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

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Abstract

Diamond-like carbon (DLC) films have many advantages, such as high hardness, low friction coefficient, and high chemical stability. They have been widely used for improving the surface hardness and wear resistance of light alloys. To improve the mechanical properties of 2024 aluminum alloy, a kind of 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 microscopy, nano-indentation, friction-wear test. The results indicate that the thickness of the DLC film increased 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 the DLC film was enhanced significantly because of the changes in the content of sp^3 and sp^2 bonds within the film. At the same time, the coefficient friction of the DLC film was reduced. This work provides an experimental and theoretical basis for improving the mechanical properties and enhancing durability of aluminum alloys.

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

Aluminum alloys are a type of lightweight alloy, which have many advantages such as low density, high strength, excellent conductivity and corrosion resistance. So, they are 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 limiting 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) has the advantages of being able to achieve low-temperature surface modification, which can improve the surface hardness and wear resistance of aluminum alloys without changing the matrix properties, because the solid solution aging temperature of aluminum alloys is generally around 130 ℃ [4-5]. Among numerous hard films, 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 technology to deposit DLC film on Si surface. The DLC film with high hardness (20 GPa), low stress (-0.5 GPa) and high deposition rate (40 nm/min) was obtained through changing the matrix bias and deposition atmosphere.

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Nelson et al. [11] used PECVD technology with 13.56 MHz RF power supply to deposit DLC film on the Si matrix. The effects

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of sample orientation on the structure and properties of DLC film were investigated in detail. The results showed that the horizontally placed samples demonstrated relatively lower surface roughness than the vertically placed samples, but they showed much higher hardness and adhesion than the vertically placed samples. Although some works have 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 technology. 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 also examined in detail and the related mechanisms are also discussed.

1 Experimental

1.1 Preparation of Materials

The chemical compositions of 2024 aluminum alloy used in this work are listed in Table 1. The aluminum rod was cut into circular specimen with Ø20 mm×10 mm using a wire cutting machine. The circular alloy samples were ground and polished with metallographic sandpapers to 2000 #. After that, the polished alloy samples were immerged in alcohol solution and cleaned by ultrasonication for 30 mins.

Table 1 Composition of 2024 aluminum alloy used in the present work (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	Balance

1.2 Experimental procedure

The clean 2024 aluminum alloy samples were placed in the chamber of PECVD equipment. The vacuum degree in the chamber was set at 3×10^{-3} Pa or less. The specimens were heated to the set temperature and 100 sccm (standard-state cubic centimeters per minute) argon was pumped into the chamber for 20 mins and a -3300 V pulse voltage was applied on the samples for 40 mins to eliminate the residual air and the oxide film on the surfaces of 2024 aluminum alloy. Tetramethylsilane with a flow rate of 40 sccm was pumped into the chamber for 40 mins. After that, the injection of tetramethylsilane was stopped and the mixed gases were pumped into the chamber. The mixed gases ratio of argon to acetylene are 20:40, 20:60, and 20:80. The deposition time is 5 hrs, and the working pressure is 2 Pa and the deposition temperature is 100 °C. The other experimental parameters are the same.

1.3 Characterization method

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

2 Results and discussion

Fig. 1 is a schematic diagram of coating 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 DC power. The pumps and atmosphere control system consist of mechanical pump, molecular pump, gas flowmeters and control panels.

Fig. 2 shows the cross-sectional morphology and film thickness of DLC film under the different deposition atmosphere. On the left side of the image is 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 the film, which effectively improve the adhesion between the film and matrix. The main element in the transition layer between the DLC film and the matrix is Si. Silicon atoms belong to the cubic diamond type. It has the same crystal structure as carbon atoms, which make it easier for the bonding of carbon atoms and silicon atoms. In addition, Si and Al are adjacent to each other in the periodic table of chemical elements. They have a similar electronegativity. Silicon and aluminum atoms can form solid solutions, resulting in the improved bonding strength between DLC film and matrix.

