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ARTICLE

Effects of Acetylene Gas on Mechanical Properties of DLC Film Prepared by Plasma-Enhanced Chemical Vapor Deposition

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Abstract: To improve the mechanical properties of 2024 aluminum alloy, a kind of diamond-like carbon (DLC) film was deposited on the surface of 2024 aluminum alloy by plasma-enhanced chemical vapor deposition technique. The effects of acetylene gas on the microstructure, hardness, wear resistance, and adhesion of DLC film were investigated by field emission scanning electron microscope, nano-indentation tester, and friction-wear tester. The results indicate that the thickness of the DLC film increases gradually with increasing the proportion of acetylene. There is an obvious transition layer between the DLC film and matrix. When the ratio of argon to acetylene is 1:3, the hardness of DLC film is enhanced significantly because of the content changes of sp^3 and sp^2 bonds within the film. At the same time, the friction coefficient of DLC film is reduced.

Key words: plasma-enhanced chemical vapor deposition; DLC film; aluminum alloy; wear resistance; hardness

1 Introduction

Aluminum alloy is a type of lightweight alloy, which has many advantages such as low density, high strength, excellent conductivity, and corrosion resistance. So, it is widely used in aerospace, automotive manufacturing, and construction industries. However, aluminum alloys still have many issues such as low surface hardness and poor wear resistance, which restrict their development. It has become a hot research topic to improve the surface hardness and wear resistance of aluminum alloys[1–3].

Surface modification is an important way to effectively improve the surface hardness and wear resistance of aluminum alloys. Compared to other surface modification methods, plasma-enhanced chemical vapor deposition (PECVD) is able to achieve low-temperature surface modification, which can improve the surface hardness and wear resistance of aluminum alloys without changing the matrix properties. The solid-solution aging temperature of aluminum alloys is generally around 130 °C[4–5]. Among numerous hard films, diamond-like carbon (DLC) film is an amorphous carbon material, which has excellent hardness, friction resistance, and chemical stability. It has been widely used for enhancing the surface hardness and wear resistance of light alloys and bearing alloys[6–9]. Currently, researchers have conducted some researches on the preparation of DLC films. Damasceno et al[10] used PECVD technique to deposit DLC film on Si surface. DLC film with high hardness (20 GPa), low stress (approximately 0.5 GPa), and high deposition rate (40 nm/min) was obtained through changing the matrix bias and deposition atmosphere. Nelson et al[11] used PECVD technique with 13.56 MHz radio frequency power supply to deposit DLC film on the Si matrix. The effect of sample orientation on the structure and properties of DLC film was investigated in detail. The results showed that the horizontally placed samples demonstrate relatively lower surface roughness than the vertically placed samples, but they show much higher hardness and adhesion than the vertically placed

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samples. Although some work has been done to enhance the resistance of light alloys by DLC films, the further research is still needed on the mechanism and regulation of mechanical properties of DLC films.

In this work, DLC films were prepared on the surface of 2024 aluminum alloy by PECVD technique. The mechanical properties and microstructures of the DLC films formed on 2024 aluminum alloy were investigated. The influences of acetylene gas on the mechanical properties of DLC film were examined in detail and the related mechanisms were also discussed.

2 Experiment

The chemical composition of 2024 aluminum alloy used in this work is listed in Table 1. The aluminum rod was cut into circular sample with *Φ*20 mm×10 mm using a wire cutting machine. The circular samples were ground and polished with metallographic sandpapers of 2000#. After that, the polished samples were immerged in alcohol solution and cleaned by ultrasonication for 30 min.

The clean 2024 aluminum alloy samples were placed in the chamber of PECVD equipment. The vacuum degree in the chamber was set at $\leqslant 3\times10^{-3}$ Pa. The samples were heated to the set temperature. The argon of 100 cm^3/min at standard state was pumped into the chamber for 20 min, and a pulse voltage of −3300 V was applied on the samples for 40 min to eliminate the residual air and the oxide film on the surfaces of 2024 aluminum alloy. Tetramethylsilane with a flow rate of 40 cm^3/min at standard state was pumped into the chamber for 40 min. After that, the injection of tetramethylsilane was stopped and the mixed gases were pumped into the chamber. The ratios of argon to acetylene in mixed gases are 1:2, 1:3, and 1:4. The deposition time was 5 h, the working pressure was 2 Pa, and the deposition temperature was 100 °C. This experimental method is based on PECVD process parameters established in our previous research[12].

