the titanium substrate. Results also showed that with the increase of plasma power, the thickness of both the TiC interfacial layer and the diffusion layer increases. The interfacial structure of the TiC layer can also be seen from the spalled area shown in Fig. 5. The porous and rough layer beneath the diamond coating is actually a TiC layer, and there are even some cracks penetrating deep into the substrate. The interfaces between the diamond coating, the TiC layer and the Ti substrate are vulnerable areas where the spallation, cracking and delamination of diamond coatings easily occurs.

4.2. Effects of processing parameters on the residual stress

Different Young’s modulus values of diamond, \( E_d \) (between 500 and 1000 GPa, from Refs. [29,30]) were used, and the Poisson ratio of diamond, \( \nu_d \), was chosen as 0.2. The Young’s modulus of the deposited diamond coating is affected mainly by the quality of the diamond coating, which is controlled by the different processing parameters. For the Ti substrate, \( E_{Ti} \) is 100 GPa, and \( \nu_{Ti} \) is 0.36. Fig. 2 shows the calculated residual stress in the diamond coating as a function of deposition temperature and elastic modulus. Generally, the calculated thermal stress is of the order of 3–7 GPa, under the current deposition temperature of approximately 800–1000 K. The thermal stress in diamond films deposited on Ti is extremely large, and in the following section, we hope to reduce the stress by applying a graded interlayer.

If the expansivity data is described by a three-order polynomial, which fitted the curve quite well:

\[
\alpha(T) = a + bT + cT^2 + dT^3
\]  

(2)

Then the misfit strain, \( \Delta \varepsilon \), follows the relation:

\[
\Delta \varepsilon = (a_d - a)(T_1 - T_2) + (b_d - b_2) \frac{(T_1^2 - T_2^2)}{2} \\
+ (c_d - c_2) \frac{(T_1^3 - T_2^3)}{3} + (d_d - d_2) \frac{(T_1^4 - T_2^4)}{4}
\]  

(3)

The coefficient of thermal expansion of pure Ti and diamond (Fig. 1) can be expressed [24,25]:

\[
\alpha_{Ti} = 0.0036T + 7.4833
\]  

(4)

\[
\alpha_{diamond} = 3 \times 10^{-9}T^3 - 8 \times 10^{-6}T^2 + 0.0089T + 1.0866
\]  

(5)

In applying this equation for the cooling condition of diamond-coated titanium, the misfit strain values can be calculated using Eq. (5). If it is assumed that the misfit is entirely accommodated within the film with an equal biaxial stress state, then the thermal stress in the film will be given by the following equation [28]:

\[
\sigma_d = \frac{\Delta \varepsilon E_d}{(1 - \nu_d)}
\]  

(6)

Fig. 6 shows the Raman spectroscopy data obtained from diamond coatings deposited for 12 h with \( CH_2:H_2 \) 196:4 and a power of 1 kW. The calculated stress is approximately \(-3.4\) GPa according to the peak shift. Fig. 7a shows the XRD results (\( d \) values as a function of \( \sin^2 \psi \)) of the same diamond coating by the \( \sin^2 \psi \)–20 method. If we choose the elastic modulus of diamond as 800 GPa (value obtained from nano-indentation), and Poisson ratio of 0.2, then the measured residual stress is approximately \(-3.19\) GPa, agreeing well with that determined with Raman analysis. Both
Raman and XRD analysis show an extremely large compressive stress existed in the deposited diamond coating. The $d - \sin^2 \psi$ curves for the TiC (4 2 0) interlayer and Ti (2 1 0) substrate in Fig. 7b and c show clearly that compressive stress dominates in the TiC interlayer whereas tensile stress dominates in the Ti substrate. The measured residual stresses in the TiC interlayer and Ti substrate are $-380$ and $+120$ MPa, respectively. $E_{\text{TiC}}$ is 450 GPa and $\nu_{\text{TiC}}$ is 0.3. Table 1 lists the stress variation of the diamond coatings and the TiC and Ti with the increase of diamond deposition duration. The measured stresses decrease with increasing thickness of the diamond film due to the relaxation of the extrinsic stress [9,30]. By comparison, the stress of the Ti is tensile and releases slightly with increasing thickness of the diamond coatings.

