The structure and adhesion of hydrogenated amorphous carbon (a-C:H) films synthesized on CoCrMo alloy by plasma immersion ion implantation and deposition at different flow ratios of acetylene to argon

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Abstract

Hydrogenated amorphous carbon (a-C:H) film is deposited on CoCrMo alloy by plasma immersion ion implantation and deposition (PIII-D) at different flow ratios of acetylene to argon (C₂H₂/Ar). The results show that Ar fraction in the C₂H₂–Ar gas mixture has an important effect on the structure and the adhesion of the a-C:H films. When Ar fraction in the C₂H₂–Ar gas mixture is less than 50%, the fabricated a-C:H film composition transfer from graphite-like to diamond-like which contains higher sp³ binding thanks to Ar ion bombardment, and the adhesion strength decreased with the increment of Ar fraction. But when Ar fraction in the C₂H₂–Ar gas mixture is beyond 50%, the fabricated film contains more sp² bonding for thermally driven and exhibits higher adhesion strength with the increment of the Ar fraction.

1. Introduction

Amorphous carbon film (a-C:H) has widespread application as protective coatings in areas such as optical windows, magnetic storage disks, car parts, biomedical coatings and as micro-electromechanical devices (MEMs) for its favorable tribological and mechanical properties [1–6]. For improving the properties of medical implants, a-C:H is also a very promising coating material because it is chemically inert, extremely hard, wear resistant and biocompatible [7]. Total hip replacement is one of the most challenging types of human implants for there are more than 400000 artificial joint operations made every year in the world and today there are some 25000000 people who have either a partial or a total hip replacement [8]. But the particles from the implanted joints caused by friction process lead to long-term loosening between the implant and the bone. And the practical lifetime of the current artificial joint is not enough and the joint will be a failure in 10 to 20 years by mechanical wear and joint loosening. Because of this, a wear-reducing coating on the metal component, which is also biocompatible, should dramatically extend hip implant life. It is easy to see that even minor improvements in the lifetime of the artificial joint can yield massive socio-economical benefits [9]. The a-C:H coating seems to be the potential candidate for improving chemical and mechanical wear resistance of the joints.

The aim of this paper is to study the microstructure and adhesion of amorphous carbon film (a-C:H) deposited on medical grade forged CoCrMo alloy at different acetylene/argon flow ratios by plasma immersion ion implantation–deposition.

2. Experimental

Medical grade forged CoCrMo alloy was cut from cylindrical bars with diameters 13 mm and thickness 2 mm, and then grinded and polished to a mirror-like surface. The amorphous carbon film was fabricated using plasma immersion ion implantation–deposition (PIII-D) technique [10] on CoCrMo alloy. The system was pumped to a base pressure of 3.0 × 10⁻¹³ Pa. Prior to film deposition, the CoCrMo alloy substrate underwent Ar⁺ sputter cleaning for 10 min to remove surface contaminants and surface oxide using a RF power of 600 W. The plasma was sustained by radio frequency at a power of 600 W. The –15 kV bias pulse voltage (150 Hz, 40 μs) was applied on the substrate during the film deposition. The process time was 2 h and oil cool was used to cool the substrate during the film deposition. The a-C:H films were synthesized at different acetylene/argon flow ratios. The detailed deposition parameters and the thickness of the films were listed in Table 1.

The film thickness was tested by AMBIOS XP-2 profile meter. The bonding characteristic was assessed employing Raman spectra and X-ray photoelectron spectroscopy (XPS). Vickers indenter and scratch tests were performed to determine the film adhesion strength between film and substrate. The diamond Vickers indenter forced on the film with sustained load for 15 s at 0.98 N, 1.96 N, 2.94 N, 4.9 N and 9.8 N. The scratch test was performed with sphericity steel
indenter with a continuously increasing load up to 100 N at a loading rate of 100 N min\(^{-1}\) and a transverse velocity of the sample of 4 mm min\(^{-1}\).

