

Article

Enhanced Wear and Corrosion Resistance of AZ91 Magnesium Alloy via Adherent Si-DLC Coating with Si-Interlayer: Impact of Biasing Voltage

Changqing Cui ^{1,*} and Chunyan Yang ²¹ College of Mechanical Engineering, Baicheng Normal University, Baicheng 137000, China² College of Computer Science, Baicheng Normal University, Baicheng 137000, China; chqoo@163.com

* Correspondence: bsccq@bcnu.edu.cn; Tel.: +86-15593190528

Abstract: Magnesium alloys are the lowest-density structural metals with a wide range of applications, such as aircraft skins, engine casings and automobile hubs. However, its low surface hardness and non-corrosion resistance in natural environments limit its wide range of applications. In this work, Si-DLC coatings (Si: 15 at.%) are fabricated on AZ91 alloy using a hollow cathode discharge combined with a DC bias voltage from 0 to −300 V to increase the deposition rate and modulate the structure and properties of the coatings. The Si interlayer with a thickness of around 0.6 μm is deposited first to enhance the adhesion. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy are used to investigate the effect of DC bias on the microstructure evolution of Si-DLC coatings. Meanwhile, corrosion and wear resistance of the coatings at various bias voltages have been investigated using electrochemical workstations and pin-on-disk wear testers. It is shown that the bias-free coating has a loose structure and is less resistant to corrosion and wear. The bias coating has a compact structure, small carbon cluster size, high chloride ion corrosion resistance, and high wear resistance against Al₂O₃ spheres. The corrosion potential of the coating bias at −300 V is −0.98 V, the corrosion current density is $1.35 \times 10^{-6} \text{ A} \cdot \text{cm}^{-2}$, the friction coefficient is 0.08, and the wear rate is 10^{-8} orders of magnitude. The formation of SiC nanocrystals and high sp³-C, as well as the formation of transfer films on the surface of their counterparts, are the main reasons for the ultra-high wear resistance of the bias coatings. The wear rate, coefficient of friction, and corrosion rate of the coating are 0.0069 times, 0.2 times, and 0.0088 times that of the AZ91 alloy, respectively. However, the bias coating has only short to medium-term protection against the magnesium alloy and no long-term protection due to cracks caused by its high internal stress.

Keywords: DLC coatings; magnesium alloys; bias voltages; corrosion; wear



Citation: Cui, C.; Yang, C. Enhanced Wear and Corrosion Resistance of AZ91 Magnesium Alloy via Adherent Si-DLC Coating with Si-Interlayer: Impact of Biasing Voltage. *Coatings* **2024**, *14*, 341. <https://doi.org/10.3390/coatings14030341>

Academic Editor: Ludmila B. Boinovich

Received: 16 February 2024

Revised: 7 March 2024

Accepted: 11 March 2024

Published: 13 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Due to the growing need for lightweight materials to decrease fuel consumption and improve power output, magnesium alloys have garnered attention in industries such as aerospace (black boxes), automotive (wheel hubs), and electronics (shells). With a density two-thirds that of aluminum, magnesium alloys offer advantages beyond their low density and high strength-to-weight ratio, including excellent machinability, dimensional stability, thermal conductivity, and damping characteristics [1–4]. However, the poor surface properties of Mg alloys themselves severely hinder their wide applicability, and corrosion and wear resistance of Mg alloys are critical issues that have been addressed in recent years. Surface coatings, especially the diamond-like carbon (DLC), have more advantages due to their ultra-low friction coefficient, amorphous structure, excellent anti-corrosion and wear resistance, which is very suitable for Mg-based alloy protection. Li et al. deposited DLC films on AZ91 at different C₂H₂ flows after a Si bottom layer was fabricated first [5], and the DLC films prepared at low flow rates have higher hardness and better wear resistance but poorer corrosion resistance. Molak et al. [6] deposited Si-DLC

coating on oxidized AZ91E alloy based on the dissociation of precursor gases ($\text{Si}(\text{CH}_3)_4$ and C_2H_2) near the hot fiber. The coating shows more favorable anti-corrosion properties. Dai et al. [7] deposited Cr-DLC films on Mg-Al-Zn alloy by magnetron sputtering and linear ion source. It is shown that all films exhibit higher adhesion and wear resistance to AZ31 than pure DLC films but are less resistant to corrosion due to defects in the thickness. Wu et al. [8] synthesized Me-DLC and Me/Ti-DLC films, and the superior anti-corrosion ability of Me/Ti-DLC film was proved. Pillari et al. [9] coated DLC film on the Mg nanocomposites by sputtering graphite under an argon gas atmosphere. It was shown that the film is very uniform and has an improved surface hardness compared with the substrate.

Others have used bias voltages to regulate the DLC coating properties. Zou et al. [10] deposited DLC films on AZ91 at various negative pulse bias voltages to enhance their wear resistance, which demonstrated that the sp^3 content and the corresponding hardness increases with negative bias from 0 to 100 V and then decreases with increasing bias voltage. Su et al. [11] prepared Mo-DLC films at different bias voltages to overcome the poor tribological properties of DLC films in pure methyl alcohol. The optimized bias voltage of 600 V results in the highest sp^3 hybridization bonds and nanohardness, as well as the lowest abrasion rate. Li et al. [12] fabricated Si-DLC coating on AZ31 alloy. The -500 V bias coating has the highest sp^3 phase and superior short-term anti-corrosion capability in a 3.5 wt.% NaCl solution. Xia et al. [13] reported that the sp^3 content in DLC films falls with increasing negative bias. Clearly, the above investigations related to bias voltages are quite different for different deposition processes.

Although DLC coatings have been demonstrated to have a positive effect in improving the corrosion and wear resistance of various substrates, there have been very few reports related to a simultaneous investigation of corrosion and wear resistance by applying bias voltages to Mg-based substrates during hollow cathode discharges. In particular, Si-doped DLC coatings have the potential to form SiC phases for enhanced wear resistance. The goal of this work will be to focus on the effect of dc bias on the structure and properties of Si-doped DLC coatings prepared from hollow cathode discharges, with important implications for scaling up applications of Mg-based alloys.

