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On the adhesion and wear resistance of DLC films deposited on nitrile butadiene rubber: A Ti-C interlayer

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ABSTRACT

To promote the adhesion strength between diamond-like carbon (DLC) films and nitrile butadiene rubber (NBR) substrates, titanium-doped carbon (Ti-C) films prepared by dual-target magnetron sputtering under varied substrate bias voltages were used as an interlayer on the rough NBR. The surface topography and structure of Ti-C films were investigated by atomic force microscopy (AFM) and Raman spectra. Raman analysis indicates that the increase of substrate bias voltage leads to an increase of the number or the size of sp^2 clusters in the Ti-C interlayer. The adhesion strength and tribological properties of DLC films coated on NBR substrate were scrutinized by a scratch tester and a ball-on-disk tribometer, respectively. It was found that DLC film with a Ti-C interlayer at a certain bias voltage exhibited superior wear resistance with a low coefficient of friction (CoF) during the sliding of 6000 laps. No clear damages in the coatings were observed from the wear tracks. Besides, the scratch test also revealed a reliable adhesion when the interlayer was prepared at -150 V, as confirmed by a scratch crack width of ~ 50 μm as compared to that of the pure DLC film increasing to ~ 120 μm . Therefore, a Ti-C interlayer could significantly enhance the adhesion and wear resistance of DLC thin films deposited on NBR.

1. Introduction

Nitrile butadiene rubbers (NBR) seals are widely applied in numerous fields, such as automotive, aerospace, engineering and biomedical industries [1,2], for the purposes of leakage prevention, pressure maintenance and exclusion of dirt. The NBR seals applied on engineering materials are usually under dynamic working conditions and suffer from high friction and severe wear, which may lead to substantial material loss and early failure of seals. Due to the low friction, high hardness, chemical inertness and excellent mechanical properties, diamond-like carbon (DLC) films are attractive as protective coatings deposited on rubbers to reduce the friction and wear rates, decrease environment pollution and extending the lifetime of seals [3–8]. However, the high residual stress and poor adhesion between DLC and the rubber easy to triggers the peel-off or delamination of the film from the rubber substrate, thus impairing its industrial wide applications. Besides, the strong adhesion between DLC films and rubber substrates is crucial to optimizing the functionality of the film. Consequently, strong research interests to enhance the interfacial adhesion between DLC films and rubbers have been motivated in the last decade [9–12].

Numerous strategies have been proposed to improve the adhesion of DLC films coated on rubber including optimizing the deposition process parameters, doping elements into DLC films and incorporating an interlayer [9,12,13]. Incorporating the interlayers may effectively reduce the properties difference between DLC film and rubbers substrate and promote the mechanical performance of the protective films [14,15]. Incorporating an interlayer could also act as a buffer to reduce the stress and enhance the mechanical integrity of the films, as well as improve the hardness, wear resistance and corrosion barrier properties of coatings [16]. Lubwama et al. [9] deposited DLC and Si-DLC with and without Si-C interlayers on nitrile rubber by a closed field unbalanced magnetron sputtering ion plating system, and the coatings with Si-C interlayers showed strong adhesion with an adhesion rating of 4A. Note that Ti has a good compatibility with substrates and reacts readily with carbon [17], promote the tough nanocomposite of TiC nano-crystallites through an amorphous carbon matrix [18,19]. In comparison with W, Cr and Si, Ti is a stronger carbide-forming element that may form strong Ti-C bonding with the dangling C of surface C-C chains of rubbers substrate after plasma cleaning/etching. Doping Ti in DLC or forming TiC nanocrystallites may largely reduce the residual stresses in DLC

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films, contributing to stronger interface adhesion. In addition, Ti-C interlayer has a better match in thermal expansion between the DLC film and rubbers substrate, in comparison with the case of DLC film directly deposited on a rubber substrate. Furthermore, rare efforts have been made to the interlayer deposited on rubber, which may significantly improve the adhesion between DLC film and rubber and promote the application of DLC films on the rubber.

In this study, DLC films with and without Ti-C interlayer were deposited on NBR rubber via magnetron sputtering in Ar plasma atmosphere. The effect of substrate negative bias voltage applied to the Ti-C interlayer on the surface topography, structural properties, adhesion properties and tribological behavior of films have been explored. The adhesion between DLC films and NBR substrate was determined by the scratch test, followed by the observation of the scratch cracks by using a scanning electron microscope (SEM, Phenom ProX). The tribological properties of the films were evaluated by a ball-on-disk tribometer.