PECVD technique was used to deposit a DLC film of a certain thickness containing hydrogen on 2024 aluminum alloy surface. Field emission scanning electron microscope (SEM, EIGMA) was used to observe the cross-section morphology of DLC film, and energy dispersive spectrometer (EDS) was used to analyze the element distribution of DLC film at different depths. The positions and intensities of the D and G peaks in DLC thin film were obtained using an XploRA PLUS Raman spectrometer with a laser wavelength of 532 nm. The hardness of the DLC thin film was analyzed by I_D/I_G and the content of sp^3 bonds in the film was determined. The nano-hardness and Young's modulus of DLC film were measured using G200 nano-indentation instrument. 20 points on the DLC film were randomly selected. The indentation depth of the indenter was 2000 nm. The MST-3000 friction and wear machine was used to test the wear resistance of DLC film on the 2024 aluminum alloy. A zirconia grinding ball with diameter of 4 mm was used for friction and wear testing. The rotating friction speed was 200 r/min, the duration was 180 min, and the load was 3 N. The prepared samples were fixed on the friction and wear equipment to ensure the test accuracy. The load was adjusted by changing the mass of weights. The horizontal bar at the end of the equipment was adjusted after installing the weight. The horizontal ball was placed in the center of circle to avoid inaccurate results. The adhesion test between DLC film and matrix was conducted using the MST-4000 scratch tester. The termination load was 100 N, the loading speed was 100 N/min, and the scratch length was 5 mm.

Table 1 Chemical composition of 2024 aluminum alloy (wt%)

Cu	Mg	Mn	Fe	Zn	Si	Ti	Cr	Al
3.81	1.40	0.40	0.40	0.14	0.22	0.05	0.05	Bal.

3 Results and Discussion

Fig. 1 is a schematic diagram of PECVD apparatus. It consists of a pulse power supply system, a vacuum chamber, sets of pumps, an atmosphere control system, an inflation system, and a control system. The power system consists of a pulse power and a direct-current power. The pumps and atmosphere control system consist of mechanical pump, molecular pump, gas flowmeters, and control panels.

Fig. 2 shows the cross-sectional morphologies and thicknesses of DLC films under different deposition atmospheres. The left side of the image shows the bakelite powder. As shown in Fig. 2, DLC film is uniform and dense. There is a clear transition layer between the aluminum alloy matrix and film, which effectively improves the adhesion between the film and matrix. The main element in the transition layer between the DLC film and the matrix is Si. Si atom belongs to the cubic diamond type. It has the same crystal structure as C atoms, which makes it easier to bond with carbon atoms. In addition, Si and Al are adjacent to each other in the periodic table of chemical elements. They have the similar electronegativity. Si and Al atoms can form solid solutions, resulting in the improved bonding strength between DLC film and matrix.

The carbons content in Fig. 2b is significantly lower than that in others, because there is a certain amount element hydrogen in the film when the DLC film was prepared by PECVD technique. The specific results of hydrogen content

