Effect of bias voltage on the properties of hydrogenated amorphous carbon films fabricated on CoCrMo alloy by electron cyclotron resonance plasma enhance chemical vapor deposition (ECR-PECVD)

Xingrui Deng, Y.X. Leng *, H.Sun, Nan Huang

Abstract

In order to increase the wear resistant of the artificial joints, amorphous hydrogenated carbon (a-C:H) films have been deposited on Co-Cr-Mo alloy substrates at different bias pulsed voltage by electron cyclotron resonance plasma enhance chemical vapor deposition (ECR-PECVD). The structure and properties of a-C:H film including sp³ content, residual stress, mechanical property, adhesion force and wear resistance are examined. The results show that the sp³ content and the hardness of the a-C:H film decrease with the bias increasing. But the a-C:H film residual stress increases with bias voltage. The a-C:H film fabricated at -800V bias pulsed voltage has most outstanding wear resistance. And the a-C:H film has potential application on artificial joint to reduce the wear particle and extend joint life.

Key word: electron cyclotron resonance plasma enhanced chemical vapor deposition; hydrogenated amorphous carbon; pulse bias voltage

1. Introduction

CoCrMo alloy and medical grade ultra high molecular weight polyethylene (UHMWPE) are commonly used in total joint replacement [1]. It is well known that the long-term failure of artificial joint is directly or indirectly due to the production of wear particles, particularly polyethylene wear particles which are produced at the articulating interface between the metal component and the high molecular weight plastic component [2]. Another concern is that the release of metal ions either directly from the bearing surfaces or from particles after phagocytosis may cause cancer [3]. A friction and wear reducing film on the CoCrMo alloy, which is also biocompatible, may reduce the production of the polyethylene wear particles and dramatically extend hip-implant life. Preparation of amorphous
carbon film coating on the metal femoral head is a promising method to reduce wear debris of UHMWPE cup [4]. Firkins et al. [5] have investigated the wear of UHMWPE against DLC coated (by CVD) stainless steel and reported that the coating reduces the wear of the polymer by approximately seven times.

In the present study, hydrogenated amorphous carbon coatings (a-C:H) are produced on CoCrMo alloy by ECR-PECVD to reduce the production of the joint wear particles. The working gas is the mixtures of argon and acetylene gas. In the process of the a-C:H deposition, the parameter such as the microwave power [6], working pressure[7], argon flow[8] and bias voltage etc. strongly affect the structure of the a-C:H films. It is known that the substrate bias voltage, which determines the ion energy, plays a crucial role in the film structure and properties. This paper investigates the effect of bias voltage on the structure and properties of a-C:H film deposited on Co-Cr-Mo alloy in an ECR-PECVD system.

2. Experimental procedure

Hydrogen amorphous carbon film was deposited on Co-Cr-Mo alloy substrate by ECR-PECVD. The experiments were carried out in a apparatus described previously [9]. Before deposition, the chamber was evacuated to 1.0×10⁻³Pa and Ar⁺ was introduced to sputter the substrate (-1200V bias, 10min). The mixed argon (60sccm) and acetylene (10sccm) gas was introduced into the chamber and the pressure was kept at 0.5 Pa. High-density plasma was generated by ECR system and the ions deposited on the substrates under negative pulse voltage. The deposition conditions were as follows: the base pressure 5×10⁻³Pa, substrate temperature <100°C, negative pulse bias voltage frequency 20KHz, duty 20%. The experimental parameters were shown in Table 1.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Microwave power/W</th>
<th>Ratio of Argon/C₂H₂</th>
<th>Bias voltage /V</th>
<th>Time/min</th>
<th>Thickness /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>#A</td>
<td>-500</td>
<td>40</td>
<td>-500</td>
<td>40</td>
<td>340</td>
</tr>
<tr>
<td>#B</td>
<td>400</td>
<td>6</td>
<td>-800</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>#C</td>
<td>-1100</td>
<td>60</td>
<td>-1100</td>
<td>60</td>
<td>260</td>
</tr>
</tbody>
</table>

The film thickness was measured using a stylus profilometer (Ambios XP-2). The Raman spectroscopy (Nicolet almegaxr equipment) was employed to characterize the chemical bonding and the microstructure of the a-C:H film. The residual stress was calculated according to the curvatures changes of the silicon plates [10]. The nano-hardness of the films was measured by a CSEM nano-indenter. The adhesion property was evacuated by nano-scratch test. The wear resistance was assessed by ball-on-disc reciprocating friction test (CSEM trimometer, Swiss).