2. Experimental

Black nitrile butadiene rubber (NBR) sheet with a thickness of 6 mm (Shore A hardness of 65) and silicon (100) wafer were used as substrates in this study. The NBR substrates of $20 \times 20 \text{ mm}^2$ size were cleaned consequently by using soap, alcohol and hot demineralized water (80–90 °C) in an ultrasonic cleaner for 10 min three times to remove contaminations. NBR substrate were etched in Ar plasma for 10 min at a bias of - 600 V, with a duty ratio of 75% and a frequency of 40 kHz in order to further clean the surface of the NBR for improving the adhesion. A series of Ti-C interlayer were deposited using different substrate bias of 0 V, - 50 V, - 100 V and - 150 V, respectively. Two opposite magnetron targets were used, one being a graphite target (> 99.99% in purity) and the other being a Ti target (> 99.99% in purity). Firstly, to produce a Ti-C interlayer, the Ti target was powered

by the radio frequency magnetron sputtering (RF-MS) at a power of 80 W and the graphite target was powered by the direct current magnetron sputtering (DC-MS) at a power of 100 W. The deposition time for the Ti-C interlayers was 10 min. Subsequently, DLC films were deposited on the Ti-C interlayer for 30 min via DC-MS in Ar gas. Hereafter the DLC films with a Ti-C interlayer under substrate bias voltages of 0 V, - 50 V, - 100 V and - 150 V are referred to as DT1, DT2, DT3 and DT4, respectively. The pure DLC film without applying a Ti-C interlayer was also deposited as a comparison (hereafter referred as sample DLC). The flow rate of Ar gas was set at 30 sccm and the process pressure was kept at 2.0 Pa constantly in this process. The sample holder was rotated at a speed of 4.5 rpm during the deposition.

The surface roughness and the cross section of the coated NBR samples were investigated by atomic force microscope (AFM) with a silicon cantilever (Tap 190AL-G) and scanning electron microscopy (SEM), respectively. The structure and the chemical bonding of the films were analyzed by Raman spectroscopy with an incident laser beam of 514 nm wavelength and by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K α source, respectively. The adhesion strength of the films was evaluated by a micro-scratch tester (CETR-UMT, Bruker) with a diamond stylus of 12.5 μm in radius. The films were peel-off under a progressively increasing load at room temperature. The scratch rate was 0.02 mm/s, and the load increased linearly from 0.1 N to 3 N in 100 s. The surface topography of the scratch tracks was analyzed by SEM. The tribological behavior of the DLC film coated NBR samples was investigated via a ball-on-disc (CETR-UMT, Bruker) tribometer under dry air condition. The counterpart was a commercial zirconium oxide ball (1.6 mm in diameter). The wear tracks were configured at 5 mm radius, and the tribo-test lasted 100 min at a rotational speed of 60 rpm and a normal load of 0.3 N. To measure the wear volume, the wear tracks were transversely scanned by a Dektak-XT profilometer with a stylus force of 3 mg. Three depth profiles, 120°

Fig. 1. AFM images with a scan area of $10 \times 10 \mu\text{m}^2$ of NBR, DLC, DT1, DT2, DT3 and DT4 film coated on NBR.

apart from each other, were scanned across each wear track for calculating the average wear volume.

3. Results and discussion

3.1. Morphology

The surface morphology of NBR substrate and DLC films coated NBR was observed by AFM as shown in Fig. 1. The surface roughness of the raw NBR was as high as 189 nm. In contrast, the surface roughness of pure DLC film coated NBR dropped to 89 nm. This is because that the sputtered atoms were filled more into the valleys and accumulated around the islands leading to the decrease in the roughness. However, the DLC films coated with the Ti-C interlayer show a slightly increase of roughness compared to the pure DLC film, this is mostly influenced by the grain size of TiC nanocrystallites [20]. Moreover, it can be seen that the surface roughness was increased progressively from 82 nm to 116 nm with the increasing negative substrate bias. This is related to the plasma ionization density and the energy of the atoms in the

scattering process. The surface roughness of the substrate is an important parameter which may influence the adhesion strength and formation of smooth DLC films [21].

