

Deposition of diamond coating on pure titanium using micro-wave plasma assisted chemical vapor deposition

YONGQING FU, BIBO YAN, NEE LAM LOH

Materials Lab, School of MPE, Nanyang Technological University, Singapore, 639798

CHANG Q. SUN, PETER HING

School of SAS, Nanyang Technological University, Singapore, 639798

The nucleation and growth of diamond coatings on pure Ti substrate were investigated using microwave plasma assisted chemical vapor deposition (MW-PACVD) method. The effects of hydrogen plasma, plasma power, gas pressure and gas ratio of CH₄ and H₂ on the microstructure and mechanical properties of the deposited diamond coatings were evaluated. Results indicated that the nucleation and growth of diamond crystals on Ti substrate could be separated into different stages: (1) surface etching by hydrogen plasma and the formation of hydride; (2) competition between the formation of carbide, diffusion of carbon atoms and diamond nucleation; (3) growth of diamond crystals and coatings on TiC layer. During the deposition of diamond coatings, hydrogen diffused into Ti substrate forming titanium hydride and led to a profound microstructure change and a severe loss in impact strength. Results also showed that pre-etching of titanium substrate with hydrogen plasma for a short time significantly increased the nuclei density of diamond crystals. Plasma power had a significant effect on the surface morphology and the mechanical properties of the deposited diamond coatings. The effects of gas pressure and gas ratio of CH₄ and H₂ on the nucleation, growth and properties of diamond coatings were also studied. A higher ratio of CH₄ during deposition increased the nuclei density of diamond crystals but resulted in a poor and cauliflower coating morphology. A lower ratio of CH₄ in the gas mixture produced a high quality diamond crystals, however, the nuclei density and the growth rate decreased dramatically. © 1999 Kluwer Academic Publishers

1. Introduction

Loosening of the device is the most common failure mode for prosthesis and tends to cause wear, corrosion, fretting, fracture and inflammation [1]. Titanium alloys are widely used as the prosthesis materials due to a good combination of mechanical properties, corrosion resistance, high elastic modulus and low density [2]. Ti-6Al-4V is used extensively in femoral prosthesis because of its high strength compared to pure titanium. However, the known toxicity of vanadium and the association of aluminum with numerous neurological disorders have raised considerable concerns about the safety of this alloys. Moreover, titanium alloys are notorious for their poor tribological properties [3].

The deposition of a well adherent diamond coating is a promising way to solve these problems. Diamond (or carbon) is highly biocompatible and has emerged as a potential biomaterial [4, 5]. The extreme hardness and inertness, superior heat conductivity, good biocompatibility and low friction coefficient of diamond coating may help to protect the titanium substrate. The diamond-coated titanium implants have been successfully implanted into the body of a pig for 52

weeks showing a good biotolerance and high resistance against corrosion and metallosis [6]. However, there is still extensive work to be done before the successful application of diamond-coated titanium implants, for example, the improvement of adhesion between diamond coating and Ti substrate, the homogeneous and large-area deposition of diamond coating on irregular-shaped implants [7, 8].

The reaction gases used in PACVD diamond deposition contain relatively low concentrations of volatile carbon compounds with a high concentration of hydrogen. Atomic/ionic hydrogen is important for the growth of diamond coating [9]. It etches graphite and/or suppresses gaseous graphite precursors and promotes the formation of diamond [10]. However, it is well known that hydrogen is easy to dissolve into Ti substrate and form titanium hydrides, which have a strong influence on the microstructure and mechanical properties [11, 12]. It is also worth to study the effects of the reactant layers, such as carbides, on the properties of diamond coatings.

The aim of this research work is to deposit diamond coatings on pure Ti substrate using microwave plasma assisted chemical vapor deposition (PACVD) method.

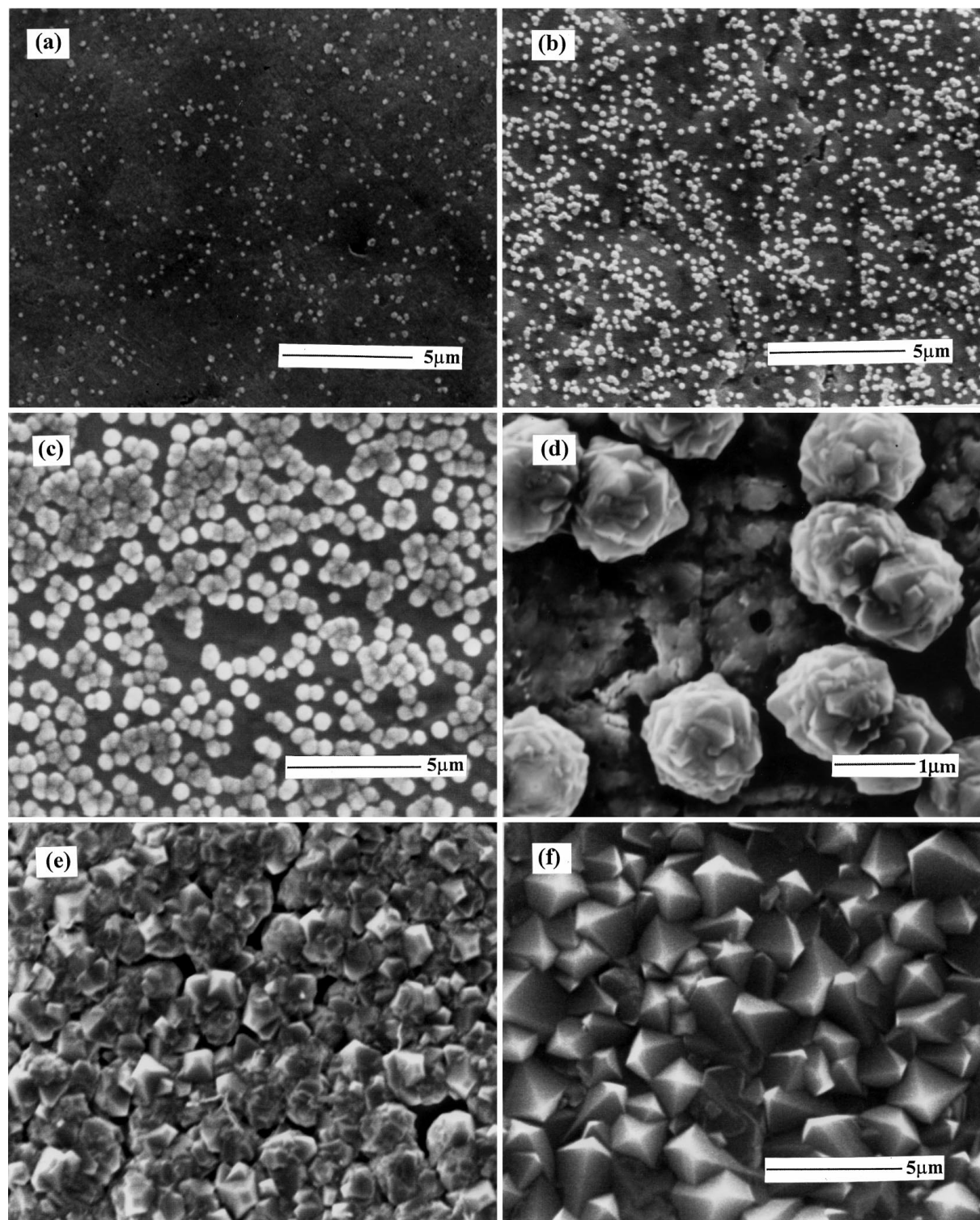


Figure 1 The surface morphology of diamond nucleation and growth with the different deposition duration. (a) After 30 minutes; (b) after 1 hour; (c) after 4 hours; (d) secondary nucleation on diamond crystals; (e) after 8 hours; (f) after 12 hours indicating the formation of a well-faceted diamond coating (deposition conditions: plasma energy of 1 kW, gas pressure: 30 Torr, gas ratio of 196 : 4).

The effects of hydrogen, plasma power, gas pressure and gas ratio of CH_4 and H_2 on the nucleation and growth, microstructure and mechanical properties of diamond coatings were investigated.

2. Experimental

Pure titanium plate with a thickness of 3 mm was mechanically ground with sand papers and polished with diamond pastes (6 to 1 μm), then ultrasonically cleaned by acetone and ethanol before deposition. Deposition

of diamond coating on Ti substrate was carried out by a MPS4 microwave plasma assisted diamond CVD system (Coaxial Power Systems Ltd., UK). The output frequency was 2.45 GHz. The detailed experimental parameters used in the deposition are listed in Table I. The surface temperature of substrate during the deposition of diamond coating was monitored by an optical pyrometer.

The surface morphology of the deposited coating was investigated by a JEOL scanning electron microscope attached with energy dispersive X-ray spectrometry

TABLE I Deposition conditions for diamond coatings on Ti substrate

Microwave power	1 and 2.2 kW
CH ₄ /H ₂	0.5, 1, 2, 5, and 10%
Gas pressure	30 and 50 Torr
Deposition time	30 min to 12 h
Pre-treatment by H plasma	15 min, 4 h and 12 h

(EDX). The coating quality was evaluated with a micro-Raman spectroscopy with the 514.5 nm line of Argon ion laser [13]. The internal stresses in diamond coatings were estimated from the quantity of diamond Raman line shift, $\Delta\nu$, with the following expressions [14, 15]:

$$\sigma = -2.63 \times 10^{10} \Delta\nu \quad \text{for } \{100\} \quad (1)$$

$$\sigma = -1.0 \times 10^{10} \Delta\nu \quad \text{for } \{111\} \quad (2)$$

The coating crystalline structure was obtained by X-ray diffraction with CuK α 40 kV/30 mA. Micro-hardness measurement was performed by a Vickers hardness tester with the normal loads of 300, 500 and 1000 g, respectively. The adhesion strength of diamond coatings on Ti substrate was evaluated by a scratch tester (with a load rate of 100 N/min and speed of 10 mm/min) and a Rockwell indentation tester (with a normal load of 150 kgf). The mechanical properties of hydrogen treated samples as well as the diamond coated Ti substrate were evaluated by a Charpy impact tester. The dimension of the specimen for impact test is 10 × 3 × 80 mm³ with a V-notch depth of 3 mm.