3. Results and discussion

Fig. 1 The deposition rate of a-C:H film deposited at different bias voltage

Fig. 1 shows the deposition rate of the a-C:H film deposited at different bias voltage. It can be seen that the film deposition rate decreases with the increase of bias voltage. As a general rule, the deposition rate is determined by the balance between the deposition of hydrocarbon radical and ion, which depends on the number of active species
generated in the plasma, and the etching by ion bombardment, which is related to the kinetic energy of ions [11]. With increasing the bias voltage, the energy of Ar ions increases intensively and the etching is enhanced. Therefore, the deposition rate decreases with the bias voltage.

![Fig. 2 Raman spectra of the a-C:H film deposited at different bias voltage](image)

Raman spectroscopy is widely used, being a routine, non-destructive and is the best way to obtain the detailed bonding structure of a-C:H. In this paper, the Raman spectra was measured using 514.5nm Ar laser and recorded in the region from 1000 to 2000 cm\(^{-1}\). Fig. 2 shows the Raman spectra of the a-C:H films deposited at different bias voltage. The so-called G and D peaks lie at around 1560 and 1360 cm\(^{-1}\), respectively, for visible excitation. The spectra in the wave number ranging from 900 to 1800 cm\(^{-1}\) were fitted by D and G peaks using Gaussian-curve function. The ratio of integrated intensities of D peak and G peak (I\(_D\)/I\(_G\)) was calculated, and was used to assess the sp\(^3\)/sp\(^2\) bonding ratio in a-C:H films.

Table 2. Results of Raman spectra deconvolution

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Bias voltage</th>
<th>D peak</th>
<th>G peak</th>
<th>I(_D)/I(_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak position /cm(^{-1})</td>
<td>FWHM/cm(^{-1})</td>
<td>Peak position /cm(^{-1})</td>
</tr>
<tr>
<td>#A</td>
<td>-500</td>
<td>1351</td>
<td>333</td>
<td>1553</td>
</tr>
<tr>
<td>#B</td>
<td>-800</td>
<td>1371</td>
<td>372</td>
<td>1560</td>
</tr>
<tr>
<td>#C</td>
<td>-1100</td>
<td>1378</td>
<td>350</td>
<td>1565</td>
</tr>
</tbody>
</table>

Table 2 shows the peak position and I\(_D\)/I\(_G\) which is calculated by deconvolution the Raman spectra. It can be seen that the position of the G peak and D peak shift towards higher wave number and the ratio of the I\(_D\)/I\(_G\) increases from 1.1 to 2.4 with the bias increasing. Many researcher reported that the sp\(^3\)/sp\(^2\) ratio is directly associated with the I\(_D\)/I\(_G\), and the bigger the I\(_D\)/I\(_G\) is, the less sp\(^3\)/sp\(^2\) ratio it has [12]. The results indicate that the sp\(^3\) content decreases with the bias increasing. In general, the growth process of a-C:H film consists of the chemical adsorption process of neutral species on the growing surface and the physical implantation process at the subsurface, in which the ion energy plays a dominant role [13–14]. At a high negative bias voltage, the dissipation of the excessive heat generated by the impinging of the energetic ions would relax density phase, which leads to the formation of loose carbon networks, and the sp\(^3\) content of the film decreases [15]. Accordingly, the sp\(^3\) content decreases with the bias voltage increasing.
The mechanical properties of the a-C:H film are of great interest for its use as a coating material. The nano-hardness of the films was measured by a CSEM nano-indenter with the loading rate of 2.4mN/min and maximum depth of 100nm. Fig. 3 shows the load/displacement curves and the nano-hardness for a-C:H coated CoCrMo samples. It can be seen that the slope of each sample is approximately constant. It means that the samples are in the elastic deformation regime. The nano-hardness of the a-C:H films is in the range of 14GPa to 20 GPa. It indicates that the a-C:H films is a kind of hard a-C:H film [17] with 40% sp³ content approximately. Furthermore, the slope and the nano-hardness of the films are both decreasing with the increasing bias voltage.