Fig. 2 shows the details of the fractured cross-sections and the surface morphology of DLC, DT1, DT2, DT3, and DT4 films deposited on NBR under different substrate negative bias voltages. It can be seen that the top surface morphology of the films shows rather coarse and inhomogeneous because of the rough interface of NBR. Furthermore, the SEM images reveal the thickness of DLC-coated films increased from 198 nm to 450 nm due to the addition of Ti-C interlayer. Moreover, DLC with a Ti-C interlayer exhibits a dense microstructure, which was owing to the roughening of the growing interface that promotes more bonding. It is believed that the mechanical interlocking provides higher adhesion strength, indicating the addition of an interlayer potentially promotes the adhesion between the DLC film and rubber [22,23].

3.2. Composition and structure

XPS, a kind of common composition analysis technology of surface,

Fig. 2. SEM images showing the fractured cross-sections of (a) DLC, (b) DT1, (c) DT2, (d) DT3 and (e) DT4 film coated NBR.

Fig. 3. XPS survey spectra and high-resolution XPS scan spectra. XPS survey spectra (a) and high-resolution XPS scan spectra over C1s (b), Ti2p (c) and O1s (d) of the Ti-C layer deposited on Si wafers under different substrate negative bias voltages (0 V, -50 V, -100 V, -150 V marked as T1, T2, T3 and T4, respectively).

is quite sensitive to the characteristics of the film surface. Here, XPS was used to investigate the chemical composition of the interlayer. A series of Ti-C layers were deposited on silicon wafers under the bias voltage of 0 V, -50 V, -100 V and -150 V, respectively, and referred to as T1, T2, T3 and T4 thereafter. Fig. 3a shows a representative XPS survey spectrum of T1, T2, T3 and T4 and Si wafer substrate as reference. The XPS survey spectrum of the interlayers confirms the existence of C, Ti, O and Si. The presence of Si and O is attributed to the thin SiO₂ layer of the Si wafer used, as revealed by the reference spectrum. The composition of the Ti-C interlayer is estimated to be 5.2–8.3 at.% Ti and 94.8–91.7 at.% C, excluding Si and O. The content of Ti increases with increasing the substrate bias voltage due to re-sputtering of carbon.

In order to obtain more detailed chemical bonding information in the interlayer, the relative element composition was determined by multiplex high-resolution scans over C1s, Ti2p and O1s, which were fitted with Gaussian-Lorentzian line shapes and the background was subtracted via Shirley methods, as shown in Fig. 3b, c and d, respectively. Fig. 3b demonstrates that the C1s could be perfectly fitted by a combination of two peaks at 284.6 eV and 283.2 eV. The C 1s peak at 284.6 eV was attributed to C-C bonding [23], and the peak at 283.2 eV may be related to the C in C-Ti-O. Considering the absent TiC peak in both C 1s and Ti2p XPS spectra, a C-Ti-O solid solution is considered to be more likely to form [24]. Furthermore, Ti element together with O may exist as small atomic clusters dissolved in the DLC matrix to render a solid solution structure, rather than bond with C atoms to form TiC nanocrystallites [25]. Fig. 3c shows that the Ti2p could be fitted by four peaks at 458.03 eV, 459.53 eV, 464.11 eV and 465.11 eV. Moulder et al. reported that the binding energy of Ti2p^{3/2} titanium is around 453.8 eV [26]. Thus, pure titanium does not exist in the film. According to the previous studies, the range of binding energy of titanium compounds is around 458 eV [27,28], thus the peak of 458.03 eV can be attributed to the titanium carbon compounds in this work. The peak

around 459.53 eV is related to titanium oxides, due to the sensitivity of titanium to oxygen. Moreover, the Ti2p peak at 464.11 eV and 465.11 eV are related to Ti2p^{1/2}, and the difference between Ti2p^{1/2} and Ti2p^{3/2} is about 6.08 eV, in accordance with the value of 6.09 eV reported by Lebugle et al. [27]. Fig. 3d shows that the O1s could be fitted by three peaks at 531.14 eV, 532.17 eV and 533.02 eV, respectively. The O1s peak at 531.14 eV and 532.17 eV corresponded to the titanium oxide due to the easy reaction of titanium with oxygen. The peak at 533.02 eV can be ascribed to the carbon-oxygen compound, which probably arose from the moisture absorbed on the samples' surface.