3. Results

3.1. Nucleation and growth of diamond coatings

Nucleation and growth of diamond coating on Ti substrate was investigated by using the following process

parameters: a plasma power of 1 kW, gas ratio of 196 : 4 (H₂/CH₄) and gas pressure of 30 Torr. Firstly, diamond coatings were deposited on Ti substrate without polishing with diamond pastes. Results showed that after about 2 to 3 hours, only a few diamond crystals nucleated on the titanium substrate. With the successive application of 6, 3 and 1 μm diamond pastes during polishing as well as ultrasonically cleaning with diamond dust, the nucleation rates have been increased dramatically. After deposition for about 30 minutes, many diamond crystals have nucleated on titanium surface as shown in Fig. 1a. The reasons for the significant increase in nuclei density after polishing with diamond pastes have been well explained by other researchers [16, 17], which include: (1) seeding; (2) minimization of interfacial energy on sharp convex surfaces; (3) breaking of a number of surface bonds; (4) strain field effects; (5) removal of surface oxides, etc. Experimental results also show that there is no indication of scratch paths being the preferred sites of diamond nucleation on titanium substrate.

Fig. 1a to f show the surface morphology of diamond nucleation and growth with the different deposition duration from 30 minutes to 12 hours. Nuclei densities, n_d , were estimated by counting the number of crystallites observed within a specific unit area visible under the scanning electron microscope. Fig. 2 shows the calculated nuclei densities of diamond particles and the average size of diamond crystals with the change of deposition duration. Both Figs 1 and 2 indicate that the nuclei density increases significantly at the beginning period, reaches a maximum value at about 1 hour and then gradually declines due to growth, coalescence, and secondary nucleation (see Fig. 1d) of diamond crystals, as well as the etching effect of hydrogen plasma. Almost Continuous thin films can be obtained by prolonging the deposition time for 8 hours (see Fig. 1e). After 12-hour deposition, a dense and well-faceted diamond coatings

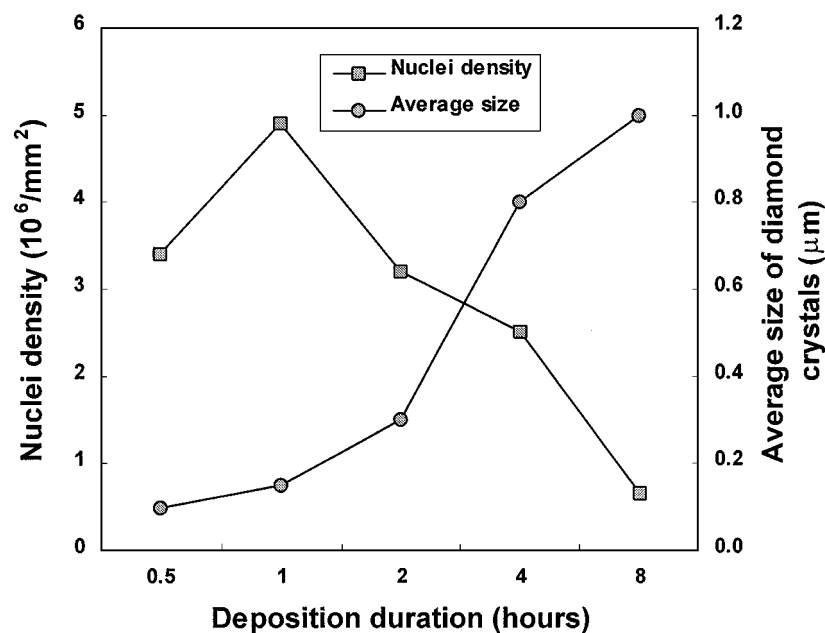


Figure 2 The nuclei density of diamond crystals with the increase of deposition duration (deposition conditions: plasma energy of 1 kW, gas pressure: 30 Torr, gas ratio of 196 : 4).

were obtained as shown in Fig. 1. SEM observation demonstrates that the diamond coatings are polycrystalline in nature with the dimension of the diamond crystals around $1\ \mu\text{m}$. The highly faceted surface morphology and the predominant $\{1\ 1\ 1\}$ orientation are also the typical characteristics of diamond films deposited under the above deposition conditions.

EDX analysis indicate that before the nucleation of diamond crystals, carbon atoms can diffuse into the substrate forming TiC phase. XRD analysis on the titanium substrate deposited for 1 h reveals the formation of TiC and TiH₂ phases in the diamond coatings as shown in Fig. 3a. Titanium is an active carbide/hydride-forming chemical element. During the PACVD process, the carbon and hydrogen atoms/ions will react with the

surface Ti atoms easily and form the titanium carbide and titanium hydride before the nucleation of diamond crystals. Low-angle XRD analysis (i.e., with thin-film attachment) of diamond coatings deposited for 12 h with X-ray impinging angles of 1° , 3° and 9° are shown in Fig. 3b. XRD diffraction patterns confirm the formation of pure polycrystalline diamond coating on the surface layer. Beneath the diamond coating, there is a titanium carbide and titanium hydride layer. The content of titanium hydride is still high after about 12-hour deposition. The $(1\ 1\ 1)$ peak of diamond is much stronger than (220) peak.

The Raman spectrum of diamond coating deposited for 12 hours are shown in Fig. 4a, which clearly demonstrates the presence of the characteristic diamond and

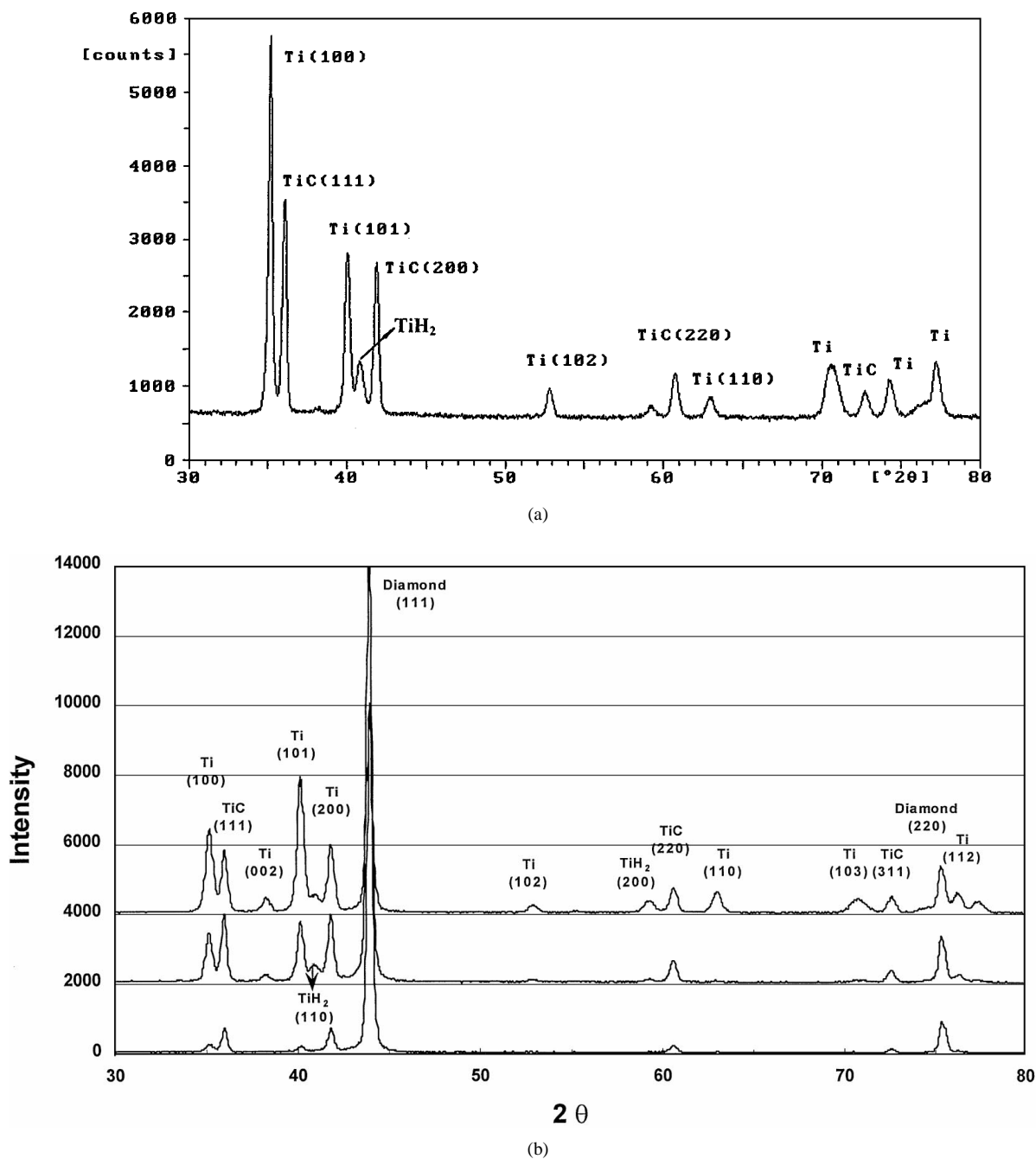


Figure 3 XRD analysis of the growth of diamond coating on Ti substrate. (a) Ti substrate with 1-hour diamond deposition indicating the formation of TiC and TiH₂ phases; (b) low angle XRD analysis of diamond coating deposited for 12 hours indicating the existence of TiC and TiH₂ phases (deposition conditions: plasma energy of 1 kW, gas pressure: 30 Torr, gas ratio of 196 : 4).