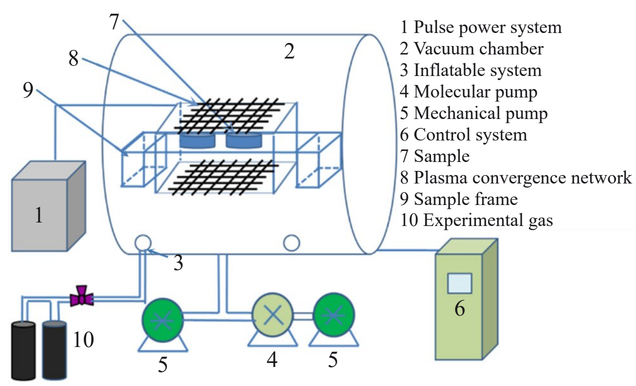

Fig.1 Schematic diagram of PECVD apparatus

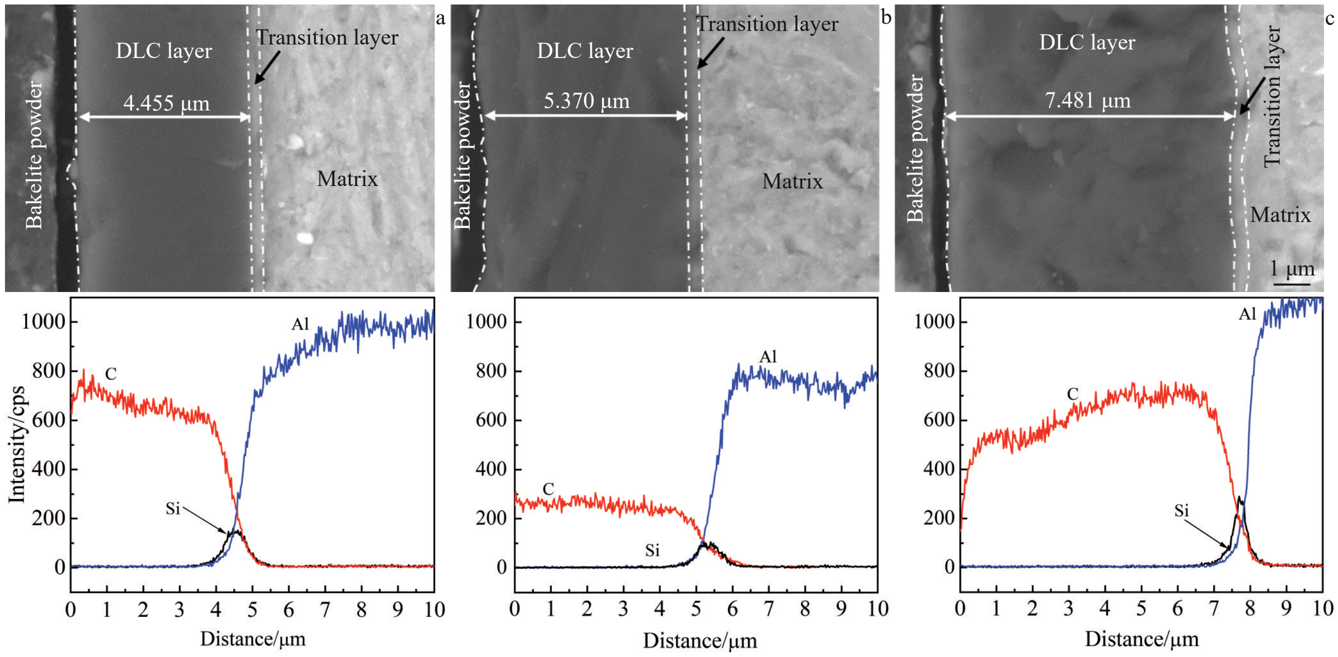

Fig.2 Cross-sectional morphologies and element contents of DLC film with different deposition atmospheres: (a) Ar:C_2H_2=1:2; (b) Ar:C_2H_2=1:3; (c) Ar:C_2H_2=1:4

cannot be obtained by EDS. Because the DLC films only contain elements carbon and hydrogen, the higher the carbon content, the lower the hydrogen content. Under other deposition atmosphere ratios, the carbon content of DLC film is relatively higher. This is because the C-H bond breaks when hydrocarbon ions are bombarded with high energy, as shown in Fig. 2a. It promotes the hydrogen formation due to active hydrogen atoms. When the gas is released from the film, carbon becomes the main element of the DLC film surface[13]. As the proportion of acetylene gas increases, the thickness of DLC film increases from 4.455 μm to 7.481 μm. This is because the total pressure in the vacuum chamber remains constant. But the number of atoms in the chamber is certain. As the acetylene increases, more hydrocarbon ions are ionized, and the relative content of argon ions is decreased. This allows more hydrocarbon ions to deposit on the surface of the 2024 aluminum alloy, and hydrocarbon ions cannot move back into the chamber due to bombardment by argon ions. Therefore, the thickness of DLC film will gradually increase with the increase in acetylene[14].

