

Preparation, Characterization and Tribological Properties of Diamond-Like Carbon Film on AZ31 Magnesium Alloy

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Abstract. In this study, DLC films were deposited using IBED with various CH₄/H₂ ratio, gas flow rates and accelerating voltages. The composition and mechanical properties of the DLC coatings were characterized using SEM, Raman spectroscopy and nano-indentor. The tribological properties of the coating were also investigated using a frictional surface microscope with an in situ observation system and friction force measurements. The DLC films were characterized by a lower I_D/I_G, higher hardness, and improved tribological properties when deposited at a lower accelerating voltage (6 kV). At the CH₄/H₂ ratio of 1:99 and 6 sccm/6 kV, minimum I_D/I_G values of 0.62, relatively low friction coefficient of 0.12, and a maximum hardness of 4056 HV were attained respectively.

Introduction

Magnesium alloys have been widely used because of their light weight, high dimensional stability, excellent machinability and so on [1, 2]. However, the poor hardness, abrasion resistance, and corrosion resistance limit their application [3]. Modification of the material surface is an effective means to improve these properties for more machine parts. Diamond-like carbon (DLC) films exhibit high hardness, low friction, excellent wear resistance and so on [4]. Liu et al. deposited a DLC film on metallic substrates using a methane ion-beam method and observed that the ultra-low wear rate was due to transfer layer formation of graphite-like carbon [5]. Dai et al. reported that magnesium alloy coated with Cr-incorporated DLC hard films had a low internal stress and excellent friction performance [6]. An increase in the hardness and reduction of the friction coefficient were observed in another study in which DLC coatings were deposited on magnesium alloys, which led to improvement of the wear resistance [7]. The drawbacks of poor hardness and wear resistance of the magnesium alloys were improved by depositing DLC films on the alloys [8, 9]. In addition, the production of a graded interfacial layer using ion-beam-enhanced deposition (IBED) can also reduce the internal stress. The DLC film can be deposited as a protective coating on magnesium alloys using physical vapor deposition, chemical vapor deposition, and other technique [10, 11]. The IBED method is a physical thin-film technique that achieves a high degree of precision and uniformity via the simultaneous bombardment of energetic atomic particles. Relative to chemical and thermal processes, the IBED method has many advantages when used to enhance the friction, adhesion, and other surface properties of high-precision parts, as it does not require post-coating refinishing.

In this study, different DLC films were deposited using IBED by changing the CH₄/H₂ gas ratio, flow rate and accelerating voltage for surface modification, and the composition and mechanical properties of the DLC coatings were analyzed. The purpose of this study was to improve the surface

performance of magnesium alloy AZ31 by enhancing the hardness and wear-resistance capacity of the DLC coating.

Experimental

The deposition of the DLC films was performed using IBED with CH₄ and H₂ sources. The mixture of CH₄ and H₂ with certain ratio was injected into the chamber. Firstly the film atoms penetrate the surface of the magnesium alloy to form the case layer. Upon implantation of the ions, they convey substantial energy to the film for substrate heating. The process of substrate heating provides a denser and more uniform coating. Then the film atoms grow out from the graded interface to form the growing DLC film by ion-beam bombardment, as illustrated in Fig. 1. Because of the graded interfacial layer, the film properties are improved, resulting in improved adhesion and lower internal stresses [12]. The substrate material used in this experiment was AZ31 (Mg–3.3%Al–0.6%Zn–0.28%Mn) magnesium alloy plates. The size of the magnesium alloy substrate was 15 mm (L) × 15 mm (W) × 3 mm (H). All the samples were ground with abrasive paper and polishing cloth. Then the samples were ultrasonically cleaned in ethanol for 10 min to remove any contamination. The current and deposition time were fixed at 40 mA and 4 h respectively. The detailed conditions are listed in Table 1.