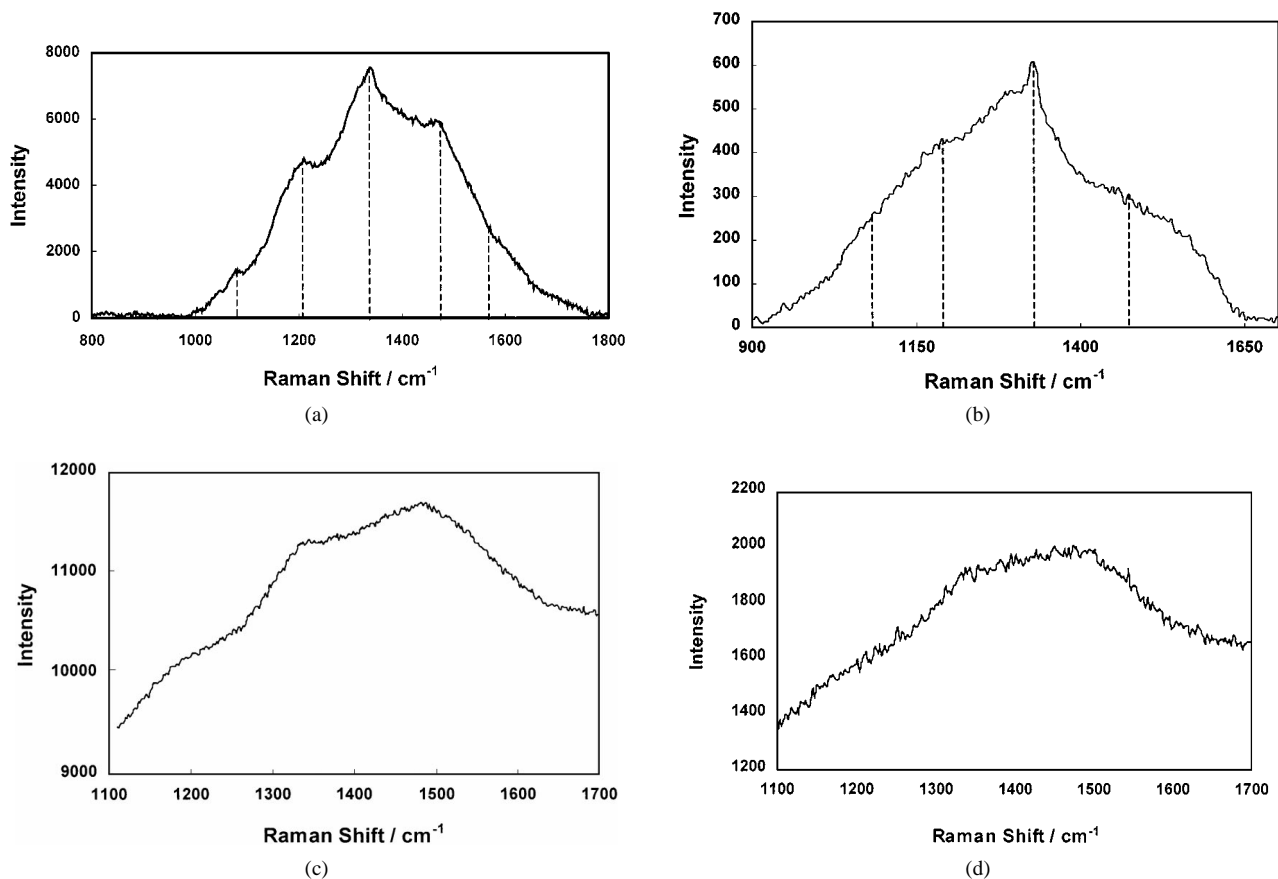


Figure 4 Raman analysis on the deposited diamond coatings. (a) Coating deposited under a plasma power of 1 kW, gas pressure of 30 Torr, gas ratio of 196 : 4; (b) coating deposited under a plasma power of 2.2 kW, gas pressure of 30 Torr, gas ratio 196 : 4; (c) coating deposited under a plasma power of 1 kW, gas pressure of 30 Torr, gas ratio of 19010; (d) coating deposited under a plasma power of 1 kW, gas pressure of 30 Torr, gas ratio of 180 : 20.

diamond-like phases in the deposited coatings. There is a sharp peak at about 1341.8 cm^{-1} which corresponds to the diamond peak. The frequency-shift of the diamond peak indicate the existence of a residual compressive stress of approximately 9.8 GPA. The peak at about 1220 cm^{-1} corresponds to the micro-crystalline structure of diamond. There is also a small peak at 1130 cm^{-1} which corresponds to Raman spectrum for nanocrystalline diamond. Raman bands around 1470 and 1550 cm^{-1} are attributed to sp^2 -bonded carbon.

Cross-section observation reveals the microstructure changes of titanium substrate during the deposition. The untreated titanium possess a polygonal grain structure with hexagonal α -grains (see Fig. 5a). Fig. 5b shows the microstructure of Ti substrate with diamond deposition for 12 hours indicating the phase transformation and significant coarsening of the α -Ti structure. It is believed that the hydrogen adsorption in Ti substrate under the diamond deposition conditions decreases the temperature for the α - β transformation [18,19]. Therefore, at a relatively low deposition temperature of 700 to $800 \text{ }^\circ\text{C}$, titanium substrate will transform into the cubic β phase and accelerated grain coarsening will occur. During a cooling in a vacuum chamber, the β - α transformation generates a martensitic grain structure with large α -martensitic plates embedded in a matrix of small α -martensitic and titanium hydride needles (see Fig. 5b).

Fig. 5c shows the high-magnification microstructure of diamond coating layer which clearly shows the

existence of three different layers: the diamond coating, the TiC layer and heat-affected and carbon/hydrogen diffused Ti layer [20]. The diamond coating is about $10 \mu\text{m}$ thick and is dense and homogeneous. TiC layer, with a thickness of a few microns, is porous and rough which is easily moved away during the grinding and polishing processes. Microhardness measurement reveals that beneath the TiC layer, there is a hardened zone in Ti substrate with a thickness of about $20 \mu\text{m}$, which is generated by the diffusion of carbon or hydrogen into the titanium substrate.

3.2. Effects of hydrogen on the microstructure and mechanical properties of diamond coatings

Hydrogen is important for the growth of diamond coating but it causes the embrittlement of Ti substrate. In order to qualify this embrittlement effect, pure hydrogen plasma, and/or the diamond deposition conditions, were reproduced in a furnace and applied to the V-notched impact specimens for 4 and 12 hours.

Pure hydrogen plasma has a significant etching effect on Ti substrate surface as shown in Fig. 6a. Fig. 6b shows the cross-section microstructure of hydrogen etched titanium substrate for 4 hours. Near the surface, there is a hydride-forming layer which composed of numerous hydride needles as shown in Fig. 6c and d. Beneath this hydride layer, the microstructure is the extremely coarse α -Ti plates embedded in a matrix of tiny

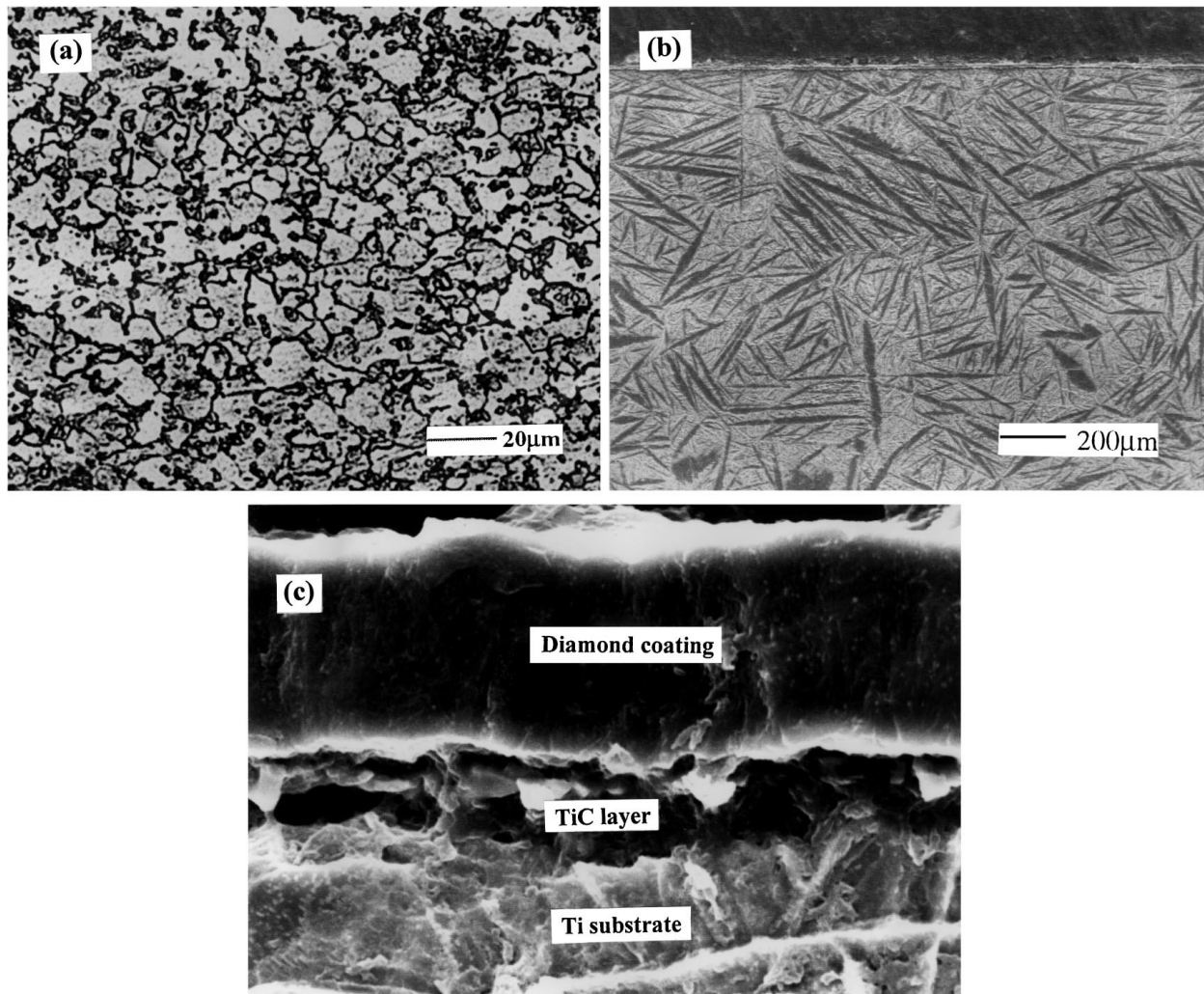


Figure 5 Cross-section observation of the microstructure of untreated, diamond coated Ti substrate and diamond coating. (a) Untreated Ti substrate; (b) Ti substrate with diamond deposition for 12 hours; (c) diamond coating indicating of the existence of three layers.