Raman spectrum is often used for the characterization of hard carbon film [29]. Here, the bonding structure of DLC films was studied by Raman spectroscopy using a 514 nm excitation wavelength. Fig. 4a shows the Raman spectra of the samples DLC, DT1, DT2, DT3 and DT4 without and with Ti-C interlayer aforementioned. Obviously, the typical Raman spectra of DLC film can be seen in the range of 800–2000 cm⁻¹, showing the prominent G and underlying D peaks (centered at approximately 1500 cm⁻¹ and 1350 cm⁻¹, respectively), which corresponds to the stretching vibration of any pair of sp² bonds whether in chains or in aromatic rings and the breaking mode of sp² bonds only in rings, respectively [28]. The Raman spectra were fitted with Gaussian line shapes. Generally, the results of Raman show that the symmetry center of the main peaks basically remained unchanged when the negative bias increased, indicating that the structure of the films was constant. Briefly, supposing the symmetry of Raman spectrum is weakening as the G peak widens, the film structure tends to be graphitization. It was notable that the peak intensity changes significantly while the bias voltage varied from -50 V to -100 V, indicating that the structure of the DLC film changes substantially at this time. Due to the excess ion energy promoted atomic relaxation around the implanted atom and a reversion of diamond-like sp³ bonding to graphite-like sp²

Fig. 4. (a) Raman spectra of the DLC films without and with Ti-C interlayer at different bias voltages (0 V, -50 V, -100 V, and -150 V), and (b) the position of G peak and I_D/I_G of the fitted Raman spectra of DLC, DT1, DT2, DT3 and DT4 films.

bonding [30].

Fig. 4b shows the ratio of I_D to I_G (I_D/I_G) and the position of G peak, the continuous curves are obtained by a polynomial fitting. It is observed that the position of G peak is sensitive mainly to the configuration of sp^2 sites attributed to the higher crosslinking. Thus, the increase of sp^2 chains has a direct influence on the increase in G position, whereas the bond disorder is the opposite. At first, the G peak position shifts upward from 1554.17 cm^{-1} to 1555.17 cm^{-1} indicating a reduction of the bond angles of sp^3 , while the I_D/I_G decreases from 1.9 to 0.57 when introducing Ti-C interlayer, revealing the increase of sp^3 fraction. Then the G peak position increases slightly from 1555.17 cm^{-1} to 1556.71 cm^{-1} when the substrate bias negative voltage increased from -50 V to -100 V. Subsequently, the G peak

position shifts downward from 1556.71 cm^{-1} to 1551.99 cm^{-1} as the substrate negative bias voltage increases from -50 V to -150 V, and simultaneously the I_D/I_G increases from 0.57 to 1.71 indicates the increase of sp^2 content. The downshift in wave number of the G-peak position may stem from either an increase of fourfold coordination or an increase of bond angle disorder in threefold bonding [31,32]. Generally, combining the G peak position and the increasing of I_D/I_G suggest that the addition of Ti-C interlayer leads to the increase of C=C sp^2 graphite cluster structure and a reduction of C-C sp^3 . Meanwhile the vibration of G peak position and the I_D/I_G exhibits an opposite trend with the increasing substrate negative bias, which is related to the increase of sp^2 rings and the reduction of the number of sp^3 bonds. This can be due to that the excessive energy of incident species during the

Fig. 5. SEM images showing the scratch morphology of (a) DLC, (b) DT1, (c) DT2, (d) DT3 and (e) DT4 film coated NBR. Two arrows pointing to the points A and B on the scratch track correspond to the critical points A and B in the scratch curves in Fig. 6.

magnetron sputtering process impedes the formation of sp^3 bonds [12].

3.3. Adhesion

The adhesion strength of DLC film was investigated with scratch test in terms of a critical load at an instant of failure occurring between the film and substrate [33–35]. Scratch tests were performed using progressive loads from 0.1 N to 3 N at a scratch speed of 0.02 mm/s and for a scratch length of 2 mm. Fig. 5 shows the scratch morphology of DLC coatings with and without the Ti-C interlayers deposited on NBR substrate. Two arrows pointing to the points A and B on the scratch tracks correspond to the critical points A and B in the scratch curves shown in Fig. 6. It was observed that the DLC film had lower adhesion compared to the DLC films with Ti-C interlayer. For instance, a distinct delamination was observed along the scratch morphology. The scratch width of DLC was 120 μm on the two arrows pointing to the points A and B, which is associated to the large strain of NBR. Generally, the DLC films with a Ti-C interlayer showed a higher adhesion, and the scratch width was < 100 μm . Especially, it was found that the DT4 sample exhibits a

superior adhesion performance, confirmed with a scratch width of only 50 μm . Raman spectroscopy analysis determined that the addition of Ti-C interlayer lead to an increase of sp^2 cluster, which relieve compressive residual stresses. A reduction of residual stresses can result from energetic ion bombardment of DLC films which can improves film adhesion [36].