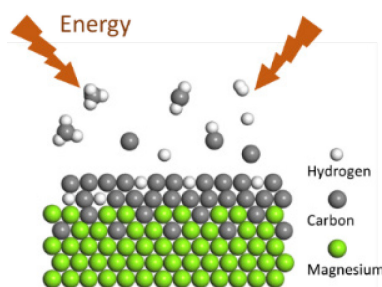


Fig. 1. Schematic diagram of ion implantation process.

Table 1. Parameters for different processing conditions.

		CH ₄ /H ₂ = 99:1						CH ₄ /H ₂ = 1:99		
Gas flow rate (sccm)	3	6	9	3	6	9	3	6	9	
Accelerating Voltage (kV)	6	6	6	9	9	9	6	6	6	

The detailed bonding structure of the DLC film was analyzed using Raman spectroscopy (NRS-4100). The surface hardness was determined using a JSPM-4210 nano-indentation. The cross-sectional morphology were analysed by a scanning electron microscopy (SEM; HITACHI, TM3000). The friction features were investigated with a reciprocating probe.

Results and Discussion

Raman spectroscopy is generally used to analyze the detailed bonding structure of DLC coatings. A shift of the G-peak position to higher wavenumbers and an increase of the intensity ratio I_D/I_G are consistent with an increase in the sp^2/sp^3 ratio [13]. Fig. 2 displays the G-peak position and the D-peak to G-peak (I_D/I_G) ratio of DLC coatings deposited at different conditions. The I_D/I_G ratios increased and the G-peak position shifted toward higher wavenumber with increasing accelerating voltage at CH₄/H₂ ratio of 99:1, and I_D/I_G decreased and the G-peak position shifted toward lower wavenumber with increasing gas flow rate at 6 kV. I_D/I_G decreased when the gas flow rate increased from 3 sccm to 6 sccm at CH₄/H₂ ratio of 1:99. The I_D/I_G and G-peak position were lower for the deposition at CH₄/H₂=99:1 than at CH₄/H₂=1:99. For the accelerating voltage of 6 kV and gas flow rates of 3 and 9 sccm, the I_D/I_G ratios were 2.12 and 1.25, respectively. Thus, the I_D/I_G ratio of DLC film deposited at 6 kV was lower than that deposited at 9 kV. The I_D/I_G ratio decreased with decreasing H₂ ratio. The I_D/I_G ratio decreased to a minimum value of 0.62 at 6 sccm/6 kV.

When a DLC coating is deposited at high accelerating voltage, the ions may have too much energy. The ions with higher energy cause the sp^3 bonds to break down into stable graphite-like sp^2 bonds with low-energy states. The high gas flow rate leads to a high amount of sp^3 C–C bonding. There are possible of other effects, such as the CH_x group ions reacting with dangling C-bonds, orbital hybridization between carbon atoms, and the formation of sp^3 C–C bonds at the surface of the magnesium alloy. Therefore, the DLC films deposited at lower accelerating voltage exhibited higher hardness. The I_D/I_G ratio is lower at $CH_4/H_2=1:99$ because of the increase in hydrogen promoting the formation of sp^3 C–C bonding. It is known that a low gas flow rate enhances dissociation of CH_4 because of the resident time at the plasma and leads to graphitization of the film structure because of H ion/atom/molecule enrichment [14, 15].

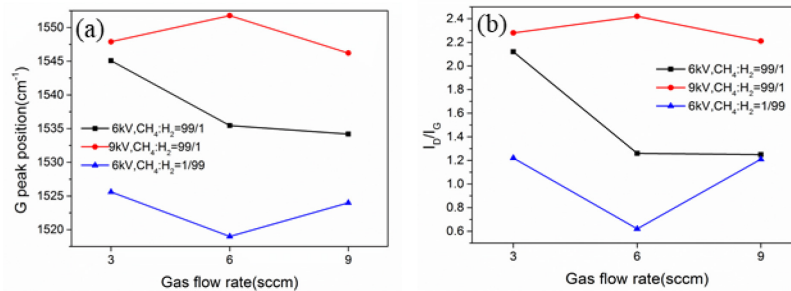


Fig. 2. (a) G-peak position and (b) I_D/I_G of DLC coatings deposited at different gas ratio, flow rate and accelerating voltage.