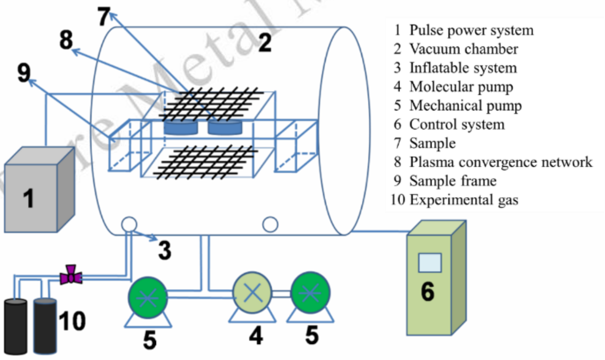

Fig. 1 Schematic diagram of PECVD

The carbons content in Fig. 2(b) is significantly lower than the others. Because there is a certain amount hydrogen element in the film when the DLC film was prepared by PECVD technology. The specific results of hydrogen content cannot be obtained by EDS. Because the DLC films only contain carbon and hydrogen elements, the more carbon there is, 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 in Fig. 2(a). It promotes the hydrogen formation due to active hydrogen atoms. When the gas released from the film, carbon became the main element of the DLC film surface [12]. As the proportion of acetylene gas increases, the thickness of DLC film increases from 4.455 μm to 7.481 μm. This is due to the total pressure in the vacuum chamber remains constant. But the number of atoms in the chamber is certain. As the acetylene increases, the more hydrocarbon ions are ionized. And the relative content of argon ions is decreased. This allows more hydrocarbon ions were deposited on the surface of the 2024 aluminum alloy without being bombarded by argon ions to move back into the chamber. Therefore, the thickness of DLC film gradually will increase as increasing the acetylene [13].

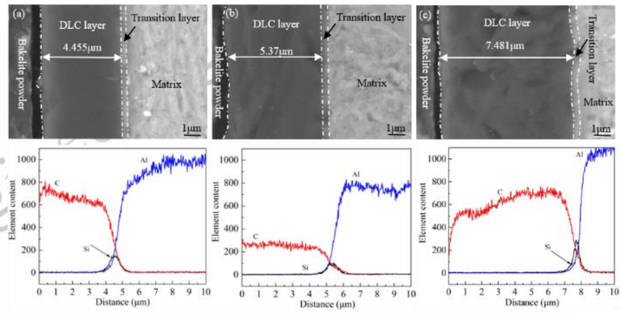

Fig. 2 Sectional morphologies and thickness results of the DLC film at the different deposition atmosphere

(a) $Ar:C_2H_2$=1:2 (b) $Ar:C_2H_2$=1:3 (c) $Ar:C_2H_2$=1:4

The structural characterization of the samples was carried out for understanding the above-described behavior. Fig. 3 shows the Raman spectrum after fitting with Gaussian function under different deposition atmosphere. 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} [14]. 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 increases as the I_D/I_G decreases [15-16]. DLC film prepared by PECVD technology can easily ionize acetylene gas. And the ionized hydrocarbon ions are adsorbed by the surface of aluminum alloy to form sp^3 bonds and hydrogen containing compounds [17]. As shown in Fig. 3, the positions of D and G peaks are different under different deposition atmosphere. When the mixture gas ratio increased from 1:2 to 1:4, the positions of the D and G peaks increase from 1362 cm^{-1} and 1580 cm^{-1} to 1395 cm^{-1} and 1600 cm^{-1}, respectively. The high band of the hydrogenated DLC film shows the bands of CH_2 and CH_3 recombine after C-H bonds were 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 are 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.