2. Materials and Methods

AZ91 alloy (Shanghai Hechuan Metal Material Co., LTD., Shanghai, China, casting) was used as a substrate, and its chemical composition can be found in reports [6,14]. Before deposition, all AZ91 sheets measuring $15\text{ mm} \times 15\text{ mm} \times 3\text{ mm}$ were first grounded by using various grades of metallographic abrasive paper, followed by cleaned ultrasonically in acetone and absolute ethyl alcohol for 10 min. Subsequently, the AZ91 sheet was placed on a holder in the chamber and etched by Ar^+ plasma for 20 min at a bias voltage of -1.3 kV . The roughness of the alloy before etching was about 85 nm (Ra), and after etching, it was about 7.5 nm (Ra), a significant reduction in roughness. To further improve the adhesion between the DLC coating and the substrate, an adhesion-promoting Si bottom layer with a thickness of around $0.6\text{ }\mu\text{m}$ was fabricated in a mixture of Ar and $\text{Si}(\text{CH}_3)_4$ (TMS) before a Si-doped DLC layer (Si-DLC), which was synthesized in a mixture of Ar, C_2H_2 , and TMS for 45 min. Because Si is not conductive like metals, it is likely that SiC nanocrystals will be formed to enhance wear resistance. Moreover, the compatibility between the Si intermediate layer and Si-DLC is better than other metallic layers. Moreover, the thickness is referred to by our previous investigation, which proves that the Si bottom layer is well compatible with the DLC layer only if the thickness is larger than $0.5\text{ }\mu\text{m}$. Therefore, we design the thickness of the Si layer to be $0.6\text{ }\mu\text{m}$. The deposition method is a mesh hollow cathode discharge [12]. A metallic cage was positioned atop the AZ91 alloy to form a hollow cathode. The metal cage has a substantially higher plasma density inside than outside due to the hollow cathode effect. A bias voltage was applied between the AZ91 alloy and the metallic cage, which can induce a very high ionic energy incident on the AZ91 alloy surface, enhancing the adatom mobility and increasing the energetic ion bombardment on the coating surface. This method has a high gas ionization rate and deposition efficiency

and can be applied to matrices of various shapes to achieve uniform deposition over a large area without a dead-angle. Moreover, the coating is well bonded to the substrate, and the coating structure is dense. In particular, it has been empirically demonstrated that fine SiC nanocrystals can be formed in DLC coatings as long as the Si content is greater than 10% compared with conventional PVD techniques. The precise parameters are as follows. For the Si layer, Ar/TMS rate of 20/60, working pressure of 0.5 Pa, mesh voltage of -1.3 kV, bias voltage of -100 V, and deposition time of 10 min. For the Si-DLC layer, Ar/C₂H₂/TMS rate of 20/60/10, working pressure of 1.0 Pa, mesh voltage of -1.3 kV, and bias voltages were fixed at 0 V, -100 V, -200 V, and -300 V, respectively. The ratio of the atomic percentages of carbon and silicon in the coating is about 5.67.

The coating's structure was examined via a transmission electron microscope (TEM, FEI Talos F200X, Houston, OR, USA) and Raman spectroscopy (InVia, Renishaw, London, UK). The morphology was observed via a scanning electron microscope (SEM, FEI, Hillsboro, OR, USA). The chemical composition and chemical states were characterized by energy disperse spectroscopy (EDS, EDAX-Falcon, Mahwah, NJ, USA) and X-ray photoelectron spectroscopy (XPS, AXIS Mode, Waltham, MA, USA). The Raman spectra were decomposed by the Gaussian function into two Gaussian peaks (D band and G band) [12]. The XPS was performed with an Al X-ray source at a pass energy of 160 eV after the Ar⁺ erosion. The corrosion behavior and the tribological properties were assessed by an electrochemical workstation (Princeton VersaSTAT3, Ametek, Berwyn, IL, USA) and a pin-on-disk tribometer (SFT-2M, Chinese Academy of Sciences, Lanzhou, China), respectively. A traditional three-electrode cell consisting of a Pt sheet, a saturated calomel electrode (SCE) and test samples was conducted in a 3.5 wt.% NaCl solution. A steady-state potential was implemented with a polarization sweep rate of 1 mV/s, ranging from -0.5 V_{ECS} to $+0.5$ V_{ECS}. The electrochemical impedance spectrum (EIS) was executed over a frequency range of 10^5 Hz to 0.1 Hz at a perturbative potential of 10 mV. A normal load of 200 g was applied to a 6 mm Al₂O₃ sphere rotated at 300 rpm in ambient air for 15 min under dry sliding for the duration of the wear test. A 3D profilometer (CR 30-T1000, Suzhou Betejia Optoelectronic Technology Co., LTD., Suzhou, China) was employed to measure the cross-section of the wear tracks, and the wear rate was calculated using Equation (1).

$$W = V / (F \times D) \quad (1)$$

where W is the wear rate ($\text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$), V is the wear volume (mm^3), F is the applied normal load (N), and D is the total sliding distance (m).

3. Results

3.1. Structure

SEM images of the surface and cross-section of the Si-DLC coating are shown in Figure 1. It can be seen that Figure 1a,b show a similar appearance, as do Figure 1c,d. Figure 1a shows that the unbiased coating has a loose structure, and its surface exhibits many deep voids and large carbon clusters, like many cauliflowers. Compared with the unbiased coating, Figure 1b shows that the size of the carbon grains and voids decreases, and the coating becomes more compact. For the -200 V coating in Figure 1c, driven by the larger deposited kinetic energy, more carbon atoms are deposited on the surface of the coating and spread across its surface to fill a large number of holes. At the same time, at the -200 V bias bombardment, the size of the carbon clusters is further reduced, and the coating becomes increasingly dense. However, the deposition energy provided by the -200 V bias is still insufficient, so the holes are still visible in the upper left and lower right corners of Figure 1c. As the bias is increased to -300 V, see Figure 1d, the coating is very dense without any defects and the carbon clusters are very fine.