The residual stress of the a-C:H films is an attractive element affecting adhesion force. According to Stoney’s equation [10], the residual stress in the a-C:H film was determined by the curvature of Si sheet, which the a-C:H film deposited on. Fig. 4 shows the silicon curvatures and the residual stress of the a-C:H film at different bias voltage. It is obvious that the Si sheets are convex form. The calculation result indicates that the a-C:H film residual stress increases with the bias voltage, and reached the maximum value 1.9GPa at the negative bias of 1100 V. The origin of the residual stress is mainly the thermal stress in the a-C:H film fabricated by PECVD [16]. The thermal stress is attributed to the difference of thermal expansion coefficient of film and substrate. Obviously, high bombarding energy caused by bias voltage leads to high temperature of the substrate after deposition. Consequently, the residual stress increases with the bias.

The scratch furrow morphology of the a-C:H film deposited at different bias, a: #A(-500V); b: #B(-800V); c: #C(-1100V)
Adhesion property is crucial for the film which used on the artificial joint. The adhesion force was assessed with the nano-scratch test on the a-C:H-coated CoCrMo alloy. Scratches were performed by a spherical indenter \((r=2\,\mu m)\) on the face direction in order to delaminate the coatings. The normal load of indenter was increased linearly from 0 to 100 mN and the scratch trace was 1 mm. Fig. 5 shows the scratch furrow morphology of the samples. In fig. 5a, it can be seen that there is only slight crack on the end of the scratch trace of sample \#A (-500V). It indicates that the adhesion force is strong and this attributes to the low internal stress and high hardness of the film. In fig. 5b and fig. 5c, it shows that sample \#B (-800V) and sample \#C (-1100V) have large delamination and the failure of sample \#B is more serious. It is reasonable that the high stress of the sample \#B and \#C releases when the indenter load on the film and it lead to the formation of crack and delamination. Therefore, the high bias voltage leads to weak adhesion force between film and substrate.

![Fig. 6 Morphology of the wear tracks and the friction coefficient, a: \#A(-500V); b: \#B(-800V); c: \#C(-1100V) ](image)

Wear property was estimated by ball-on-disc reciprocating friction test on the a-C:H-coated CoCrMo alloy. SiC ball \((Φ 6mm)\) was used as the grinding-ball. The sliding speed was 30 mm/s, the normal load was 2N and the sliding cycle was 20000 laps. Fig. 6 shows the morphology of the wear track by optical microscope. In fig. 6a, it could be seen that the film deposited at -500V wear severely but does not fail. The wear track on sample \#B (-800V, fig. 6b) is slight without any visible detachment or delamination. The sample \#C(-1100V, fig. 6c) wear severely with considerable localized spallation resulted from fatigue. The results indicate that the film fabricated at -800V has excellent wear resistance.

The delamination of the films can not be seen in the Fig. 6a, b and c. It indicates that the adhesion force is strong enough in the friction process. The film fabricated at -500V has the maximum \(sp^3/sp^2\) ratio which can provide high hardness. However, low \(sp^2\) content reduce the effect of lubrication. So, the abrasive wear is prominent and deep wear tracks form in the friction process. The film fabricated at -1100V has low \(sp^3\) content and hardness. Therefore, cracks appear in the friction process under normal load. The cracks propagation in the friction process leads to fatigue failure. The film fabricated at -800V with appropriate ratio of \(sp^2\) and \(sp^3\) can provide not only good lubrication but also high hardness. The results indicate that proper bias voltage (-800V) is advantageous to increase the wear resistance of the a-C:H films.

4. Conclusion

Diamond-like carbon films were successfully deposited on CoCrMo alloy using a ECR-PECVD method with a mixture of argon and acetylene. The influence of bias voltage on the structure and property of a-C:H films was investigated. The Raman result shows that the \(sp^3\) content and the hardness of the film decrease with the bias increasing. The residual stress increases with bias voltage in terms of impinging of the energetic argon ions. High residual stress leads to weak adhesion force between substrate and film. The most excellent friction property is obtained from the a-C:H film fabricated at -800V. And the a-C:H film has potential application on artificial joint to reduce the wear particle and extend joint life.

Acknowledgment

This work is financially supported by NSFC 10876030 and National High Technology Research and Development Program of China 2006AA02A135.
References