α -Ti plates and hydride needles. Low-angle XRD analysis (shown in Fig. 7) on the 4-hour hydrogen-etched Ti samples clearly reveals the formation of TiH_2 and $\text{TiH}_{1.924}$ phases. With an increase in the penetration depth, it can be observed that titanium hydrides always exist in titanium substrate. With an increase of the hydrogen etching duration from 4 to 12 hours, the content of hydride increases significantly.

Fig. 8 shows the Charpy impact values, α_k , of three types of specimens, i.e., titanium substrate, titanium treated with hydrogen plasma and titanium with deposition of diamond coating for 12 hours. With the deposition of diamond coatings on the titanium specimen, the impact energy drops dramatically. This is attributed to the significant coarsening of the microstructure of Ti substrate after the deposition of diamond coating. A more significant decrease in impact strength can be found for the hydrogen plasma treated specimens. The reason is attributed to the embrittlement of Ti substrate due to hydrogen interstitial diffusion and the formation of titanium hydride needle as well as the significant coarsening of the titanium microstructure [21]. SEM observation on the fractured surface reveals the ductile to brittle changes after the hydrogen plasma treatment and diamond deposition. Fig. 9a shows the fracture surface of untreated Ti substrate showing the

ductile fracture mode with elongated dimples. The fracture surfaces of diamond coated and hydrogen etched Ti specimens show a typical brittle fracture mechanisms. Fig. 9b shows the fracture surface of diamond coated specimen indicating the fracture along many large and coarse α -Ti plates. Examination on the fracture surfaces of hydrogen plasma treated specimen shown in Fig. 9c reveals that the fracture occurs along numerous hydride needles as well as the coarse titanium substrate.

The impact strength of hydrogen plasma treated specimen and diamond coated specimen can be restored slightly by a dehydrogenation annealing treatment at a temperature of 800°C under a vacuum chamber (see Fig. 8). However, examination on the impact fracture surface of annealed specimen reveals no much difference for the fracture mechanisms before and after annealing treatment. The slightly increase in the impact strength is probably attributed to the removing of the interstitial hydrogen and decomposition of titanium hydride during annealing processes [22]. However, this annealing treatment can not change the nature of the coarse structure, thus no much contribution to the increase in the impact strength. Studies are being done on how to recrystallization of coarse microstructure after diamond deposition but not to cause the peeling of diamond coating during treatment.

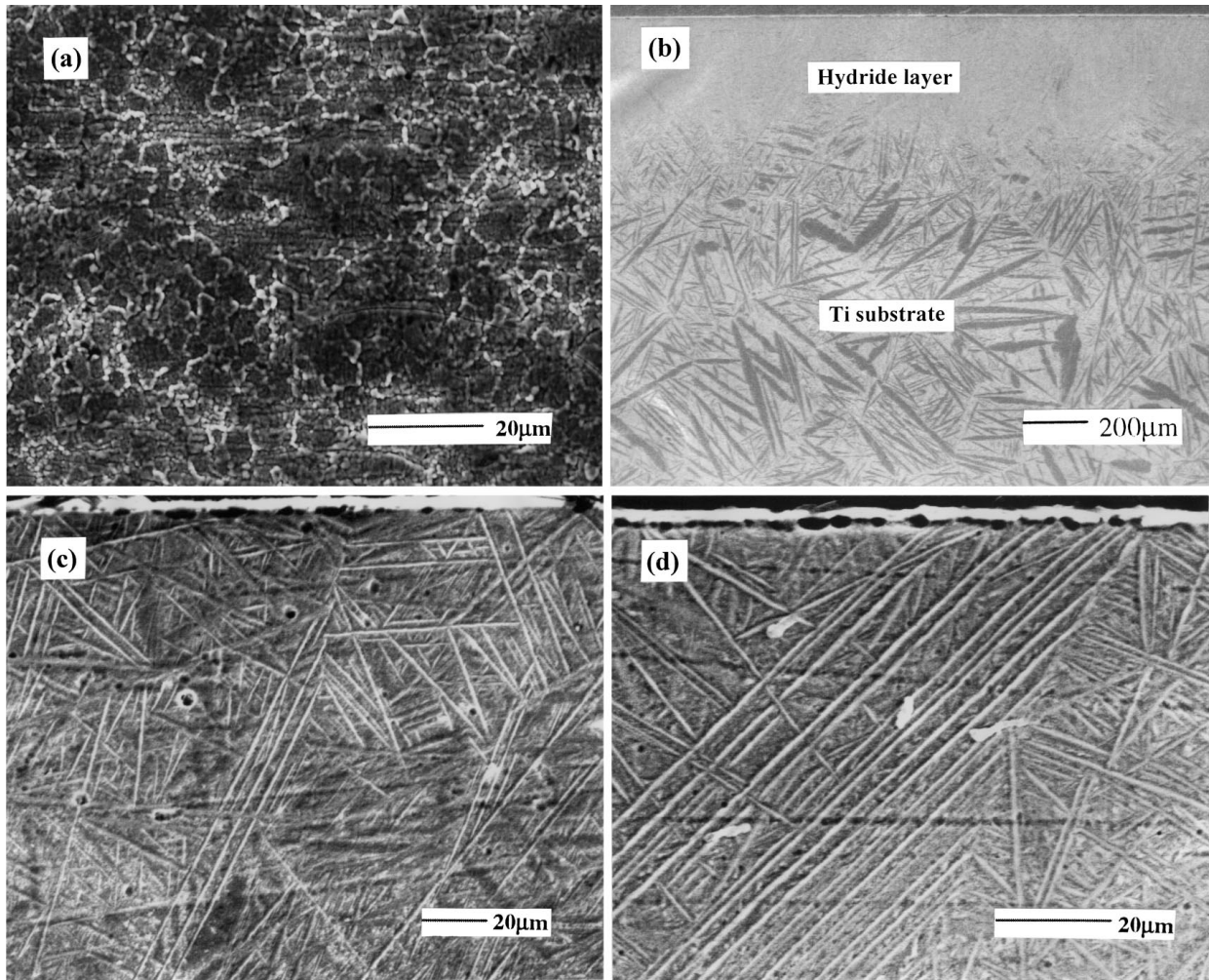


Figure 6 Effect of hydrogen plasma on the microstructure of Ti substrate. (a) Surface etching effect (pure hydrogen plasma for 4 hours); (b) cross-section of hydrogen etched Ti substrate; (c) and (d) numerous hydride needles existed on the surface layer.

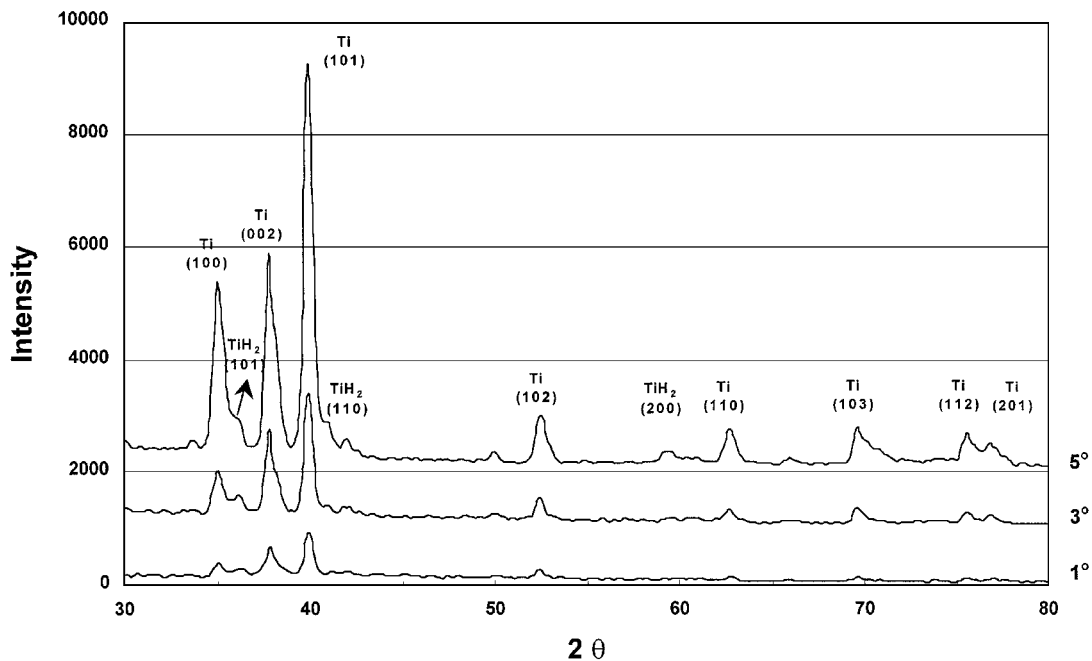


Figure 7 Low-angle XRD results on hydrogen etched Ti surface (4 hours) indicating the existence of titanium hydrides.