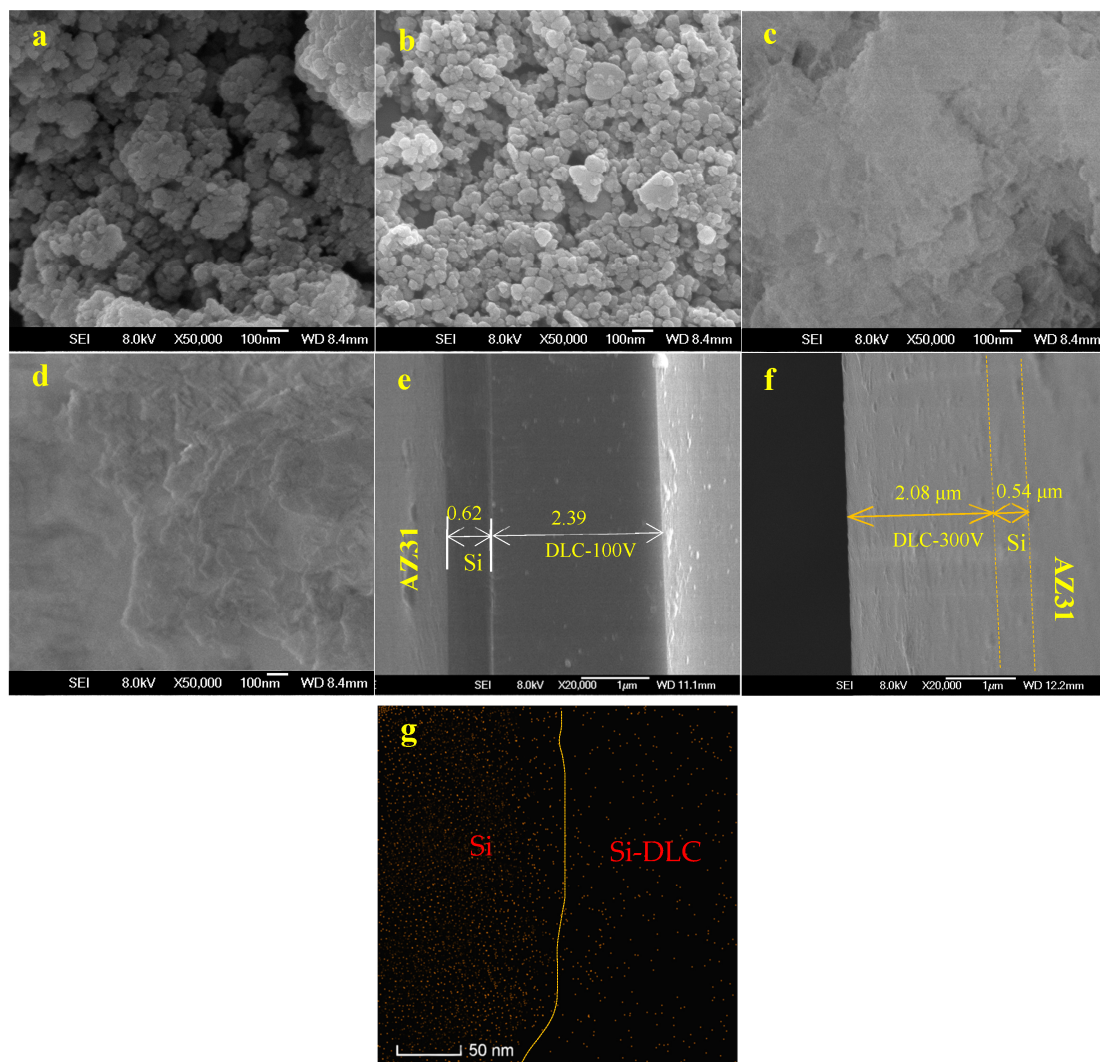


Figure 1. SEM images of the surface and cross-section of the Si-DLC coating. Results at (a) 0 V; (b) −100 V; (c) −200 V; and (d) −300 V. (e) Cross-section of −100 V; (f) cross-section of −300 V. (g) Mapping of the Si distribution across the −300 V coating cross-section.

Figure 1e shows Si under layer with a thickness of roughly 620 nm was grown on the −100 V sample, and the thickness of the Si-DLC layer is around 2.39 μm . The coating thickness is uniform, and the interface between each layer is well-defined. Figure 1f shows the thickness of the Si layer of the −300 V coating is around 540 nm and the Si-DLC layer with a thickness of around 2.08 μm . It is also clearly understood from Figure 1f that the −300 V coating shows smooth, dense, and compact structures, and the interfaces between each layer are not visible and clear. It is very vague, without any defects, indicating that the coating is well combined between the layers and the coating is well adhered to the AZ91 substrate. Figure 1f shows the mapping pattern of the Si elements across the −300 V coating cross-section. It is clear that the Si elements are distributed very evenly. In summary, the bias voltage leads to a reduction in the size of the carbon grains, in the size and number of defects, and in the thickness of the coating, which also makes the structure dense and compact.

Figure 2a depicts a surface TEM image of an unbiased coating. The coating shows the rough carbon clusters, and the corresponding Fast Fourier Transform (FFT) pattern in Figure 2b shows an unclear halo, indicating its coarse amorphous carbon structure. Figure 2c illustrates that the −200 V coating has a finer structure with smaller carbon clusters, and the corresponding FFT pattern in Figure 2d is still a halo, suggesting its fine

amorphous structure. In the case of the -300 V coating in Figure 2e, the surface presents very different, that is, many black nanocrystallines embedded in tiny amorphous carbon clusters, and the FFT pattern in Figure 2f shows a series of diffraction rings, corresponding to SiC (101), (102), (104), (105), and (108) (#PDF 49-1430), which were confirmed by the diffraction ring radius. Results from the HRTEM images and the corresponding FFT patterns consistently confirm that the Si-DLC layer is an amorphous structure. When the bias voltage is increased, the carbon grain size decreases, a large number of nanocrystals appear, and the phase structure changes from amorphous carbon to nanocrystalline SiC.