The structural characterization of the samples was conducted for understanding the above-described behavior. Fig. 3 shows the Raman spectra after fitting with Gaussian function under different deposition atmospheres. In general, the positions and the intensity ratio (I_D/I_G) of D and G peaks after Gaussian function fitting are discussed. D peak appears at 1350 cm^{-1} and G peak appears at 1590 cm^{-1}[15]. The hardness of DLC thin film is reflected by the ratio of I_D/I_G. And the ratio of sp^3 to sp^2 bonds increases as the I_D/I_G decreases[16–17]. DLC film prepared by PECVD technique can easily ionize acetylene gas, and the ionized hydrocarbon ions are adsorbed by the surface of aluminum alloy to form sp^3 bonds and

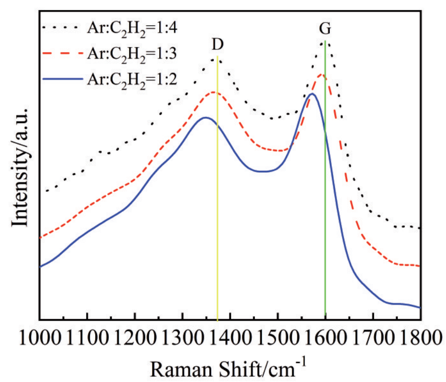

Fig.3 Raman spectra of DLC film with different deposition atmosphere

hydrogen-containing compounds[18]. As shown in Fig. 3, the positions of D and G peaks are different under different deposition atmospheres. When the mixture gas ratio changes from 1:2 to 1:4, the position of D peak increases from 1362 cm^{-1} to 1395 cm^{-1}, and the position of G peak increases from 1580 cm^{-1} to 1600 cm^{-1}. The high-frequency band of the hydrogenated DLC film shows that the bonds of CH_2 and CH_3 recombine after C-H bonds are broken. As the proportion of acetylene gas increases, more and more C-H bonds are broken, resulting in the increased hydrogen content in the films, which is consistent with the above results. When the ratio of argon to acetylene is 1:2, 1:3, and 1:4, the I_D/I_G is 3.12, 2.76, and 2.94, respectively. It means that when the ratio of argon to acetylene is 1:3, the ratio of sp^3/sp^2 in DLC film is the highest.

The wear resistance of DLC film can be determined by the friction coefficient. The friction coefficient of 2024 aluminum alloy matrix is 0.31[19]. Fig. 4 shows the time-dependent

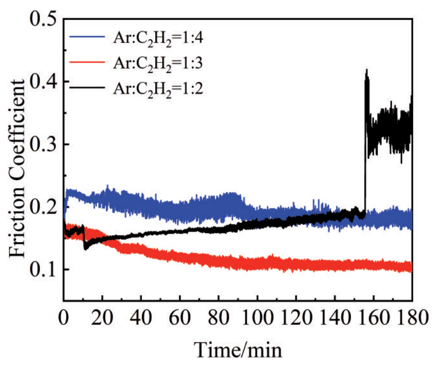

Fig.4 Friction coefficient of DLC film with different deposition atmospheres

average friction coefficient between DLC thin films and zirconia grinding balls under different deposition atmospheres. After the friction test runs for 155 min, the friction coefficient is rapidly increased from 0.15 to 0.31 when the argon to acetylene is 1: 2. It is the same as the surface friction coefficient of 2024 aluminum alloy matrix. This is because the DLC film is so thin, which is easy to wear and expose the matrix. DLC film is continuously bombarded by argon ions during the deposition. It will cause severe stress, which forms and remains in the DLC film. When a force is applied on the film, this stress will make it more susceptible to damage[3]. When the argon to acetylene is 1:3 and 1:4, the friction coefficients of DLC thin films are 0.11 and 0.19, respectively. The main factors influencing the friction coefficient of DLC films are composition, thickness, and surface roughness. So, when the ratio of argon to acetylene is 1:3, the DLC film shows the lowest friction coefficient and the best wear resistance.

The adhesion between the DLC films and the matrix can be determined by the loading force that corresponds to the acoustic signals. It is usually believed that the loading force corresponding to the location where the first acoustic signal occurs is the adhesion between the film and the matrix. Fig.5–Fig. 6 show the acoustic signal curves and the scratches profiles of the DLC films with different deposition atmospheres. As shown in Fig. 5, when the ratio of argon to acetylene are 1:2, 1:3, and 1:4, the adhesion are 2.2, 9.8, and 6.6 N, respectively. But there is significant peeling around the scratch when the ratio of argon to acetylene is 1:2 (Fig. 6a). This is because the high-energy hydrocarbon ions pass through the surface layer from the lattice gap and remain in the sub-layer to form interstitial atoms, which increases the internal stress and makes the film deform. So, there is a large-scale film peeling under external force[20–21]. The intensity of acoustic signals caused by the peeling of the film at the scratch tip does not exceed the minimum value set by the