Table 2 and 3 display the hardness of the DLC coatings deposited at different conditions by nano-indenter [16]. The surface hardness clearly increased with increasing gas flow rate at 6 kV. The hardness of the DLC coating was higher at 6 kV than at 9 kV. The hardness increased to a maximum of 4056HV at 6 sccm/6 kV. The hydrogen content is considered to play an important role in determining the bonding structure of C atoms by helping to stabilize the sp^3 -C structure [17]. A low sp^2/sp^3 ratio implies low internal stress and high hardness. At the higher H_2 ratio, the DLC coatings exhibited higher hardness. The Vickers hardness of AZ31 magnesium alloy is only 78HV. The hardness of all the DLC coatings were much higher than that of uncoated substrate.

Table 2. Hardness of DLC coatings deposited at 6 kV.

Accelerating Voltage (kV)	CH ₄ /H ₂ = 99:1			CH ₄ /H ₂ = 1:99		
	3	6	9	3	6	9
Gas flow rate (sccm)						
Hardness (HV)	1011	1036	1044	1320	4056	1334

Table 3 Hardness of DLC coatings deposited at 9 kV

CH ₄ /H ₂ = 99:1			
Accelerating Voltage (kV)	9		
Gas flow rate (sccm)	3	6	9
Hardness (HV)	1006	806	1018

SEM images showing the cross-sectional morphology of the AZ31 magnesium alloy and DLC films deposited at different conditions are presented in Fig. 3. Compared with the uncoated AZ31 magnesium alloy, no obvious cracks or delamination were observed for any of the DLC coating surfaces, indicating that the DLC films were successfully deposited on the substrates as protective coatings. The DLC film surfaces were uniform over a large area. The average thickness of the DLC film was approximately 0.284 and 1.145 μm , respectively, at 3sccm/6 kV and 9sccm/6 kV shown on Fig. 3(b) and (d). The thickness of the DLC layer was approximately 1.034 μm at 6 sccm/6 kV shown on Fig. 4(c). The DLC coating deposited at 6 sccm/6 kV was denser than that of others.

The friction behaviors of the uncoated and DLC-coated AZ31 magnesium alloys were examined using a reciprocating probe and wear tester. The load, sliding speed, sliding distance, and repeated time were 1 N, 20 mm/s, 2 mm, and 300 s, respectively. Fig. 4 shows that the friction coefficient

varied with time for the uncoated magnesium alloy and DLC coatings. The friction coefficient was highest in the first cycle because of the run-in process. The curve of the friction coefficient fluctuated because of the appearance of wear particles during the friction process. The friction coefficient of the uncoated magnesium alloy was significantly higher than that of DLC films. During the friction process, the friction coefficient on the uncoated magnesium alloy clearly changed and increased to a maximum of 0.28 as observed in Fig. 4(a). Compared with the uncoated AZ31 magnesium alloy, the DLC films had lowest average friction coefficient of approximately 0.11 at 9 sccm/6 kV because of higher sp^2/sp^3 ratio. The sudden increase in friction coefficient may be due to a lower film density and a thinner film as observed in Fig. 5(b). The fluctuations were caused by cracking of the DLC coatings under applied loading. The cracks were detected on the surface especially on uncoated AZ31 magnesium alloy surface.