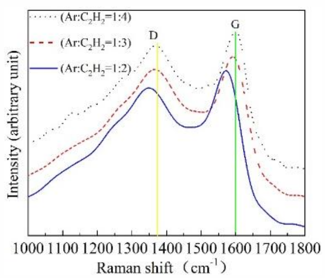

Fig. 3 Raman spectrum of the DLC film at the different deposition atmosphere

The wear resistance of the DLC film can be determined by the friction coefficient. The friction coefficient of 2024 aluminum alloy matrix is 0.31[18]. Fig. 4 shows the time-dependent average friction coefficient between DLC thin films and zirconia grinding balls under different deposition atmosphere. After the friction test was run for 155 mins, the friction coefficient was rapidly increased from 0.15 to 0.31 when the argon to acetylene was 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 that it is easy to wear and expose the matrix. The DLC film is continuously bombarded by argon ions during the deposition. It will cause severe stress, which generated and remained in the DLC film. It will make the film damage easier when a force was applied on the film [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. The main factors that affect 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, which means it has the best wear resistance.

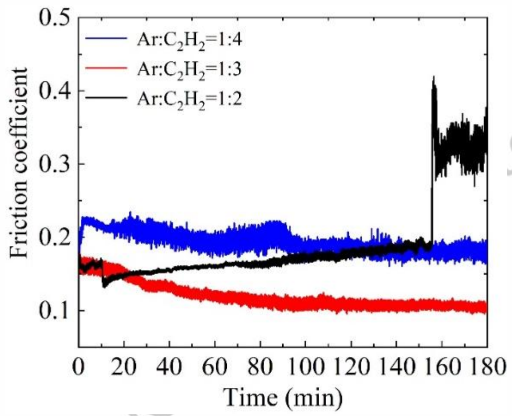

Fig. 4 Friction coefficient of the DLC film at the different deposition atmosphere

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 and Fig. 6 show the acoustic signal curves and the scratches profiles of the DLC films with different deposition atmosphere. 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 N, 9.8 N, and 6.6 N, respectively. But there is significant peeling around the scratch when the ratio of argon to acetylene is 1:2 (Fig. 6). 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. It increased the internal stress and made the film deformation. So, there is a large-scale film peeling under external force [19-20]. The acoustic emission signals intensity caused by the peeling of the film at the scratch tip did not exceed the minimum value set by the instrument. It is defaulted as noise signals during the film peeling process. When the atmosphere ratio is 1:2, the peeling phenomenon get serious. But there are three acoustic emission signals observed in Fig. 5a. This is because there are three locations where the DLC film continuously peels off at the front of scratch in Fig. 6a. The value of the acoustic emission signal appeared after the third position is much smaller than its value. In Fig. 6b, the DLC film almost have not 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 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 good mechanical properties such as adhesion and toughness than other samples.

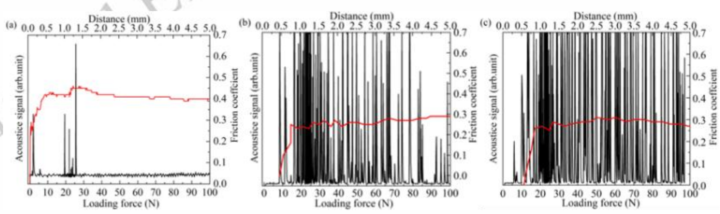

Fig. 5 Acoustic emission signal to progressive load on the DLC film at the different deposition atmosphere

(a) $Ar:C_2H_2$=1:2 (b) $Ar:C_2H_2$=1:3 (c) $Ar:C_2H_2$=1:4

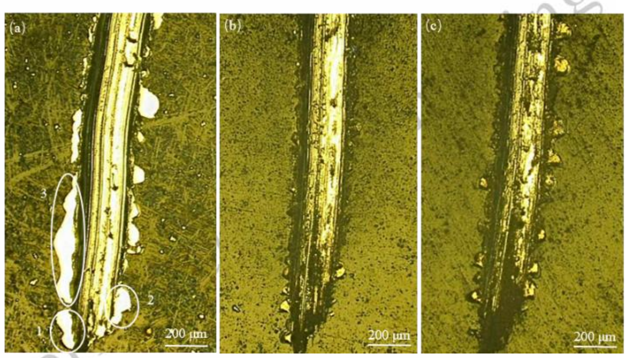

Fig. 6 Scratch morphology of the DLC film at the different deposition atmosphere

(a) $Ar:C_2H_2$=1:2 (1, 2, and 3 indicate the locations where film is peeling) (b) $Ar:C_2H_2$=1:3 (c) $Ar:C_2H_2$=1:4