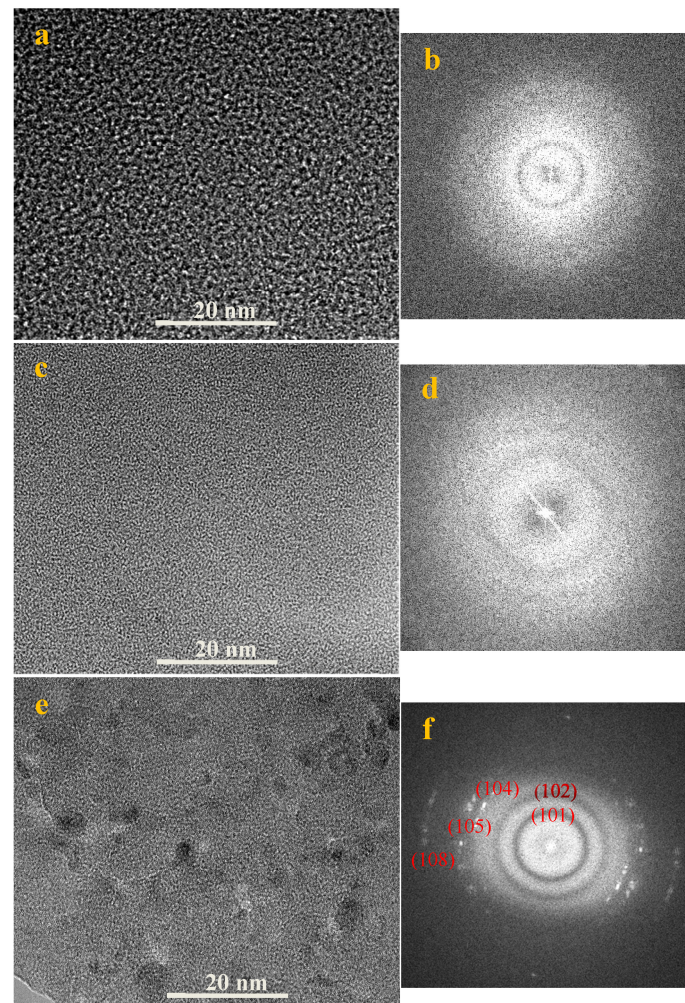


Figure 2. TEM observations and the corresponding FFT images of the Si-DLC coatings at (a) 0 V; (b) FFT pattern of 0 V; (c) -200 V; (d) FFT image of -200 V; (e) -300 V; (f) FFT image of -300 V.

The Raman spectrum of the DLC coatings always consists of sp^2 and sp^3 bonds, and the sp^3 fraction is directly related to the hardness of DLC coatings. Figure 3 shows the Raman spectra and fitting curves for the Si-DLC coatings, which show two distinctive asymmetric peaks from 1000 to 1800 cm^{-1} , consisting of a D peak around 1360 cm^{-1} and a G peak around 1580 cm^{-1} . The position of Raman G and D bands, full width at half maximum (FWHM) of peak G, hydrogen content, as well as intensity ratio of I_D/I_G , are shown in Table 1. From Figure 3 and Table 1, it can be found that, with the bias increasing from 0 to -300 V, the positions of G and D peaks move towards high wavenumber, FWHM for G peak and the ratio I_D/I_G decrease, and the saliency of the D and G peaks of -300 V coating is the most intense. The positions of the G and D peaks are shifted to higher wavenumbers, indicating an increase in the internal stress of the coating, while a decrease in the I_D/I_G ratio indicates an increase in the sp^3 phase content. Moreover, the higher

while narrower Raman peak can be attributed to a more ordered structure in the deposited coating with more Raman activity and longer phonon lifetime.

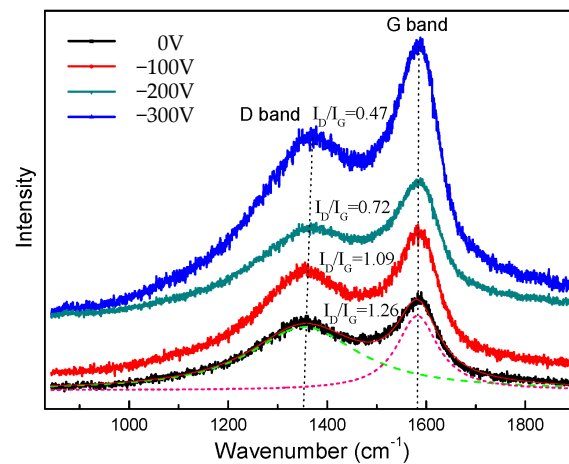


Figure 3. Raman spectra of the Si-DLC coatings.

Table 1. Gaussian fitting parameters obtained from the Raman spectra.

Samples	Position (D Peak) (cm ⁻¹)	Position (G Peak) (cm ⁻¹)	I _D /I _G	FWHM of G Peak (cm ⁻¹)	H at. %
0 V	1351.7	1580.1	1.26	74.69	18.35
−100 V	1358.5	1582.3	1.09	70.18	14.07
−200 V	1365.2	1584.6	0.72	67.92	10.84
−300 V	1367.5	1587.1	0.47	65.67	6.29

Table 1 clearly shows that the DLC_{−300V} coating has the lowest I_D/I_G value of 0.47, indicating its highest sp³ phase concentration, which illustrates that the higher bias produces more high-energy particles and has a strong implantation effect on the subsurface of the coating, which is helpful for generating the sp³ bond structure [11]. Moreover, the G peak wavenumber of the DLC_{−300V} coating has the highest wavenumber at 1587.1 cm^{−1}, indicating the highest internal stress of the coating. In addition, the decrease of FWHM (G peak) of the DLC_{−300V} coating indicates that the disorder degree of the above DLC coatings decreases with bias increasing, which is highly consistent with TEM observation in Figure 2c. In summary, the inter-stress, sp³ concentration, and hardness of the Si-DLC coating increase with bias from 0 to −300 V.

3.2. Corrosion Behavior

Figure 4a exhibits the Tafel polarization curves (TPC), which obtain polarization parameters of the coatings [5,15,16]. The electrochemical parameters are listed in Table 2. Figure 4a shows that all samples exhibit similar shapes in the cathode reaction region, but they are very different in the anode reaction region. The AZ91 alloy and the −100 V coating show normal and smooth shapes, indicating a homogeneous corrosion process, while the unbiased, −200 V and −300 V coatings exhibit abrupt points in the anode reaction region corresponding to −1.22 V, −0.79 V, and −0.74 V. The −1.22 V indicates the Cl[−] ions penetrate into the inner coating and react on the coating to generate corrosion products [17]. As the reaction progresses, the corrosion product accumulates on the surface of the coating, resulting in a decrease in the corrosion current density (*I*_{corr}) after −1.22 V. In the case of −200 V and −300 V coatings, there is a sudden rise at −0.79 V and −0.74 V, suggesting that the coating is broken, while at the same time, cracks appear and chloride ions enter the interior of the coating, with the result that the value of *I*_{corr} increases rapidly. In addition, the TPC of the coating shows a large shift towards the lower value of *I*_{corr} and higher potential compared with the AZ91 substrate, especially for the −300 V coating, which has

the lowest I_{corr} value and highest potential (E_{corr}), indicating its best corrosion resistance among the groups.