A very interesting observation is that pre-etching with hydrogen plasma for a short time can significantly increase the nuclei density of diamond crystals during the following deposition. In our tests, Ti samples

were hydrogen etched for about 15 minutes, then used for the deposition of diamond coatings. Fig. 10a shows that after fifteen-minute deposition, there are many diamond crystals formed on the pre-etched surface. After

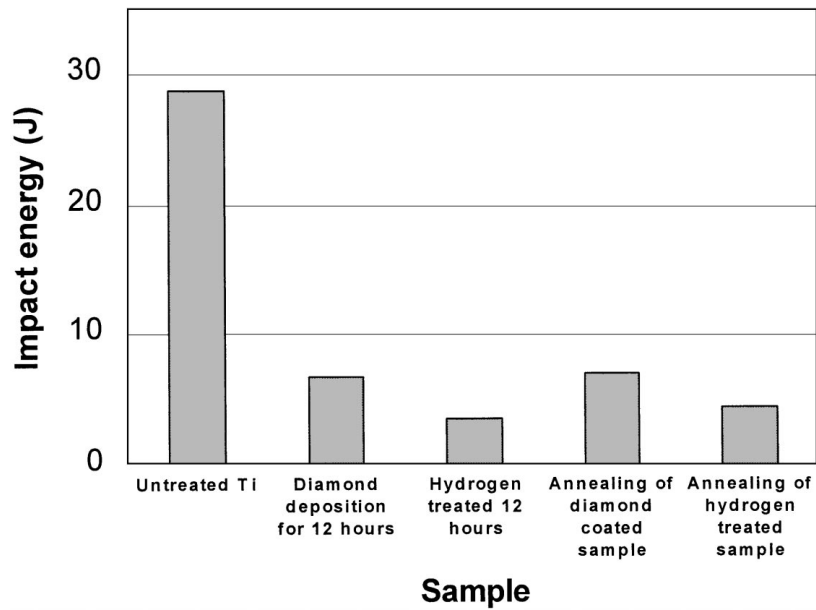


Figure 8 Charpy impact values of three types of specimens: untreated Ti substrate, titanium substrate with diamond coated for 12 hours and Ti substrate with hydrogen plasma treated for 12 hours.

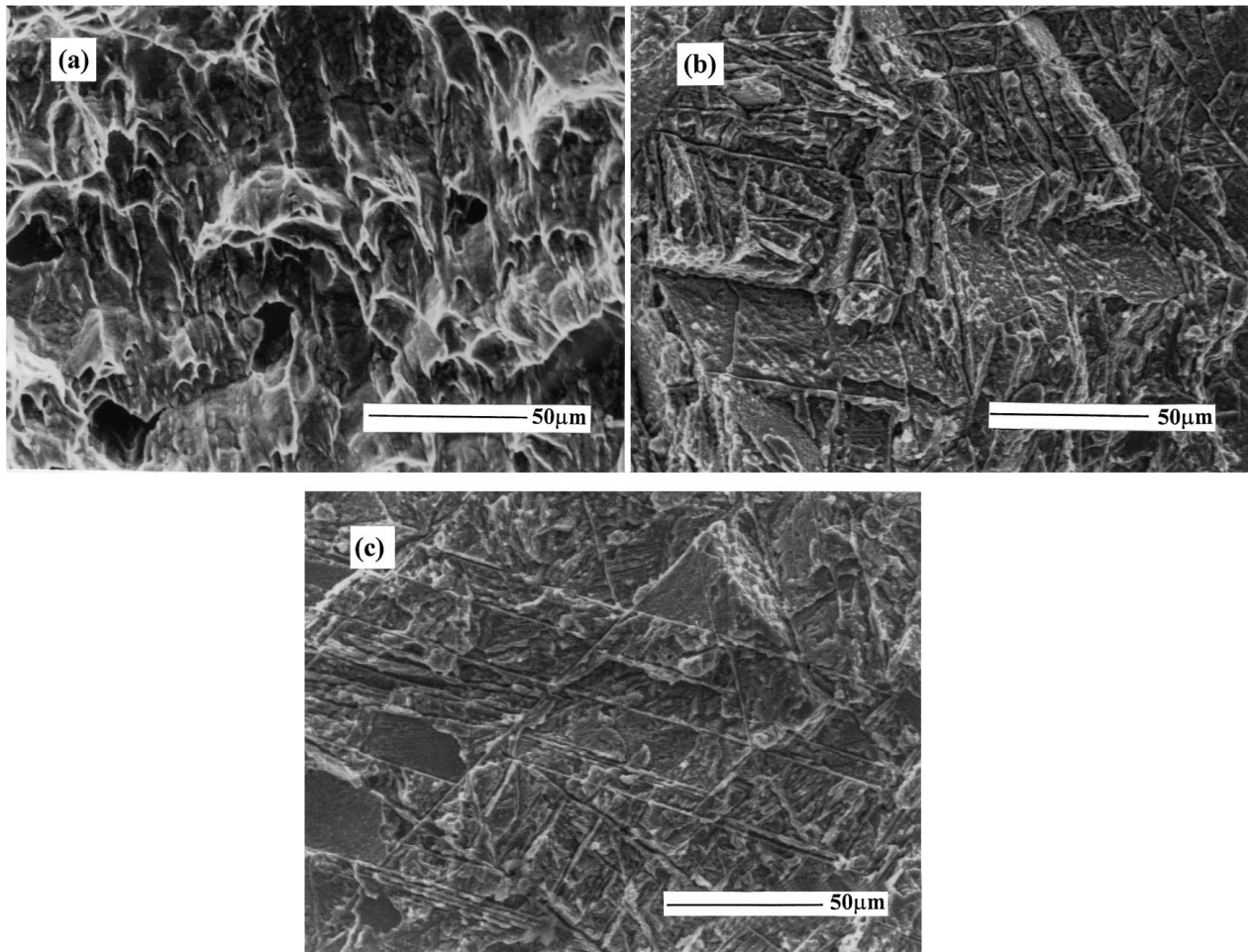


Figure 9 The morphology of the fracture surfaces. (a) Untreated Ti substrate; (b) Ti with diamond deposition for 12 hours; (c) Ti with hydrogen plasma treated for 12 hours.

another 15 minutes, almost all the surface are covered with nucleated diamond particles (see Fig. 10b). Compared with Fig. 1a and b, it can be observed that the nucleation rate of diamond crystals has been increased significantly with pre-hydrogen plasma etching for a

short time. The reasons why the nucleation rates are increased with the pre-hydrogen plasma treatment can be attributed to: (1) after the plasma etching, the surface become rough, which probably provide nucleation sites for the deposition of diamond crystals; (2) due to the

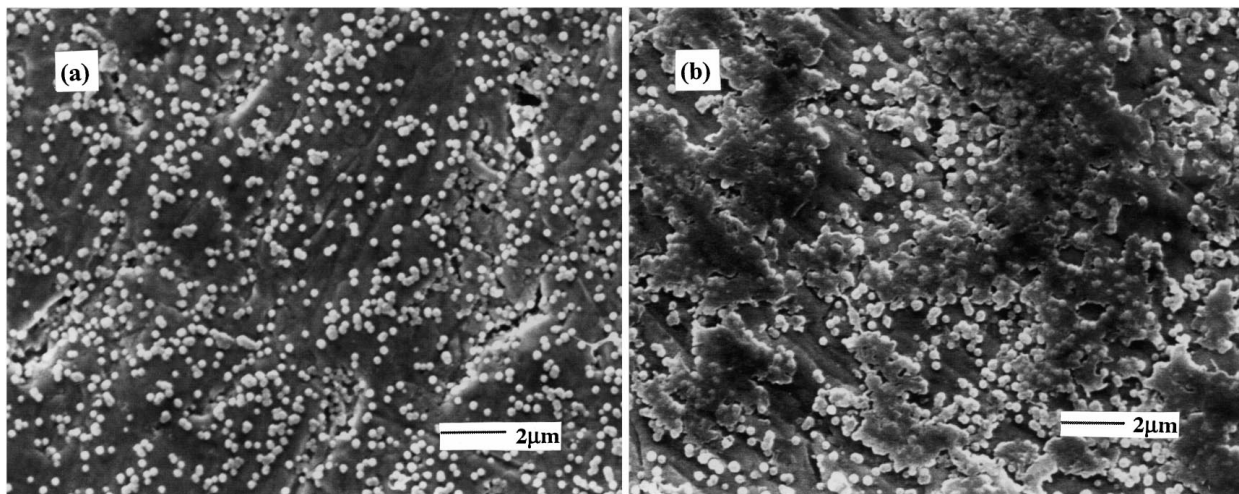


Figure 10 The nucleation of diamond crystals on the pre-hydrogen etched Ti surface. (a) Deposition for 15 minutes; (b) deposition for 30 minutes.

reaction of hydrogen plasma with titanium, hydrogen can diffuse into titanium substrate and combine with titanium forming the hydride on the surface layer. When the carbon atoms arrive on Ti surface, they are not so easily to react with Ti atoms forming TiC phase, and they will be etched by hydrogen plasma forming the diamond crystals thus increasing the nucleation rate. However, pre-etching with hydrogen is not good since the involvement of hydrogen will cause severe loss in impact strength.

3.3. Effect of plasma power on growth of diamond coating

The microwave power density is an important parameter which controls the H and C atom concentration and plays a crucial role in the quality and growth rate of diamond coatings [23]. Fig. 11a shows the surface morphology of Ti specimen treated after 4-hour deposition under a plasma power of 2.2 kW (gas ratio of 196 : 4 (H_2/CH_4), gas pressure of 30 Torr). EDX analysis reveals that some diamond particles form on the rough TiC layer. The nuclei density is observed much lower under a very high plasma power (optical pyrometer

shows the surface temperature can reach to 1200 °C). XRD analysis shows the strong peaks of TiC indicating that under high plasma power, formation of titanium carbide is more predominant as shown in Fig. 12.