Fig. 6 shows the scratch curve from scratch test of DLC film with and without Ti-C interlayer deposited on NBR, with the critical point A and B corresponding to the locations A and B marked in Fig. 5. However, the critical load cannot be well defined due to the high elasticity of NBR substrate, and the scratch morphology of the critical point could be defined as a qualitative analysis method. As shown in Fig. 6, the friction increases linearly with the applied load. The first critical point of DLC film occurs at the length of 0.38 mm and the corresponding normal load is 0.67 N, indicating the poor adhesion as compared to the critical loads (0.91–1.79 N) of the DLC films with Ti-C interlayer. It can be explained by the brittleness and high residual tensile stresses of DLC film [9]. Furthermore, the highest critical load (1.79 N) in DT4 film indicates the enhanced interfacial adhesion.

Fig. 6. The scratch curve of DLC film with and without Ti-C interlayer deposited on NBR.

Fig. 7. (a) CoF of NBR, DLC film with and without Ti-C interlayer coated on NBR, (b) the enlarged view of CoF.

Fig. 8. Depth profile of the wear track on raw NBR, DLC film and DT films coated NBR. The labels R and M define the borders of the wear tracks.

Fig. 9. SEM images showing the wear tracks of NBR, DLC-coated on NBR (DLC, DT1, DT2, DT3 and DT4).

3.4. Tribology

The coefficient of friction (CoF) as a function of sliding distance in dry conditions under 0.3 N normal load is shown in Fig. 7. The rapid decrease in CoF of the raw NBR rubber at the beginning of the tribo-test

was associated to the effect of flash temperature rising on the contact area [37]. CoF subsequently reaches the steady value of ~ 1.2 . It can be seen that the CoF of the DLC coated NBR sample exhibits a low value of ~ 0.25 at the beginning of the test and rapidly increases to ~ 1.0 within 300 laps, indicating a poor adhesion and rapid breakdown of the DLC

Fig. 10. (a) SEM image showing the wear track of DT4 with the dashed lines indicating the borders of the wear track, (b, c) higher magnification SEM images showing the wear morphology of DT film in the wear track.

film. This initial rise in CoF of the sample DLC is attributed to the initial high roughness and reduced contact area between the interfaces. While sliding, the rough surface features were smoothed as a result of the

elastic and plastic effects of the frictional forces acting on the coating, which in turn increase the contact area that is strongly influencing the CoF [3]. Obviously, a lower CoF was observed in DLC coated-rubber with the addition of the Ti-C interlayers, while the CoF of the films exhibit various characteristics owing to the different adhesion strength affected by the negative bias voltages of the interlayer. At the beginning of sliding, the CoF of the DT1 sample started from ~ 0.18 and then increased rapidly to the value of ~ 0.7 after 2400 laps, and finally reached to ~ 0.9 . The CoF of DT2 and DT3 samples exhibited the similar trend starting with a low CoF value of ~ 0.15 within 1500 laps and subsequently jumping to the value of ~ 0.9 at the end of the tribotest. In particular, the DT4 film showed the lowest CoF of ~ 0.18 and it was stable within 6000 laps. The difference of the CoF between the different films is associated to the addition of the Ti-C interlayer leading to the increase in volume of the sp^2 content, which is beneficial to the reduce of the compressive stress in the DLC film that contributes to the improved adhesion performance of the DT4 film.

Fig. 8 shows the depth profile of the wear track of all the samples after tribo-test. It can be seen that the largest wear depth up to $119 \mu\text{m}$ is observed in the raw NBR, indicating its poor wear resistance. The DLC-coated rubbers also show high wear depth ($115 \mu\text{m}$) and a high CoF, which are associated to the poor adhesion strength between film and rubber leading to the early delamination of films. The wear depth of the DT films substantially decreases after the addition of a Ti-C interlayer, in the range from $1.2 \mu\text{m}$ to $68 \mu\text{m}$. The DT4 film exhibits the lowest wear depth of $1.2 \mu\text{m}$, which is mainly the plastic deformation of the rubber substrate [38]. This large difference in wear rate may be attributed to the different degrees of adhesion enhancement of the films that keeps the films functional with prolonged lifetime [39]. In contrast, early delamination of the films will result in the poor wear resistance. To conclude, the addition of Ti-C interlayer could enhance the adhesion strength of DLC films and help the films maintain superior tribo-performance.