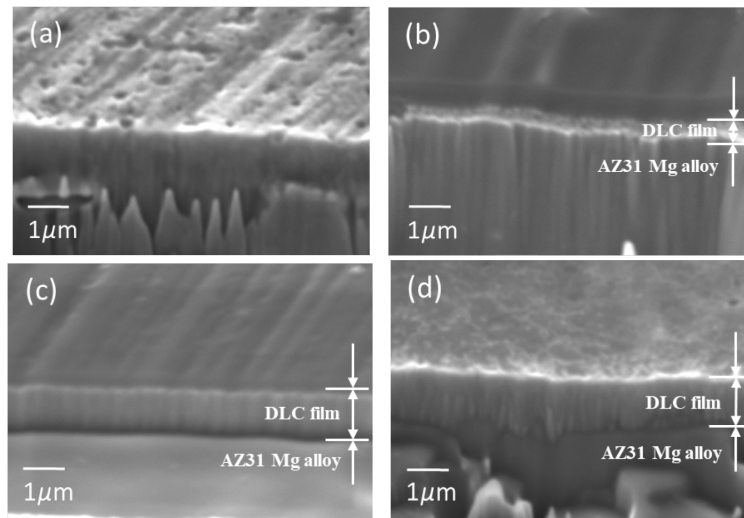


Fig. 3. Cross-section SEM images of (a) AZ31 magnesium alloy substrate, DLC films deposited at the CH_4/H_2 ratio of 1:99 and at (b) 3 sccm/6 kV; (c) 6 sccm/6 kV; (d) 9 sccm/6 kV.

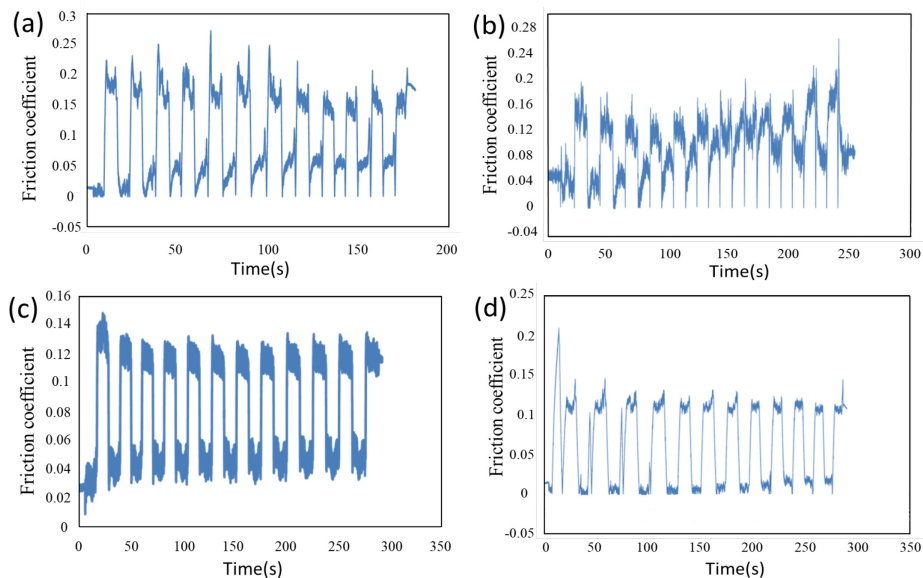


Fig. 4. Friction coefficient varies with time of (a) naked magnesium alloy substrate; DLC films deposited at the CH_4/H_2 ratio of 1:99 and at (b) 3 sccm/6 kV; (c) 6 sccm/6 kV; (d) 9 sccm/6 kV.

In Fig. 5, images of the wear morphology of the uncoated magnesium alloy and DLC films are presented. The numbers of cracks and grooves parallel to the sliding direction could be determined. The wear traces are deep and broad in Fig. 5 (a), indicating the low hardness. The area of the wear trace was $735 \mu\text{m}^2$. Surface profiles of wear tracks of the uncoated magnesium alloy substrate and DLC films deposited at different conditions are presented in Fig. 6. The area of the wear track was $615 \mu\text{m}^2$ at 9 sccm/6 kV. For the gas flow rates of 3 and 6 sccm, the wear track areas were 350 and

332 μm^2 , respectively. The wear areas are consistent with the hardness, which can protect the surface from wear. Once cracks appeared on the DLC films, spallation more easily spread along the surface. Less abrasive debris or spike particles were observed in the wear morphology images of the DLC coatings than that of the uncoated magnesium alloy. The lowest I_D/I_G and highest hardness values at 6 sccm/6 kV corresponded with the least debris in Fig. 5(c). The good wear resistance may originate from the combined protection of the smooth surface morphology and high hardness of the DLC films.