Fig. 7 shows the nano-indentation hardness (H) and Young's modulus (E) of films under different deposition atmosphere. 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 GPa, 5.46 GPa, and 5.15 GPa. And the E values are 40.7 GPa, 40.3 GPa, and 37.3 GPa, respectively.

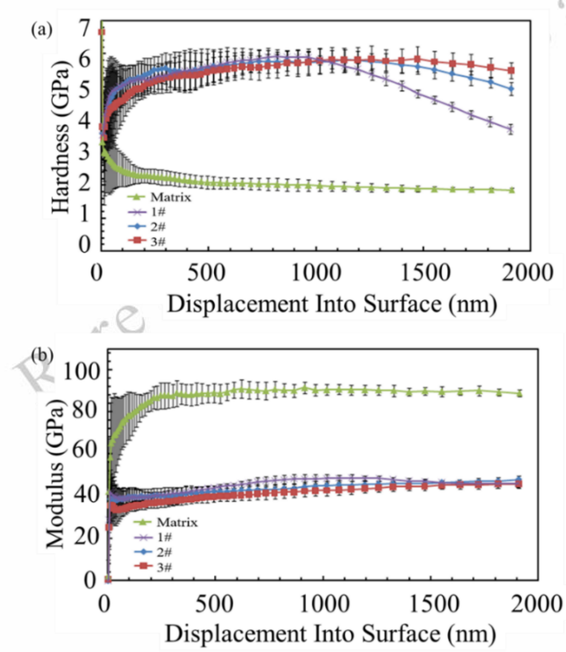

Fig. 7 Nano-indentation hardness and Young's modulus of the DLC film at the different deposition atmosphere

(1#: Ar:C_2H_2=1:2; 2#: Ar:C_2H_2=1:3; 3#: Ar:C_2H_2=1:4)

Table 2 Mechanical properties of the DLC film at different deposition atmosphere

No.	Coefficient friction	Hardness /GPa	Modulus /GPa	Adhesion /N	H/E	H^3/E^2
Matrix	0.3148	2.27	87.3	/	0.026	0.0015
1#	0.1880	5.26	40.7	2.2	0.129	0.0878
2#	0.1195	5.46	40.3	9.8	0.135	0.1002
3#	0.1943	5.15	37.3	6.6	0.138	0.0981

The mechanical properties of DLC films prepared under different deposition atmosphere are summarized in Table 2. The ratio of H/E characterizes the ability of the material to deform elastically and recover. Usually, the higher the H/E value, the lower the wear. The wear failure life of the film will be longer [21]. H^3/E^2 is the resistance factor to plastic deformation. It indicates the resistance of the film 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 increased 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.

3 Conclusions

1) As the acetylene increases, the thickness of film 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 argon to acetylene is 1:3, the content of sp^3 bonds in the DLC film is the highest. Based on the H/E and H^3/E^2 ratio, it can be concluded that the mechanical properties of DLC film is also the best.

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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：类金刚石碳（DLC）薄膜具有许多优点，例如高硬度、低摩擦系数和高化学稳定性。它们已被广泛用于提高轻合金的表面硬度和耐磨性。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 DLC 薄膜。通过场发射扫描电子显微镜、纳米压痕测试仪、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 sp3 和 sp2 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。这项工作为提高铝合金的机械性能和增强耐久性提供了实验和理论基础。
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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