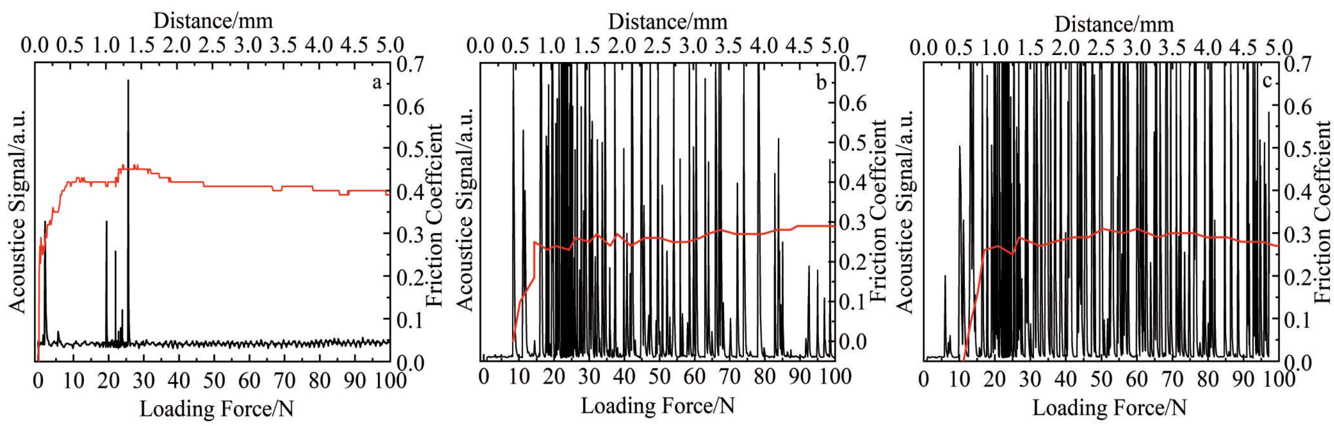

Fig.5 Acoustic signal and friction coefficient of DLC film with different deposition atmospheres: (a) Ar:C_2H_2=1:2; (b) Ar:C_2H_2=1:3; (c) Ar:C_2H_2=1:4

instrument. It is defaulted as noise signals during the film peeling process. When Ar:C_2H_2=1:2, the peeling phenomenon gets serious. But there are three acoustic signals observed in Fig. 5a. This is because there are three locations where the DLC film continuously peels off at the front of scratch, as shown in Fig. 6a. The value of the acoustic signal appearing after the third position is much smaller than that from other positions. In Fig. 6b, the DLC film almost has no peeling phenomenon around the scratch. As can be seen from Fig. 6c, there is a small amount of film peeling on both sides of the scratch. It may be that the film reaches a certain thickness. Combined with the Fig.4, when the ratio of argon to acetylene is 1: 3, the DLC thin film exhibits the best mechanical properties such as adhesion and toughness.

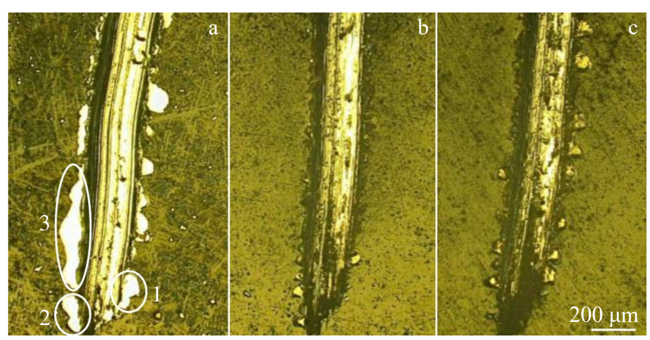

Fig.6 Scratch morphologies of DLC films with different deposition atmospheres: (a) Ar:C_2H_2=1:2; (b) Ar:C_2H_2=1:3; (c) Ar:C_2H_2=1:4 (circles 1, 2, and 3 in Fig.6a indicate the peeling locations)

Fig.7 shows the nano-indentation hardness (H) and Young's modulus (E) of films under different deposition atmospheres. The H value of the DLC film is an average value calculated by randomly selected 20 points. When the indentation depth reaches 1000 nm, the H and E values remain unchanged. It indicates that the H values are not affected by the matrix. When the ratio of argon to acetylene is 1:2, 1:3, and 1:4, the H values are 5.26, 5.46, and 5.15 GPa, and the E values are 40.7, 40.3, and 37.3 GPa, respectively.