Fig. 11b shows the surface morphology of diamond coating deposited for 12 hours indicating the preferred orientation of (1 0 0) and well-faceted diamond crystals under an extremely high plasma power. The reason for this phenomenon has not been obtained. There are many cracks formed on the surface and some part of the coating peels off from the substrate indicating an extremely large residual stress existed in the diamond coating [24]. Raman analysis confirms that under a high plasma density, the coating quality is good as shown in Fig. 4b. There is a sharp peak in Raman spectroscopy at about 1335.2 cm^{-1} which corresponds to the diamond peak indicating a much higher residual stresses existed in the coatings. The calculated residual stresses in coating is about 8.416 GPa and is less than that of the coating deposited under 1 kW, which is because of the stress relaxation due to the cracking and peeling-off of the coating. The sp^2 -type peak is very weak indicating the relatively pure diamond crystals formed under high temperature.

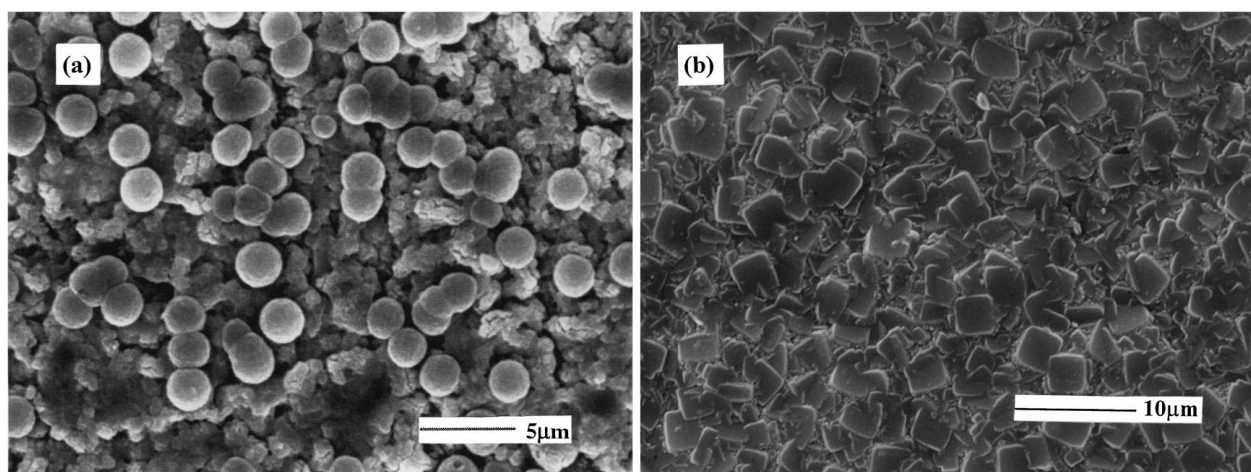


Figure 11 Surface morphology of the diamond coating deposited under a high plasma power of 2.2 kW (gas pressure 30 Torr, gas ratio of 196 : 4). (a) Deposition for 4 hours; (b) deposition for 12 hours.

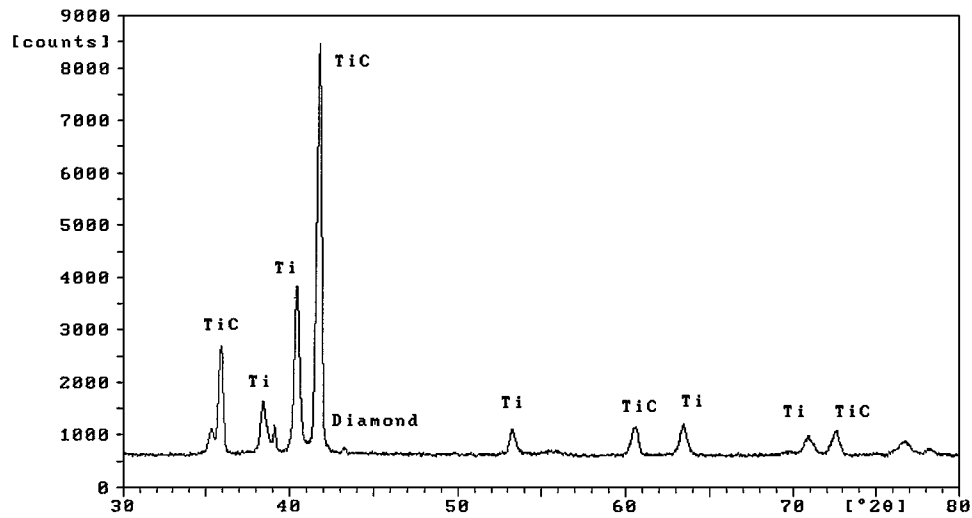


Figure 12 XRD analysis on diamond coating deposited under a high plasma power of 2.2 kW for 4 hours.

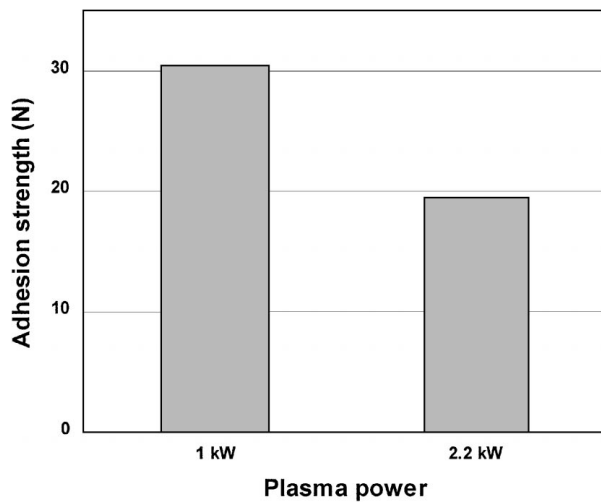


Figure 13 The comparison between the adhesion strength of diamond coatings deposited under 1 kW and 2.2 kW respectively (gas pressure 30 Torr, gas ratio of 196 : 4).

The scratch tests were performed for diamond coatings deposited under different plasma powers. The critical loads, i.e., the adhesion strength of diamond coatings under two deposition conditions are shown in Fig. 13. Diamond coating deposited under a high plasma power of 2.2 kW shows a very poor adhesion strength. The poorer adhesion strength under high plasma energy density can be explained by the high thermal stresses existed in the diamond coating and the high content of porous TiC phases existed between diamond coatings and Ti substrate.

3.4. Effect of the total gas pressure

Two types of gas pressures have been used in this study, i.e., 30 and 50 Torr. Fig. 14 shows the surface morphology of the diamond coatings deposited under 50 Torr (gas ratio 196 : 4 (H_2/CH_4)) and plasma power of 1 kW). Compared with diamond coating deposited

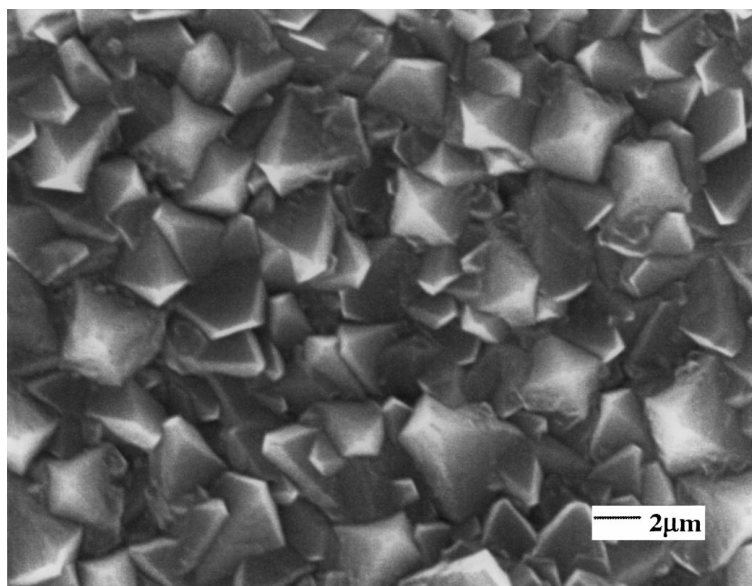


Figure 14 The surface morphology of the coating deposited under a gas pressure of 30 Torr and gas ratio of 196:4 and plasma power of 1 kW.

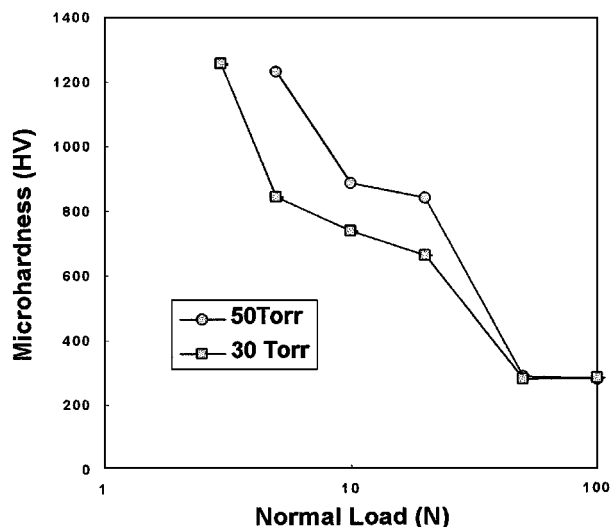


Figure 15 The microhardness results for coatings deposited under different gas pressures: 30 Torr and 50 Torr (gas ratio: 196 : 4; plasma power of 1 kW).

under a gas pressure of 30 Torr shown in Fig. 1f, the crystals of the diamond coatings are a little larger at a relatively higher deposition pressure. There is no much difference in XRD pattern and Raman spectrum between the coatings deposited under two types of gas pressures. Fig. 15 shows the microhardness results for two types of the diamond coatings. The coatings prepared under a lower gas pressure of 30 Torr has a relatively higher microhardness which is probably attributed to the smaller diamond crystals in the coating.