3. Results and discussion

3.1. Composition and bonding structure

Raman is a frequent and effective method to analyze the bonding structure of a-C:H\(^{[11]}\). Fig. 1(a) shows Raman spectra of the a-C:H films prepared at different acetylene/argon flow ratios. All the spectrum of the films show a broad peak at approximately 1560 cm\(^{-1}\) and an obvious shoulder at approximately 1350 cm\(^{-1}\), commonly referred to as G band and D band\(^{[12]}\), respectively. The G peak is due to the bond stretching of pair sp\(^2\) atoms in both rings and chains. The D peak is due to the breathing modes of sp\(^2\) atoms in rings\(^{[13]}\). As a general rule, the G band position and the intensity ratio of D peak and G peak (\(I_D/I_G\)) are important factors in determining the film structure, and a higher G peak position and a greater \(I_D/I_G\) ratio are the indicators of a higher sp\(^2\) concentration in carbon films\(^{[14,15]}\). In order to obtain the information about the position of G bond, the intensity ratio of D peak and G peak, and estimate sp\(^3\) content, Raman spectrum of the films prepared at different acetylene/argon flow ratio is fitted. Fig. 1(b) shows a typical Raman spectrum fitted by Gaussian curve function after subtracting the background. Based on the fitting parameters, the peak positions and the ratio of the integrated areas under the D and G peaks (\(I_D/I_G\)) are obtained and summarized in Table 2. As shown in Table 2, with the increasing of Ar fraction from 20\% to 67\%, G band shifts from 1549 to lower 1547 cm\(^{-1}\) and then to higher 1552 cm\(^{-1}\), and \(I_D/I_G\) shifted from 1.64 to 1.33 and then to 1.78. Since the ratio of \(I_D/I_G\) is related to the sp\(^2\)/sp\(^3\) ratios, these results indicate that the sp\(^3\) content first increases and then decreases with increasing Ar fraction. In other words, a-C:H film structure is more diamond like when Ar fraction is 50\%.

Sometimes the Raman results are not definitive enough to discern the a-C:H films\(^{[7,16]}\). In order to obtain more structure information, XPS is used. Fig. 2 shows the C1s XPS spectra of the amorphous carbon film (a-C:H) deposited at different acetylene/argon flow ratios. It can be observed that the C1s peak of the sample shifts to a higher binding energy with the increasing of Ar fraction to 50\%, but shift to lower when Ar fraction increased to 67\%. The C1s spectra can be deconvoluted into

<table>
<thead>
<tr>
<th>Sample number</th>
<th>(C_2H_2) flow (sccm)</th>
<th>Ar flow (sccm)</th>
<th>Ar fraction (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>40</td>
<td>10</td>
<td>20</td>
<td>260</td>
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<tr>
<td>3#</td>
<td>30</td>
<td>30</td>
<td>50</td>
<td>199</td>
</tr>
<tr>
<td>4#</td>
<td>15</td>
<td>30</td>
<td>67</td>
<td>75</td>
</tr>
</tbody>
</table>

### Table 2

Deconvolution results from Raman spectroscopy.

<table>
<thead>
<tr>
<th>Ar fraction (%)</th>
<th>D band</th>
<th>G band</th>
<th>(I_D/I_G)</th>
</tr>
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<tbody>
<tr>
<td>Position</td>
<td>FWHM</td>
<td>Area</td>
<td>Position</td>
</tr>
<tr>
<td>1# 20</td>
<td>1362</td>
<td>342</td>
<td>1549</td>
</tr>
<tr>
<td>3# 50</td>
<td>1359</td>
<td>326</td>
<td>1547</td>
</tr>
<tr>
<td>4# 67</td>
<td>1369</td>
<td>339</td>
<td>1552</td>
</tr>
</tbody>
</table>

![Fig 1](https://example.com/fig1.png)

(a) Raman spectra of the a-C:H films prepared at different \(C_2H_2/Ar\) flow ratios. (b) Typical Raman spectrum deconvoluted by Gaussian curve function.

![Fig 2](https://example.com/fig2.png)

C1s XPS spectra of the a-C:H films prepared at different \(C_2H_2/Ar\) flow ratios.
three peaks at approximately 284.6, 285.6, and 286.5 eV, corresponding to sp\(^2\) carbon atoms, sp\(^3\) carbon atoms, and C – O contamination formed at the surface of the samples. Then the content of sp\(^2\) and sp\(^3\) carbon atoms can be determined as the ratio of the corresponding peak area to the total C1s peak area. Fig. 3 shows the sp\(^2\) and sp\(^3\) contents as a function of Ar fraction. When Ar fraction of the mix gas is 25%, the fractional sp\(^3\) content is about 29%, and then increases to about 60% and 65% with the increasing Ar fraction to 33% and 50%, but suddenly decreases to 17% with continual increasing Ar fraction to 67%. These results also show that a-C:H film structure is more diamond like when Ar fraction is 50%. And this conclusion is extraordinarily consistent with that of Raman.