The mechanical properties of DLC films prepared under different deposition atmospheres are summarized in Table 2. The ratio of H/E characterizes the ability of the material to undergo elastic deformation and recovery. Usually, the higher the H/E value, the lower the wear. The wear failure life of the film will be longer[22]. H^3/E^2 is the resistance factor to plastic deformation. It indicates the film resistance to plastic deformation[22]. The H/E and H^3/E^2 values are directly dependent on the wear resistance and the adhesion of the film. The H/E value increases with the increasing acetylene. When the argon to acetylene is 1:3, the H^3/E^2 value reaches to the highest. It indicates that the DLC film has the best wear resistance and the highest adhesion.

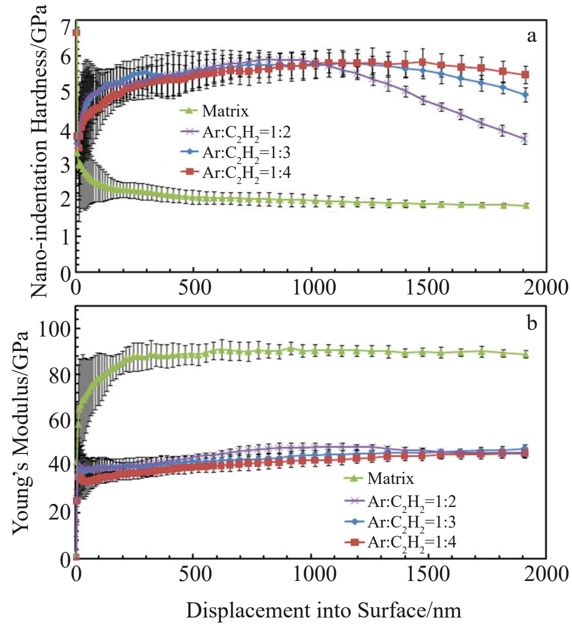

Fig.7 Nano-indentation hardness (a) and Young's modulus (b) of DLC film with different deposition atmospheres

Table 2 Mechanical properties of DLC film with different deposition atmospheres

Atmosphere	Friction coefficient	Nano-indentation hardness/GPa	Young's modulus/GPa	Adhesion/N	H/E	H^3/E^2
Matrix	0.3148	2.27	87.3	-	0.026	0.0015
Ar:C_2H_2=1:2	0.1880	5.26	40.7	2.2	0.129	0.0878
Ar:C_2H_2=1:3	0.1195	5.46	40.3	9.8	0.135	0.1002
Ar:C_2H_2=1:4	0.1943	5.15	37.3	6.6	0.138	0.0981

4 Conclusions

1) DLC film was prepared by plasma-enhanced chemical vapor deposition technique. As the acetylene increases, the thickness of DLC film on the surface of 2024 aluminu alloy increases from 4.455 μm to 7.481 μm. The film has a good bonding with the matrix. There is a clear transition layer containing Si between the film and matrix.

2) When the ratio of the argon to acetylene is 1: 3, the content of sp^3 bonds in DLC film is the highest, and the mechanical properties of DLC film are also the best based on the analysis of H/E and H^3/E^2 ratio.

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乙炔气体对等离子体增强化学气相沉积DLC膜力学性能的影响

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摘　要：为了提高2024铝合金的机械性能，采用等离子体增强化学气相沉积技术在2024铝合金表面沉积类金刚石碳（DLC）薄膜。通过场发射扫描电子显微镜、纳米压痕测试仪和摩擦磨损试验仪研究了乙炔气体对DLC薄膜的微观结构、硬度、耐磨性和粘附性的影响。结果表明，DLC薄膜的厚度随着乙炔比例的增加而逐渐增厚，且DLC薄膜与基体间存在明显过渡层。当氩气与乙炔气体的比例为1:3时，由于薄膜内sp^3和sp^2键含量的变化，DLC薄膜的硬度显著提高，同时，DLC薄膜的摩擦系数下降。

关键词：等离子体增强化学气相沉积；DLC薄膜；铝合金；耐磨性；硬度

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