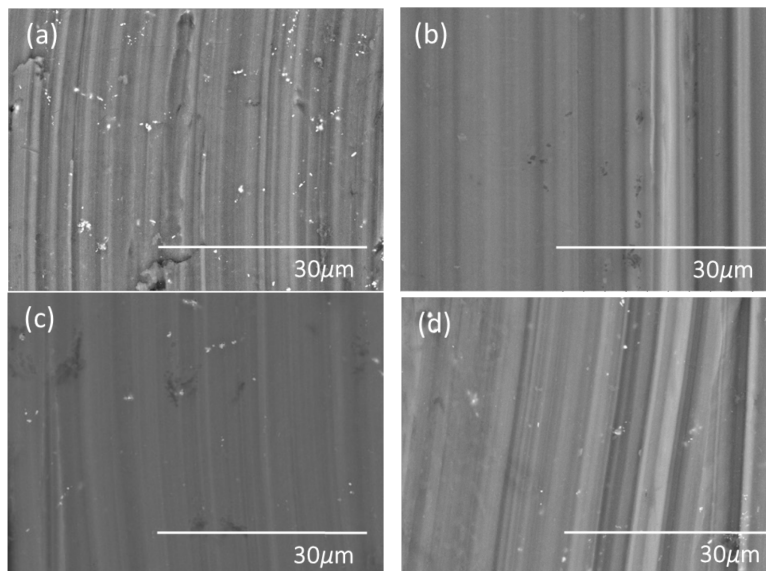


Fig. 5 Images of wear morphology of uncoated magnesium alloy substrate (a), and DLC films deposited on magnesium alloy at 3 sccm/6 kV (b); 6 sccm/6 kV (c); 9 sccm/6 kV (d) with the CH_4/H_2 ratio of 1:99.

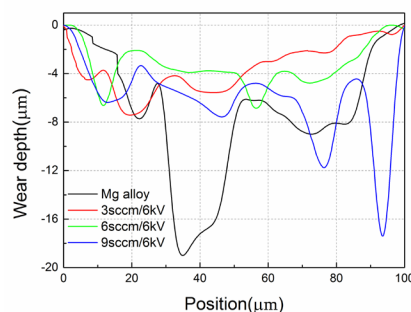


Fig. 6 Surface profiles of wear tracks of uncoated magnesium alloy substrate and DLC films deposited on the magnesium alloy at different conditions for CH_4/H_2 ratio of 1:99.

Conclusions

Different DLC coatings were deposited on AZ31 magnesium alloy using the IBED method by changing the gas ratio, flow rate and accelerating voltage. The following observations were made:

(1) The I_D/I_G decreased to a minimum of 0.62, the hardness increased to a maximum of 4056 HV and the track wear area decreased to 332 μm^2 at a lower accelerating voltage of 6 kV and at a higher H_2 ratio. The friction coefficient decreased to 0.12 for the DLC coating deposited at 6 sccm/6 kV.

(2) Orbital hybridization between carbon atoms and sp^3 C–C bonds was formed. The ions with higher energy caused the sp^3 bond to break down into the stable sp^2 bond as the accelerating voltage decreased, and unsaturated C- bonds were saturated by the site-selective adsorption of incident CH_x , resulting in a high fraction of sp^3 carbon, and high hardness in the DLC films.

(3) An increase of the gas flow rate led to reduction of friction coefficient because the increasing CH_x group ions reduced the number of C-dangling bonds on the surface. A low gas flow rate enhances dissociation of CH_4 due to the resident time at the plasma and leads to graphitization of the film structure because of H ion/atom/molecule enrichment.

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