Both the Raman and the XPS results indicate the same conclusion. When Ar fraction in the C\(_2\)H\(_2\)–Ar gas mixture is less than 50%, the a-C:H film composition transfers from graphite-like to diamond-like which contains higher sp\(^3\) binding, but when Ar fraction in the C\(_2\)H\(_2\)–Ar gas mixture is beyond 50%, the film contains more sp\(^2\) bonding with the increment of the Ar fraction. As the amount of Ar increases in the gas mixture, the fraction of the Ar ion increases along the plasma, the bombardment effect enhances correspondingly. For the Ar ion has higher energy, it was reported [2] that ion bombardment helps the formation sp\(^3\) of bonding, so the result shows that sp\(^3\) bonds in the films increase gradually as Ar fraction increases from to 20% to 50%. However, an excessively high Ar flow reduces the sp\(^3\) bond rapidly, one of the reasons is that the bombardment energy of the overlying Ar ions is more pronounced, as a result, the substrate temperature increases, it may promote film graphitization, and the process is thermally driven [15]. Thus, the film prepared at 50% Ar fraction shows the most sp\(^3\) bonding.

### 3.2. Adhesion strength

a-C:H films will be used for enhancing the wear resistance of the joint, thus strong adhesion is required. The indentation method is one of commonly used techniques for the assessment of adhesion between hard coatings and substrates. In this technique, the load for the lateral crack initiation and the slope obtained from the indentation load-lateral crack diameter are parameters, directly related to the adhesion [17]. The indentation often causes film spallation, and the information of the coating adhesion can be obtained by analyzing the dimension of the delamination. In this paper, we process the indentation test with Vickers indenter penetration. Compare with Rockwell indenter, when coating detachment occurs, the arris and corners of Vickers indenter where deformation stress induced easily can result more cracks paralleling the arris. Fig. 4 shows indent
produced in the a-C:H films under the load of 2.94 N. Samples #1 and #4 show intact mark under the 2.94 N load (Fig. 4a, d), even a slight crack couldn’t be found in the mark. However, a load of 2.94 N is enough to cause the film break off for samples #2 and #3 (Fig. 4b, c). Especially for sample #3 which is rich in sp³ bonding, the coating failure occurs and the bare substrate around the edge is exposed. Further SEM test has been done to observe the indenter under a load of 9.8 N to characterize samples #1 and #4, which are shown in Fig. 5. It shows that no slight crack could be found. Due to the plastic deformation of the substrate under the large loads, lots of slip bands could be found in the indenter, but the deformation of the film is still consistent with that of the substrate. There is more slip band appearance in the indent of sample #4 which comprises more sp² bonding. This test indicates the adherence between the film and the substrate is very strong when the film comprises more sp² bonding.

A similar conclusion can be reached based on the scratch test. Scratch test is another technique used to evaluate the adhesion strength, which is very conventional and acceptable as a comparison test of adhesion strength [18]. In this paper, the test is done using a sphericity steel indenter. Fig. 6 is a schematic drawing of scratch process (Fig. 6a) and the profile of the scratch (Fig. 6b). When the spherical steel tip drives over the film, the substrate is pressed, the friction load is induced and makes dominate effect, once critical value reached with the increasing press load, arch deformation occurred and the coating may peel off. In general, acoustic signal produced by the delamination of the films can be used to characterize the critical load. However, because the fracture of the film at the sides of the scratch trace also generates acoustic signals, this mode is not very accurate. We defined the critical load by microscopic observation of the start of cracks at the sides of the scratch trace [19].

Fig. 7 shows the optical micrograph of the surface of samples #1, #3 and #4 after being scratched with sphericity steel tip. The samples #1 and #4 are intact along the scratch length. Although some obvious channel engendered during the steel tip slid over, the coating adheres on the substrate well even when the max load was reached. However, for sample #3 it could be seen that fracture formed at the sides of the scratch trace when the load increased to 35 N. The film surface arching and peeling off accelerated as the load increases, and the substrate material is exposed at the end of the scratch.

4. Conclusion

Diamond-like carbon thin films are synthesized on CoCrMo alloy using plasma immersion ion implantation–deposition at different flow ratios of acetylene to argon (C₂H₂/Ar). The Ar fraction in the mix gas affects the structure and adhesion of the a-C:H films significantly. When Ar fraction in the C₂H₂–Ar gas mixture is less than 50%, the fabricated a-C:H film composition transfer from graphite-like to diamond-like which contains higher sp³ binding thanks to Ar ion bombardment, and the adhesion strength decreased with the increment of Ar fraction. But when Ar fraction in the C₂H₂–Ar gas mixture is beyond 50%, the fabricated film contains more sp² bonding for thermally driven and exhibits higher adhesion strength with the increment of the Ar fraction.

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