If the calculated thermal stress is of the order of $-4$ to $-6$ GPa (Fig. 2), the stress relaxation mechanism must be considered since the measured stress value is much lower. One possible explanation could be the tensile intrinsic stress generation due to the existence of grain boundaries, voids and impurities [7]. Another explanation could be the much lower yield stress of pure Ti, which allows a partial relaxation of the high thermal stress in the diamond coating [19]. The third could be the presence of TiC layer at diamond–Ti interface [2,30], which can reduce the thermal stress because the thermal expansion coefficient of TiC is
Fig. 6. Raman spectrum of diamond coatings showing the presence of the characteristic diamond and diamond-like phases in the deposited coatings.

$7 \times 10^{-6}/^\circ\text{C}$, much less than that of Ti, which is $9.5 \times 10^{-6}/^\circ\text{C}$ [2].

Residual stresses obtained from Raman analysis for the diamond coating deposited under different plasma powers are shown in Fig. 8. For the coatings deposited under 0.8 and 1 kW, the compressive residual stresses are 2.1 and 3.4 GPa, respectively, corresponding to the larger and better-defined diamond crystals shown in Fig. 8. For the coating deposited under a plasma power of 2 kW, the obtained residual stress is 1.1 GPa even though the crystals are quite large. The relatively lower residual stress is due to the stress relaxation caused by cracking in diamond coatings deposited under a high plasma power as shown in Fig. 9 [32]. Cracks propagate through the diamond crystals rather than along the boundary showing a good cohesion of the diamond crystals.

Fig. 10 shows the effect of the concentration of CH$_4$ on the residual stress of a diamond coating on a titanium substrate. The higher the concentration of CH$_4$ in the gas mixture, the larger the compressive stress in the

<table>
<thead>
<tr>
<th>Deposition duration (h)</th>
<th>8</th>
<th>12</th>
<th>21</th>
</tr>
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<tbody>
<tr>
<td>Diamond thickness (μm)</td>
<td>3.8</td>
<td>6.4</td>
<td>9.2</td>
</tr>
</tbody>
</table>

**Diamond stress**

<table>
<thead>
<tr>
<th>Raman shift</th>
<th>3.5</th>
<th>3.4</th>
<th>2.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD (3 1 1)</td>
<td>-3.42</td>
<td>-3.19</td>
<td>-2.51</td>
</tr>
<tr>
<td>TiC interlayer stress (4 2 0)</td>
<td>-0.505</td>
<td>-0.380</td>
<td>-0.303</td>
</tr>
<tr>
<td>Ti substrate stress (2 1 0)</td>
<td>0.267</td>
<td>0.120</td>
<td>0.105</td>
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| TiC interlayer stress (4 2 0) | -0.505 | -0.380 | -0.303 |
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Table 1

The residual stresses (unit in GPa) of Ti, TiC and diamond coatings deposited with CH$_4$/H$_2$ = 196:4 at a plasma power of 1 kW.

Fig. 7. $\sin^2 \psi$ plots for diamond, titanium carbide and titanium substrate. (a) Diamond; (b) TiC; (c) Ti.
diamond coating due to a higher non-diamond carbon content in the coating as shown in Fig. 10 [31,33]. Also, the increase of coating thickness with the increase of CH₄ concentration can also promote the increase of residual stress. However, increase of CH₄ concentration will cause decrease in grain size, and an increase in defects in the coating, thus causing the increase of tensile stress components. Therefore, the compressive stress value does not increase significantly under a high CH₄ concentration.

4.3. Effect of processing parameters on adhesion

Rockwell indentation tests were performed on diamond coatings deposited with a H₂/CH₄ gas ratio of 196:4 and a plasma power of 1 kW for 12 h. Fig. 11 shows the indentation morphology. Spallation of the diamond coating is observed, indicating the poor adhesion strength of diamond coatings on titanium substrates. The poor adhesion is related to: (1) high thermal stresses which cause interfacial debonding and spallation of the coating; (2) the large difference in stiffness or elastic modulus between diamond and the Ti substrate, which leads to high stresses when an external force is applied; (3) the porous and brittle interfacial TiC layer.