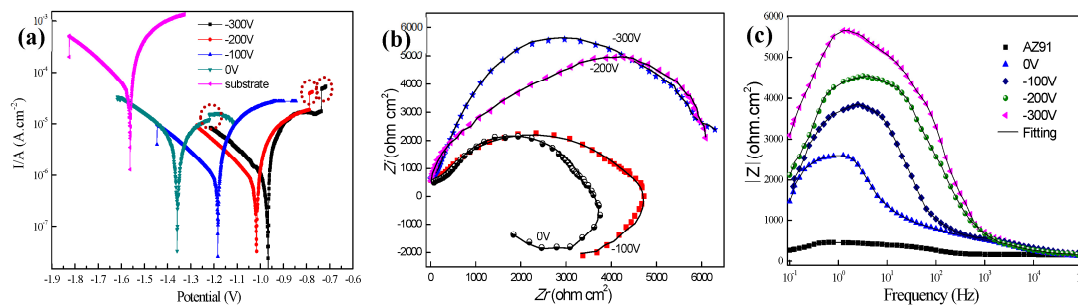


Figure 4. The results of electrochemical test in 3.5 wt.% NaCl aqueous solution. (a) Potentiodynamic polarization curves; (b) Nyquist plots; (c) Bode plots of $|Z|$ vs. frequency.

Table 2. Potentio-dynamic polarization parameters of the samples.

Samples	E_{corr} (V)	I_{corr} ($A \cdot cm^{-2}$)	R_{corr} (mm/Year)	β_c (mV)	β_a (mV)
AZ91	−1.566	7.84×10^{-4}	17.77	480	322
0 V	−1.359	9.98×10^{-6}	0.258	467	84
−100 V	−1.185	7.45×10^{-6}	0.193	311	88
−200 V	−1.016	5.89×10^{-6}	0.152	309	49
−300 V	−0.967	6.02×10^{-6}	0.156	226	40

As can be seen from Table 2, I_{corr} gradually decreases, and E_{corr} becomes nobler with increasing bias voltage. Moreover, Table 2 shows that the I_{corr} of the bias coating is two orders of magnitude lower than that of the AZ91 alloy. The coating biased at −300 V has the lowest corrosion rate, which is calculated by Equation (2) [15]. The AZ91 alloy has the highest corrosion rate at 17.77 mm/year, and the −200 V and −300 V coatings have very similar values, around 0.152 mm/year.

$$R_{corr} = \frac{MI_{corr}}{nF\rho} \times 87,600 \quad (2)$$

where M is the relative atomic mass of the substrate; n is valence; ρ represents the density of the substrate; F denotes the Faraday's constant of $26.8 A \cdot h/mol$.

Figure 4b is the Nyquist plots of the coatings. From Figure 4b, we can find that the 0 V and −100 V coatings show capacitive arcs in the high-frequency region and induced arcs in the low-frequency region, indicating that they are pitted at the surface defects [17]. In contrast, the two coatings at −200 V and −300 V exhibit only one capacitive arc over the entire frequency range. The capacitive arc diameter of the coating is much larger than that of the substrate and increases with bias, demonstrating the better anti-corrosion properties of the coating in the Cl^- environment. The −300 V coating has the largest capacitive loop diameter, implying optimal corrosion resistance.

Figure 4c illustrates the Bode-Z plots of the coatings. The model value of the impedance $|Z|$ can be used to evaluate the stability of the coating. The higher the value of $|Z|$, the more stable the coating. As seen in Figure 4c, the impedance $|Z|$ of the samples decreased with increasing frequency in the range of 10^2 to 10^5 Hz and became almost constant over 10^4 Hz. Also, it can be seen that the coated AZ91 has a higher $|Z|$ than the bare AZ91. The highest value of $|Z|$ is found for the −300 V coating, indicating that it is the most stable. These results demonstrate that the smooth surface and compact structure of DLC coating enhance the corrosion resistance of bare Mg alloy.

Figure 5 shows the SEM morphology of the specimen after electrochemical testing in a 3.5 wt.% NaCl solution. Figure 5a illustrates that the pits and cracks appeared after

the test, a large number of corrosion products paved on the AZ91 surface, which was verified by the EDS pattern in Figure 5b, as marked at the yellow circle, a large amount of Mg and O were detected in the EDS pattern, as well as Cl element, indicating the products of $\text{Mg}(\text{OH})_2$ and MgCl_2 formed. Figure 5c shows that the coating without bias presents obvious corrosion pits and cracks, indicating that the coating suffered from severe non-uniform corrosion. Figure 5d shows that the coating at -100 V has the same surface morphology as the 0 V coating, while the pits and cracks that occurred at the boundary of the holes and large particles were narrow and small. After increasing the bias to -300 V, the surface morphology remains with a large number of cracks due to high inter-stress, but there is no peeling, and the cracks are not very deep, showing uniform corrosion, as shown in Figure 5e. So, after increasing the bias, the anti-corrosion properties of the coating are enhanced, and the corrosion process becomes more uniform.

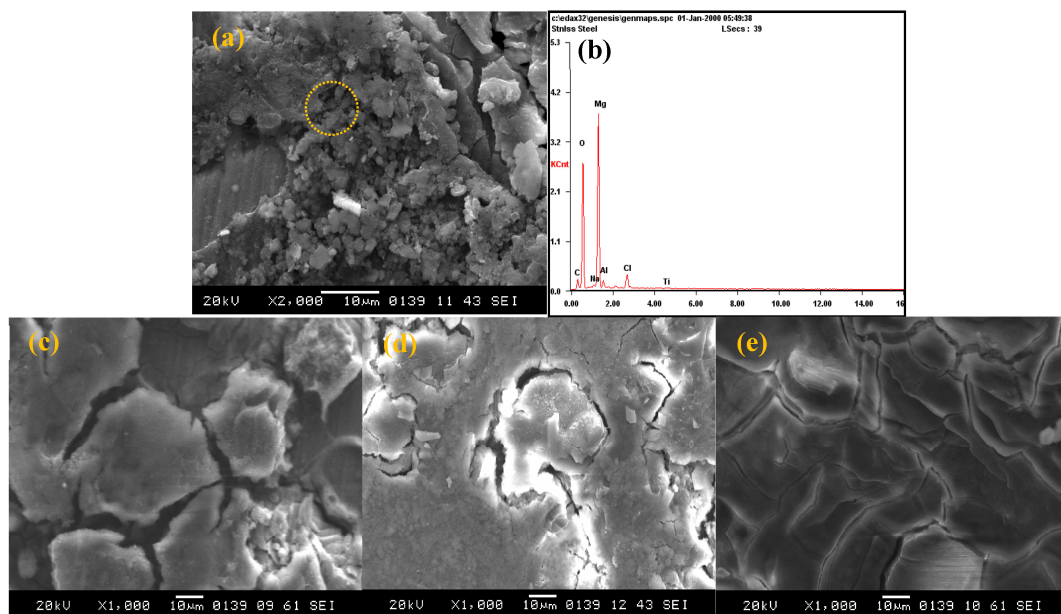


Figure 5. SEM morphology of the coating after electrochemical testing (a) AZ91; (b) EDS pattern of the yellow circle area; coatings at (c) 0 V; (d) -100 V; (e) -300 V.