Rockwell indentation tests were performed on the above diamond coatings under a normal load of 150 kg. After indentation, there are usually many cracks formed indicating the brittle nature of the deposited diamond coating. From Fig. 16a and b, it can be observed that there are only some circumferential cracks formed on the coating surface deposited under a gas pressure of 30 Torr. However, for the coating deposited with 50 Torr, a large-area spallation of the diamond coating

is observed. This indicates that the diamond coating deposited under a gas pressure of 30 Torr has a relatively higher adhesion strength compared with coating deposited under a gas pressure of 50 Torr. The better performance in adhesion strength for coatings deposited under a lower gas pressure is probably due to the relatively smaller crystal sizes.

3.5. Effects of gas ratio of CH₄ and H₂

The gas ratio has a significant effect on the nucleation and growth of diamond coatings. Fig. 17a to d show the surface morphology of diamond crystals deposited for one hour under different gas ratios (plasma power: 1 kW, gas pressure: 30 Torr). Under the specific testing conditions, the nuclei density of diamond crystals on Ti substrate increases with the ratio of CH₄ in the gas mixture as shown in Fig. 18. Fig. 19a to d show the surface morphology of the diamond coatings deposited for 12 hours under the different gas ratios. The optimum gas ratio under the above deposition condition is 196 : 4 (H₂/CH₄). With a decrease in gas ratio from 196 : 4 to 198 : 2, the quality and crystallinity of diamond crystals are excellent but the nucleation and growth rate of the diamond crystals is relatively lower. Fig. 17a shows the surface morphology of the diamond coatings deposited on Ti substrate under a gas ratio of 198 : 2 for 12 hours indicating only many well-faceted diamond particles existed on the surface of titanium substrate. With the gas ratio of H₂ and CH₄ increased from 196 : 4 to 190 : 10 and 180 : 20, the nucleation density and growth rate of diamond crystals increase significantly (see Figs 17 and 18). However, results show that the quality of the deposited diamond coating becomes poor and cauliflower structure (ballast-typed, poor-quality coatings) forms on the substrate rather than well-faceted diamond crystals as shown in Fig. 19b and c. Raman analysis results shown in Fig. 4 also confirms the above results. For the coatings deposited under the gas ratio of 190 : 10 and 180 : 20, two broad Raman peaks at about 1339 and 1570 cm⁻¹ were

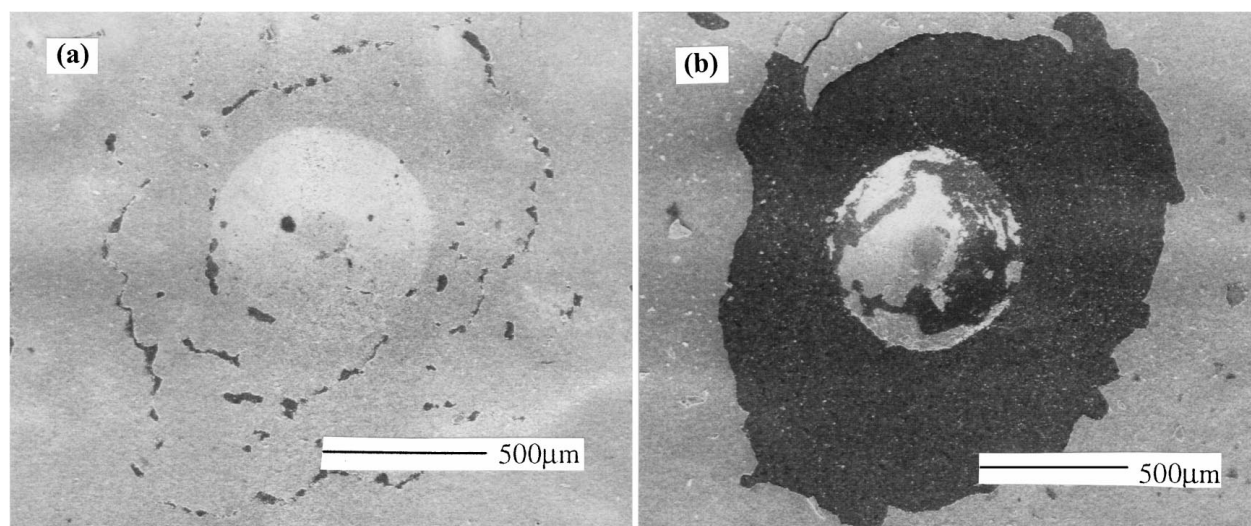


Figure 16 Surface morphology of diamond coatings after the Rockwell indentation test. (a) Coating deposited under a gas pressure of 30 Torr; (b) coating deposited under a gas pressure of 50 Torr.

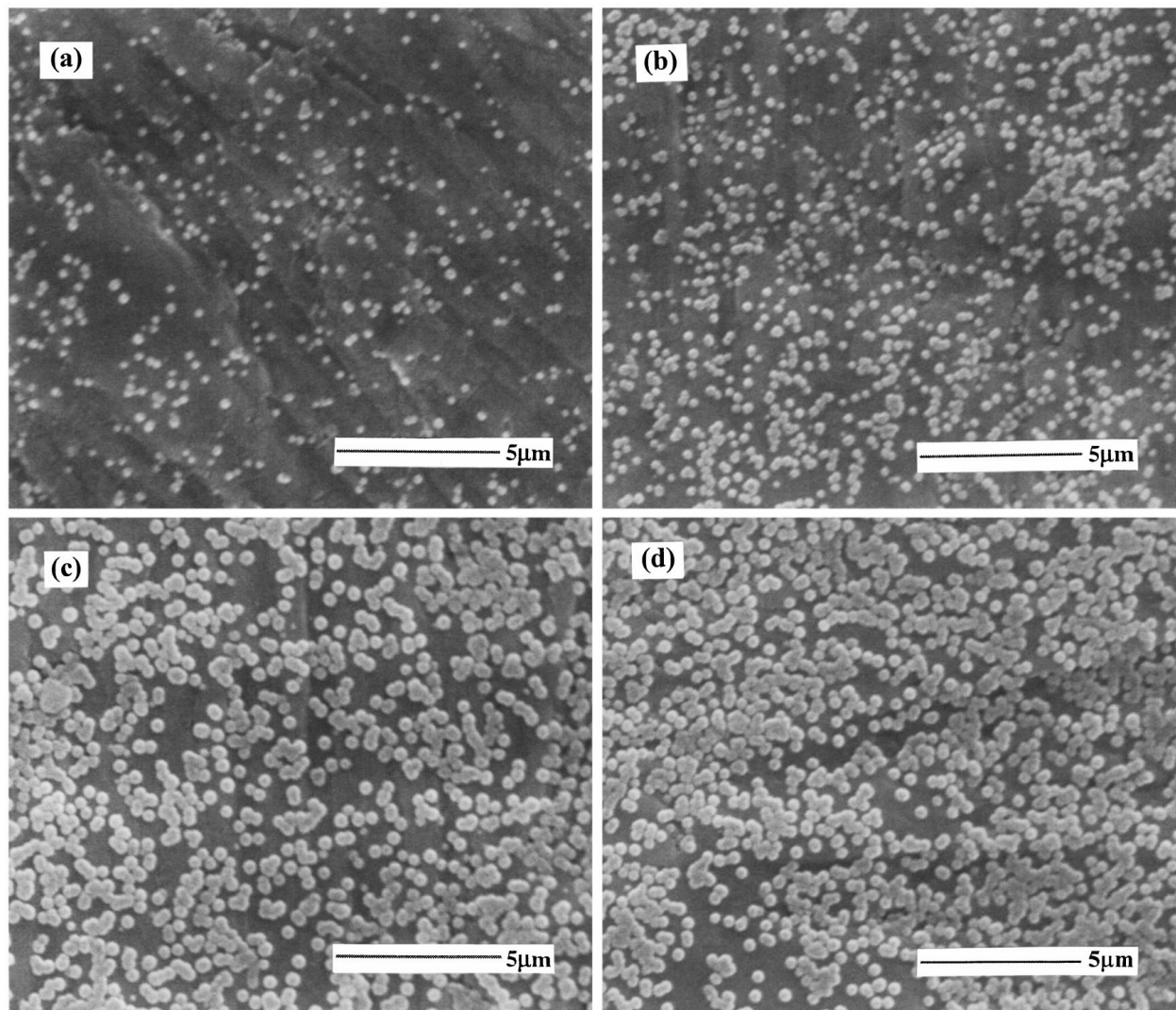


Figure 17 The surface morphology of diamond crystals deposited for one hour under different gas ratios (plasma power: 1 kW, gas pressure: 30 Torr). (a) Gas ratio: 198 : 2; (b) gas ratio: 196 : 4; (c) gas ratio: 190 : 10; (d) gas ratio: 180 : 20.

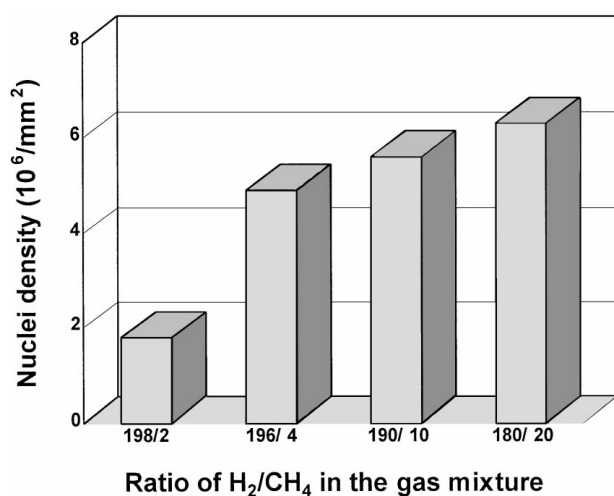


Figure 18 The nuclei density of diamond crystals on Ti substrate deposited for one hour under the different gas ratios (plasma power: 1 kW, gas pressure: 30 Torr).

found, the former from diamond (sp^3 bonding), and the latter from non-diamond carbon (sp^2 bonding). The results from Raman spectrum indicate that with an increase in CH_4 content in the gas mixture, more content

of non-diamond carbon (sp^2 bonding) formed in the diamond coating. At a gas ratio of 180 : 20 (H_2/CH_4), the Raman spectrum of the deposited coating reveals a typical characteristics of diamond-like-carbon coatings.