Indentation tests on the diamond coatings prepared under different process parameters reveal the following conclusions. At a lower plasma power, the deposition temperature is quite low, and the interfacial layer of TiC is not fully established, also the content of non-diamond components is relatively large, thus the bonding is not good (with one example shown in Fig. 12). Whereas at a high plasma power, the thermal stress is quite high and a much more porous TiC layer exists between the diamond coatings and the Ti substrate, which causes the poor adhesion. The effects of CH₄ concentration are not so significant. The higher CH₄ concentration results in an increase in the concentration of non-diamond material, resulting in a significant increase in residual stress, and thus a deterioration of the adhesion properties.
Fig. 12. Rockwell indentation morphology of diamond coatings deposited with a H$_2$/CH$_4$ gas ratio of 196:4 and a plasma power of 0.8 kW for 12 h.

However, the higher concentration of CH$_4$ results in the formation of a thicker interfacial carbide layer. The thicker carbide layer may reduce the stress gradient and/or magnitude between the substrate and the diamond films, providing for better adhesion.

4.4. Graded interlayer to improve the adhesion

Applications of different types of interlayers between the diamond layer and the substrate to improve adhesion properties are well documented [16,23,34,35], and among them, a TiN layer is frequently used. However, preliminary work found that with the application of a TiN layer or plasma nitriding of a Ti substrate, delamination easily occurs at the interface due to the large mismatch in thermal expansion coefficient between titanium nitride and the diamond coating, and the large differences in crystal structures between diamond coating and TiN phases [22,31,36]. Since plasma nitriding can provide a diffusion-barrier layer for hydrogen and carbon atoms, it can be used as the first step for diamond deposition. On the top of the plasma nitrided layer, plasma carbonitriding with variable (CH$_4$/N$_2$) gas mixtures can provide a graded carbonitride and carbide layer, which serves as the precursor for the nucleation and growth of diamond crystals [22]. Fig. 13 shows the cross-sectional morphology, indicating the gradual changes of the microstructure from the plasma nitrided layer, plasma carbonitrided layer through to the diamond coating. The residual stress obtained from Raman tests was only approximately 1.1 GPa, and compressive. Fig. 14 shows the indentation morphology of the graded coating. It can be observed that even though there are some circular cracks as well as radiating cracks (revealing the brittle nature of the deposited diamond coating), there is no spallation or delamination indicating a relatively good adhesion property. A continuous compositionally graded interlayer TiC/TiCN/TiN layer can eliminate the interfacial cracking by homogenizing the stress distribution, facilitate good bonding and improve the load bearing capacity. The pre-nitriding/carbonitriding treatment can prevent the rapid diffusion of carbon and hydrogen into the substrate, increase the hardening depth, impart better chemical stability to a titanium substrate, and also provide an excellent supporting layer for diamond coatings.

5. Conclusions

1. Diamond coatings synthesized on titanium showed large compress stress on the order of a few GPa, TiC layer showed the compressive stress in TiC and Ti substrate showed tensile stress.
2. With the increase of deposition duration from 8 to 21 h, the compressive residual stress decreased. The higher the plasma power, the higher the residual stress. The higher concentration of CH$_4$ in the gas mixture resulted in a larger compressive stress in the film due to a higher non-diamond carbon content.
3. The calculated thermal stress in the diamond coating was larger than the measured data, and this is probably because (1) the lower yield stress of pure Ti could allow a partial relaxation of the high thermal stress; (2) the lower yield stress of pure Ti could allow a partial relaxation of the high thermal stress; (3) the existence of a TiC interlayer between the diamond and Ti substrate.

4. The large residual stress in the diamond coating resulted in poor adhesion of the coatings to the substrate, but adhesion was also related to other factors, such as the thickness and nature of the TiC interlayer, the diamond grain size, orientation, etc.

5. A graded interlayer before diamond deposition was proposed to lower the thermal stress and improve the adhesion strength.

References