3.3. Tribological Property

Figure 6a shows the averaged coefficient of friction (COF) values of the coatings after the tests in ambient air, whereas Figure 6b presents wear loss for each tested coating. The mean value of the COF for each test is calculated excluding the run-in period fluctuations of the friction force. As shown in Figure 6a, it can be observed that the COF for the coatings exhibits a similar tendency. The COF of the unbiased coating first increases and then decreases at 100 s, after which the coating enters a steady state with an average value of around 0.21 . The COF fluctuates considerably. This is ascribed to the large particles (like cauliflower) on the surface and the so many holes and pits. As the sliding time increases, the so-called cauliflowers are torn and fractured from the surface by shear and normal forces. Thus, the COF decreases after 100 s. For the bias coating, the evolution of the COF along the test is quite stable for each bias coating without any abrupt changes, and the COF is significantly reduced compared to the unbiased case. The COF decreases with increasing bias, with the lowest COF around 0.08 for the -300 V coating. Figure 6b depicts that the wear loss of the deposited Si-DLC coating is relatively low. The wear rate of the -300 V biased coating was calculated to be the lowest of $9.35 \times 10^{-8} \text{ mm}^3/\text{Nm}$, and the unbiased coating is the highest of $7.98 \times 10^{-7} \text{ mm}^3/\text{Nm}$. It is noted that the wear rate of the -300 V coating is much smaller than that of the unbiased case and decreases significantly with increasing bias.

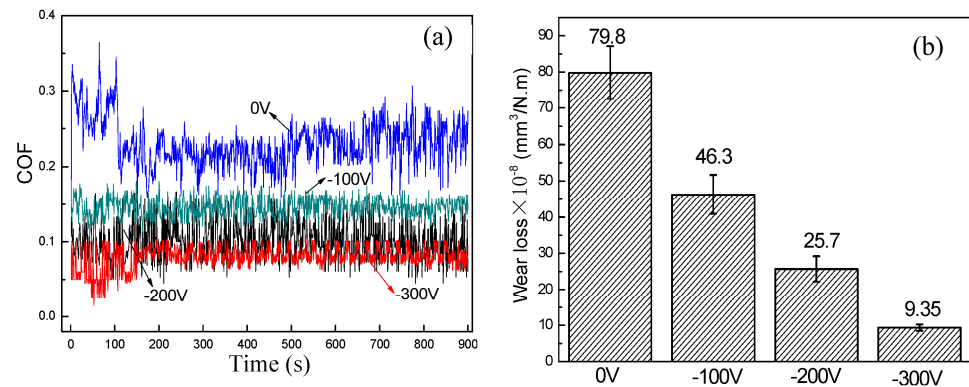


Figure 6. (a) COF of the coating; (b) wear loss of the coating.

The SEM morphology of the worn track after the pin-on-disk test is shown in Figure 7. As exhibited in Figure 7a, there are a large number of obvious scratches and furrows on the surface of the unbiased coating, with no folds and flaking at the edge, indicating high-intensity abrasive wear is visible. It can be seen in Figure 7b that the scratch on the -100 V coating surface is shallower, and the width is also narrower than that of unbiased coating, implying the -100 V coating has better wear resistance than the unbiased case. In the case of the -300 V coating in Figure 7c, at a higher magnification, the scars become much shallower, but long cracks along the direction of the friction on the surface are still visible and clear. In addition, the counterbody Al_2O_3 debris is observed on the wear surface of the -300 V coating, which is verified by the EDS pattern in Figure 7d. The EDS pattern illustrates the presence of Al, O, and C elements, with O having to come from the DLC coating and Al from the counterpart. In summary, the scratching of the coated surface becomes lighter and lighter with increasing bias voltage. Moreover, we can conclude from the wear marks that the wear mechanism of the coating is primarily abrasive.

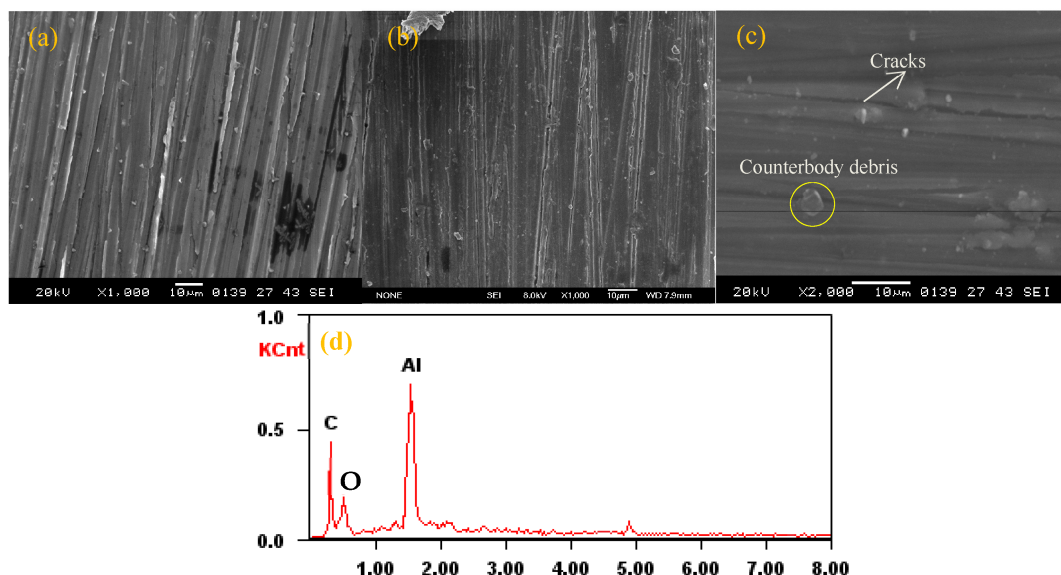


Figure 7. SEM morphology of the wear scars on the surface of the coatings at (a) 0 V; (b) -100 V; (c) -300 V; (d) EDS pattern at the yellow circle in (c).