From the above results, it is concluded that during the nucleation of diamond crystals, the gas ratio of CH_4 to H_2 should be kept high in order to obtain the maximum nucleation density. After that, the gas ratio of CH_4 and H_2 should be reduced to a low value in order to obtain a well-faceted, good-quality diamond coating.

4. Discussions

According to the experimental results shown above, the nucleation and growth of diamond coatings on titanium substrate can be listed as follows:

4.1. Etching of hydrogen plasma and formation of hydrides

The hydrogen plasma has a significant effect on the nucleation and growth of diamond coating on titanium substrate. The etched titanium surface is thought to be good for diamond nucleation [25, 26] because the

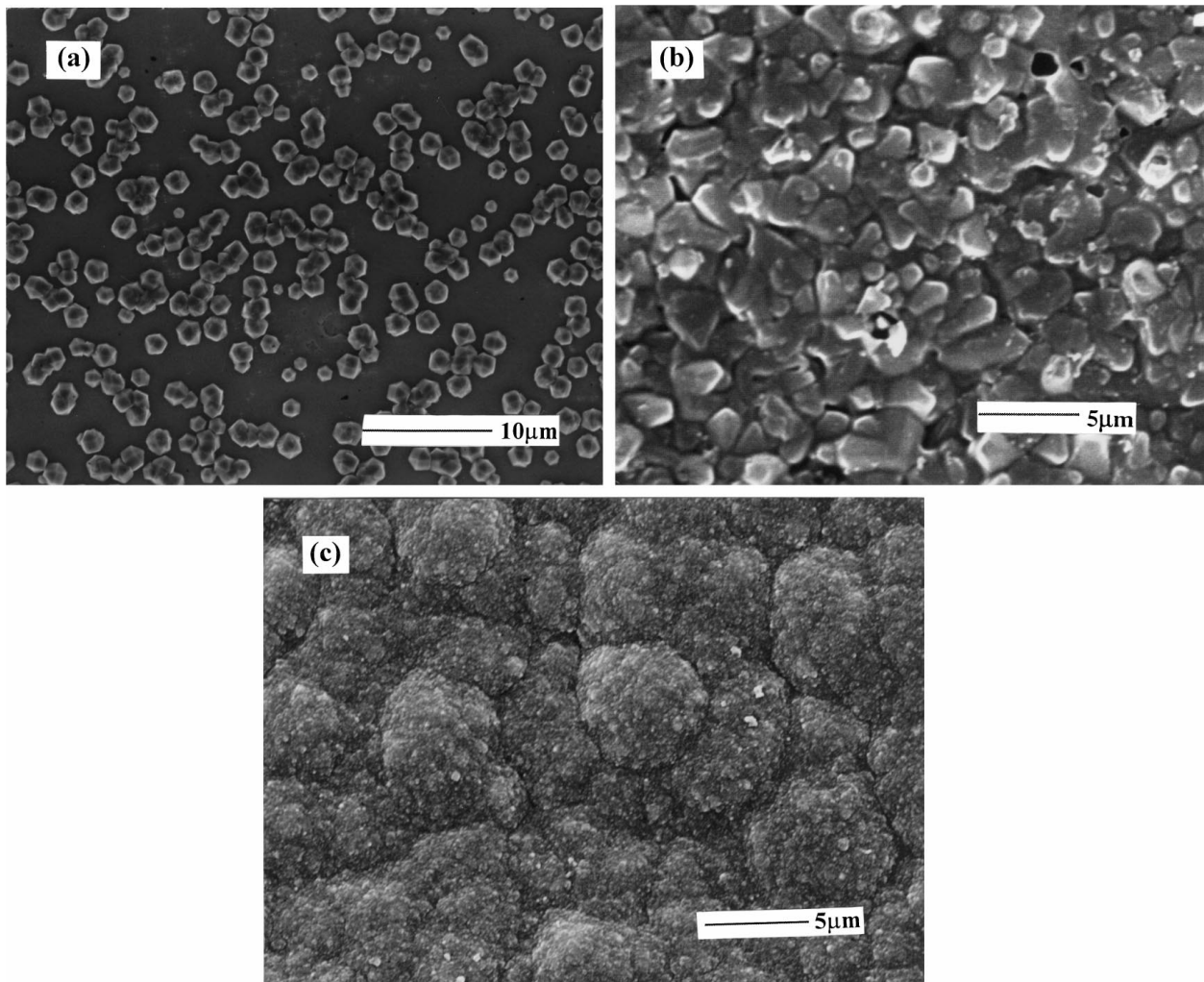


Figure 19 Surface morphology of the coating deposited for 12 hours under the different gas ratios (plasma power: 1 kW, gas pressure: 30 Torr). (a) Gas ratio of 198 : 2; (b) gas ratio of 190 : 10; (c) gas ratio of 180 : 20.

rough surfaces due to the plasma etching effect of hydrogen can provide the suitable sites for the deposition of diamond crystals. As a result of hydrogen adsorption, significant coarsening of the microstructure and the formation of titanium hydride will affect the mechanical properties and impact toughness of Ti substrate [27]. This is a disadvantage for the deposition of diamond coating on titanium substrate since it is easy to cause the fracture failure of prosthesis implants. Post heat treatments are necessary to reduce the hydrogen content and modify the microstructure of Ti substrate.

4.2. Competition between the formation of carbide and diamond nucleation

TiC formation and diamond nucleation occur almost simultaneously on Ti substrate and there is a competition between these two processes since both nucleation (and subsequent growth) of the diamond crystals and the formation of TiC phase depend on the availability of carbon [28]. It is well known that titanium is an active carbide-forming chemical element. During the PACVD process, when the carbon atom/ions arrive on the surface of the substrate, they will dissolve easily into the substrate and form TiC immediately. During the further

deposition process, more and more titanium atoms react with the arriving carbon atoms or ions forming a layer of TiC. Diamond crystals can nucleate directly on the Ti substrate or on the TiC layer. Many researchers agreed that diamond nucleation occurred on carbide layer only when the carbon concentration on the surface reaches its saturation value [29]. The competition between the formation of carbide and diamond nucleation depends on several factors, such as plasma power, surface temperature, gas ratios, gas pressure, etc. A higher plasma power or substrate temperature can promote the formation of titanium carbide and delay the early formation of diamond crystals. A higher ratio of CH_4 in the gas mixture can both promote the formation of titanium carbide and diamond crystals depending on the specific conditions.

4.3. Diamond growth on the surface of titanium carbide layer

Actually the 3D diamond growth is also a competition between the growth of diamond crystals and the diffusion of carbon into Ti substrate. The diamond crystals nucleated on the Ti substrate can easily move on the surface, grow in three dimensions, coalesce, secondary nucleation or diffuse into the substrate. From

this point of view, a copious diamond nucleation and growth rate is expected to be beneficial to reduce interfacial porosity, raise the interfacial toughness, and promote the rapid coverage of the substrate surface by diamond, which then acts as an obstacle to carbon and hydrogen penetration.

Adhesion and mechanical properties of diamond coatings are usually not good under either an extremely higher or a lower temperature. Since in the former case, the residual stress is too large, and in the latter condition, the content of micro-crystalline graphite or diamondlike is too high. Higher substrate temperature is responsible for the improvement in the quality of the diamond crystallites (in terms of reduced amount of sp^2 bonded carbon) and the faster growth rate of the diamond. However, a higher substrate temperature will cause a larger grain size of diamond and poor adhesion which is not entirely suitable for wear resistance applications.

Embedded TiC layer can be as thick or thin, porous or dense depending on the deposition conditions. A higher ratio of CH_4/H_2 content can both increase the nucleation rate of diamond crystals and the thickness of the TiC layer depending on the process conditions. Considering that the thermal expansion coefficient for TiC ($7 \times 10^{-6}/^\circ C$) is less than that of Ti-6Al-4V ($8.0 \times 10^{-6}/^\circ C$), and the CTE of diamond is about 3.2×10^{-6} , it is reasonable that stress may be reduced by a thicker carbide layer. There are some reports that the embedding layer of TiC improved the adhesion of diamond coating on Ti substrate [30]. However, this effect must depend on the nature of TiC layer. Under a high temperature, because of the formation of the porous and rough TiC layer, this layer does not contribute much to the adhesion strength and adversely results in the cracking and spallation. Therefore, optimization of processing parameters and proper design of the interface may be necessary in order to reduce and to obtain well-adhered diamond films on Ti substrate.

5. Conclusions

Diamond thin coatings were successfully prepared on Ti substrate using PACVD system. Effect of hydrogen, plasma energy density, gas pressure and gas ratio of CH_4 and H_2 on the microstructure and properties of deposited diamond coatings were evaluated. Following conclusions can be obtained:

(1) Results indicated that the nucleation and growth of diamond crystals on Ti substrate can be separated into different stages: (a) Surface etching by hydrogen plasma and the formation of hydride; (b) Competition between the formation of carbide, diffusion of carbon atoms and diamond nucleation; (c) growth of diamond crystals and coatings on TiC layer.

(2) During the deposition of diamond coatings, hydrogen can diffuse into Ti substrate and react with titanium forming titanium hydride leading to the profound microstructure changes and the severe loss in impact strength. Results also showed that pre-etching of tita-

nium substrate for a short time significantly increased the nuclei density of diamond crystals.

(3) Plasma power and total gas pressure had a significant effect on the properties of the deposited diamond coatings, which can be revealed from the adhesion strength, coating morphology, etc.

(4) A higher ratio of CH_4 increased the nuclei density of diamond crystals but resulted in a poor and cauliflower coating morphology. A lower ratio of CH_4 in the gas mixture produced a high quality diamond crystals, however, the nuclei density and the growth rate decreased dramatically.

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