4. Discussion

We next discuss the mechanisms by which coatings fail to protect and corrode. The preparation of the Si-DLC coating on the AZ91 surface prevents direct contact between the Cl^- environment and the AZ91 matrix, leading to an anode polarization process that increases the electrode potential of the matrix. Due to the large resistance of the

coating, it suppresses the passage of the current, hinders the penetration of the solution, and consequently reduces the corrosive current density of the matrix. However, for both unbiased and low-biased coatings, the coating structure is loose, and the surface has a large number of holes and other defects. When the current passes through the solution, the positive and negative ions are diffused, and Cl^- penetrates into the coating through holes and other defects, forming a galvanic cell (the substrate is the anode) between the coating and the substrate and a chemical reaction occurs to produce corrosion products. As the reaction time lengthens and the Cl^- intrusion increases, the corrosion holes gradually become larger, and the coating falls off and loses protection. When the bias voltage is at or above -200 V, the coating structure is compact, the size and number of surface defects are significantly reduced, the channel of chloride ions into the coating is reduced, and the path of chloride ions diffusing through the coating to the substrate surface is extended. As a result, the corrosion resistance of the coating is significantly improved. In short, the general corrosion process of the coating is as follows: chloride ions first penetrate the coating defects (holes, cracks), then galvanic cells form. This is followed by the formation of a large number of corrosion products, the expansion of defects such as pores and cracks, and finally, the shedding of the coating from the substrate.

XPS spectroscopy was performed on the abraded surface of the Al_2O_3 counterpart to understand the abrasion mechanism of the bias coating, as shown in Figure 8. The $\text{C}1\text{s}$ peak around 284.8 eV is related to the graphitic structure (sp^2), and the $\text{C}1\text{s}$ peak around 285.3 eV originates from the diamond structure (sp^3) [18,19]. To obtain an attribution for each carbon bond, the $\text{C}1\text{s}$ and $\text{Si}2\text{p}$ spectra were deconvoluted with a Gaussian function after subtracting the background. After deconvolution, the $\text{C}1\text{s}$ core-level spectrum shows five peaks corresponding to the C–Si bond at around 284.2 eV, the sp^2 –C bond at around 284.8 eV, the sp^3 –C bond at around 285.2 eV, the C–O bond at around 286.5 eV, and the C=O bond at around 288.3 eV. The C–O and C=O bonds are attributed to absorption from air during friction. Similarly, the $\text{Si}2\text{p}$ core-level spectrum shows two peaks corresponding to the Si–C bond at around 99.8 eV and the Si–O bond at around 101.1 eV. The concentration of the Si–C and Si–O bonds are 65.68% and 34.32% , respectively. In addition, the DLC layer itself is actively exposed to air/ O_2 from the air, and the O-containing compounds formed on the surface of the counterpart may result from transfer from the DLC coating to the counterbody. The sp^2/sp^3 ratio calculated from the C–C sp^2 peak area and the C–C sp^3 peak area [18,19] is nearly 5.0 , which is significantly higher than the deposited coating at -300 V, as referenced from Table 1, indicating a large number sp^2 –C has involved in the wear process as solid lubricant. Also, the presence of C–Si bonds with a fraction around 25.05 at.% on the surface of the counterpart implies that the SiC phase generated by the -300 V bias has been transferred to the Al_2O_3 counterbody. The sp^2 –C and SiC phases are responsible for the optimal wear resistance.

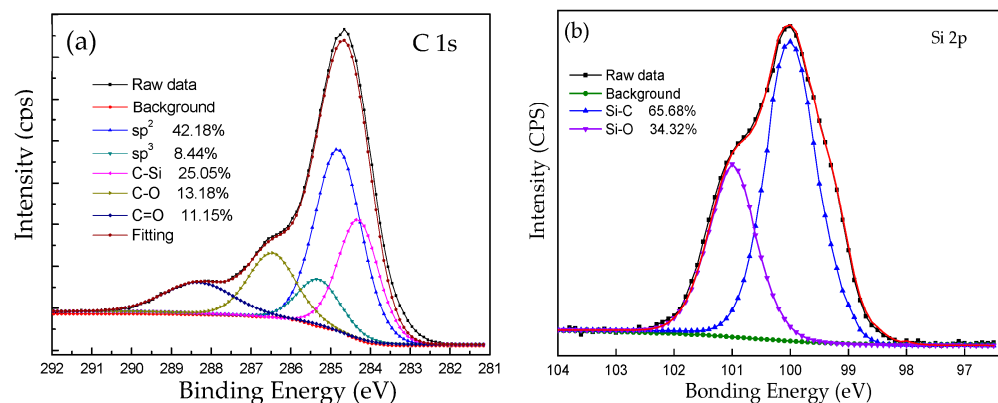


Figure 8. XPS spectra of $\text{C}1\text{s}$ (a) and $\text{Si}2\text{p}$ (b) on the surface of counterpart against -300 V coating.

5. Conclusions

The study strives to enhance the wear and corrosion resistance properties of AZ91 Magnesium Alloy for automobile hub and airplane shell applications. Si-DLC films were applied to the substrate at different biasing voltages ranging from 0 to -300 V, utilizing a hollow cathode discharge combined with a DC bias voltage. The investigation focused on uncovering the tribological and corrosion characteristics of the coated surfaces. The effect of the bias voltage on the structure, corrosion behavior, and wear resistance of the Si-DLC coating on the AZ91 alloy was systematically investigated. The increase in bias leads to denser structures, finer carbon clusters, and a reduction in the thickness and surface hydrogen content of the coating. As the bias is increased, the coating structure changes from coarse amorphous carbon to fine amorphous carbon and then to a composite structure of nanoscale SiC crystals embedded in fine amorphous carbon clusters. Moreover, as the bias increases, the size and number of defects decrease, the I_D/I_G ratio and disorder decrease, internal stress and hardness increase, corrosion resistance and wear resistance are enhanced, and the -300 V bias coating has the best corrosion and wear resistance. Surface defects, such as holes, pits, and large grains, are the main causes of deterioration of the anti-corrosive properties, whereas a transfer membrane composed of SiC nanocrystalline, C=O oily lubricating phase and sp^2 -C phase greatly improves the wear resistance, and the wear mechanism belongs mainly to abrasive wear. In summary, the application of bias voltage can be used to simultaneously modulate the corrosion resistance and wear resistance of DLC coatings, which has important implications for extending the utilization of Mg-based alloys.

Author Contributions: C.C.: conceptualization, data curation, writing—original draft, and review and editing. C.Y.: methodology, investigation, formal analysis, and review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by Jilin Provincial Department of Education “Research on pose estimation and gait planning methods for NAO robots based on sensor information fusion” (No. JJKH20240).

Institutional Review Board Statement: The study did not require ethical approval.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Bai, J.Y.; Yang, Y.; Wen, C.; Chen, J.; Zhou, G.; Jiang, B.; Peng, X.D.; Pan, F.S. Applications of magnesium alloys for aerospace: A review. *J. Magnes. Alloy.* **2023**, *11*, 3609–3619. [\[CrossRef\]](#)
2. Apelfeld, A.; Krit, B.; Ludin, V.; Morozova, N.; Vladimirov, B.; Wu, R.Z. The characterization of plasma electrolytic oxidation coatings on AZ41 magnesium alloy. *Surf. Coat. Technol.* **2017**, *322*, 127–133. [\[CrossRef\]](#)
3. Ji, P.; Long, R.Y.; Hou, L.G.; Wu, R.Z.; Zhang, J.H.; Zhang, M.L. Study on hydrophobicity and wettability transition of Ni-Cu-SiC coating on Mg-Li alloy. *Surf. Coat. Technol.* **2018**, *350*, 428–435. [\[CrossRef\]](#)
4. Li, H.T.; Wang, Q.; Zhuang, M.H.; Wu, J.J. Characterization and residual stress analysis of TiN/TiCN films on AZ31 magnesium alloy by PVD. *Vacuum* **2015**, *112*, 66–69. [\[CrossRef\]](#)
5. Li, H.T.; Sun, P.F.; Cheng, D.H. Structure and properties of DLC films deposited on Mg alloy at different C_2H_2 flows of magnetron sputtering process. *Coatings* **2021**, *11*, 815. [\[CrossRef\]](#)
6. Molak, R.M.; Topolski, K.; Spychalski, M.; Dulińska-Molak, I.; Morończyk, B.; Pakieła, Z.; Nieużyła, L.; Mazurkiewicz, M.; Wojucki, M.; Gebeshuber, A.; et al. Functional properties of the novel hybrid coatings combined of the oxide and DLC layer as a protective coating for AZ91E magnesium alloy. *Surf. Coat. Technol.* **2019**, *380*, 125040. [\[CrossRef\]](#)
7. Dai, W.; Wu, G.S.; Wang, A.Y. Preparation, characterization and properties of Cr-incorporated DLC films on magnesium alloy. *Diam. Relat. Mater.* **2010**, *19*, 1307–1315. [\[CrossRef\]](#)
8. Wu, Y.M.; Zhou, S.G.; Zhao, W.J.; Ouyang, L. Comparative corrosion resistance properties between (Cu,Ce)-DLC and Ti co-doped (Cu,Ce)/Ti-DLC films prepared via magnetron sputtering method. *Chem. Phys. Lett.* **2018**, *705*, 50–58. [\[CrossRef\]](#)
9. Pillari, L.K.; Umasankar, V.; Sarma, A.; Gupta, M. DLC coating of magnesium nanocomposites using RF sputtering. *Mater. Today Proc.* **2017**, *4*, 6737–6742. [\[CrossRef\]](#)

10. Zou, Y.S.; Wu, Y.F.; Yang, H.; Cang, K.; Song, G.H.; Li, Z.X.; Zhou, K. The microstructure, mechanical and friction properties of protective diamond like carbon films on magnesium alloy. *Appl. Surf. Sci.* **2011**, *258*, 1624–1629. [[CrossRef](#)]
11. Su, Y.Y.; Gong, X.H.; Huang, W.J.; Zhang, T.F.; Hu, R.; Zhang, P.; Ruan, H.; Ma, Y. Enhancing the tribological property of Mo-doped DLC films in methanol using appropriate bias voltage. *Diam. Relat. Mater.* **2023**, *135*, 109795. [[CrossRef](#)]
12. Li, H.T.; Sun, P.F.; Qi, A.T.; Zhang, S.J.; Zhang, F.T. Modulation of structure and corrosion behavior of Si-DLC coatings on AZ31 by applying a self-source bias. *Ceram. Int.* **2023**, *49*, 32193–32204. [[CrossRef](#)]
13. Xia, L.F.; Sun, M.R.; Liao, J.X. The effect of negative bias pulse on the bonding configurations and properties of DLC films prepared by PBII with acetylene. *Diam. Relat. Mater.* **2005**, *14*, 42–47. [[CrossRef](#)]
14. Bhowmick, S.; Sen, F.G.; Banerji, A.; Alpas, A.T. Friction and adhesion of fluorine containing hydrophobic hydrogenated diamond-like carbon (F-H-DLC) coating against magnesium alloy AZ91. *Surf. Coat. Technol.* **2015**, *267*, 21–31. [[CrossRef](#)]
15. Cui, C.Q.; Yang, C.Y. Study of Structural, Mechanical, and Corrosion Resistance of a Nanocomposite CrSiN/CrN/Cr Coating Deposited on AZ31: Effects of Deposition Time. *Coatings* **2023**, *13*, 678. [[CrossRef](#)]
16. Li, H.T.; Sun, P.F.; Cheng, D.H.; Liu, Z.M. Effects of deposition temperature on structure, residual stress and corrosion behavior of Cr/TiN/Ti/TiN films. *Ceram. Int.* **2021**, *47*, 34909–34917. [[CrossRef](#)]
17. Xu, F.M.; Luo, L.; Xiong, L.; Liu, Y. Microstructure and corrosion behavior of ALD Al₂O₃ film on AZ31 magnesium alloy with different surface roughness. *J. Magnes. Alloys.* **2020**, *8*, 480–492. [[CrossRef](#)]
18. Cao, H.S.; Qi, F.G.; Ouyang, X.P.; Zhao, N.; Zhou, Y.; Li, B.; Luo, W.; Liao, B.; Luo, J. Effect of Ti Transition Layer Thickness on the Structure, Mechanical and Adhesion Properties of Ti-DLC Coatings on Aluminum Alloys. *Materials* **2018**, *11*, 1742. [[CrossRef](#)] [[PubMed](#)]
19. Jedrzejczak, A.; Szymanski, W.; Kolodziejczyk, L.; Sobczyk-Guzenda, A.; Kaczorowski, W.; Grabarczyk, J.; Niedzielski, P.; Kolodziejczyk, A.; Batory, D. Tribological Characteristics of a-C:H:Si and a-C:H:SiO_x Coatings Tested in Simulated Body Fluid and Protein Environment. *Materials* **2022**, *15*, 2082. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.