To illustrate the wear track intuitively, the SEM images in Figs. 9 and 10 revealed that the wear morphology of NBR, DLC and DT films after 6000 laps. It was observed that the wear track diameter of the raw NBR sample larger than DLC-coated films deposited on rubber. As shown in Fig. 9, the pure DLC film has been completely worn through the rubber substrate due to the poor adhesion of the film. It is reported that the DLC films coated on the rubbers only reduce partially the inevitable viscoelastic deformation of coated rubber [38,40]. It can be seen that the films of DT1, DT2 and DT3 were also suffered from severe wear. According to the curve of friction coefficient, the film DT1 exhibited a well wear resistance at the beginning, but the film gradually peeling off around 2500 laps, and the CoF also rose sharply after the film completely peeled off. Similarly DT2 failed at around 1500 laps, which is well consistent with the adhesion strength of the DT films evaluated by scratch test as shown in Fig. 6. The wear track of DT4 film-coated NBR sample is hardly visible in a low-magnification overview (see Fig. 9f), indicating the superior wear resistance and protection to the rubber substrate. This is in sharp contrast to the heavily damaged wear track of other DT film coated NBR and raw NBR samples. Fig. 10 provides a close view of the wear track of DT4 film coated NBR sample. Note that no clear damages in the DT4 film are observed from the wear track of DT4, but few micro-cracks formed in the DT4 film due to the large elastic deformation of NBR substrate under the high contact pressure applied. The wear of DT4 film is seen very minor. In particular, no delamination or peel off of DT4 film is found, see Fig. 10b, which indicates a reliable adhesion behavior of the film. It is cleared that the Ti-C interlayer deposited at -150 V bias voltage exhibits the strong adhesion and the superior tribology performance. This variation is probably ascribed to the film structure tends to be graphitization with the increase of substrate bias, and the friction-induced heating that transforms the film into a graphite-like phase [41].

4. Conclusions

DLC films with and without Ti-C interlayer were deposited on NBR rubber via magnetron sputtering in Ar plasma. The Ti-C interlayer was sputter deposited at substrate bias voltage of 0 V, -50 V, -100 V and -150 V, respectively. The addition of Ti-C interlayer resulted in enhanced adhesion of DLC film to NBR rubber. Tribo-test results show that the DT4 film with Ti-C interlayer deposited at -150 V substrate bias voltage exhibits the lowest CoF of ~0.18 and a minor wear depth of ~1.2 µm, compared to the CoF value up to ~1.0 of DLC film coated NBR. The DLC film without a Ti-C interlayer or weakly bonded interlayer may break down in the early stage of sliding and lead to high wear. It could be concluded that the addition of Ti-C interlayer is promising to enhance the adhesion strength and superior tribological performance.

Declaration of competing interest

The authors declare no conflict of interest.

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References

- [1] C. Antonios, S.J. Sergio, B.M. Jihane, D. Chern, V. Barnier, G. Kermouche, C. Heau, M.A. Leroy, J. Fontaine, S. Descartes, C. Donnet, H. Klocker, Experimental study of wear-induced delamination for DLC coated automotive components, *Surf. Coatings Technol.* 352 (2018) 549–560, <https://doi.org/10.1016/J.SURFCOAT.2018.08.048>.
- [2] R. Brow, D.R. Stephen, V. Crowder, A. McIntyre, E. Day, Advanced Materials for Aerospace and Biomedical Applications New Glasses for Hermetic Titanium Seals, (1970), <https://doi.org/10.2172/510597>.
- [3] J. Solis, H. Zhao, C. Wang, J.A. Verduzco, A.S. Bueno, A. Neville, Tribological performance of an H-DLC coating prepared by PECVD, *Appl. Surf. Sci.* 383 (2016) 222–232, <https://doi.org/10.1016/J.APSUSC.2016.04.184>.
- [4] J.Q. Liu, Z.Y. Wu, H.T. Cao, F. Wen, Y.T. Pei, Effect of bias voltage on the tribological and sealing properties of rubber seals modified by DLC films, *Surf. Coatings Technol.* 360 (2019) 391–399, <https://doi.org/10.1016/J.SURFCOAT.2018.12.100>.
- [5] L. Qiang, C. Bai, Z. Gong, A. Liang, J. Zhang, Microstructure, adhesion and tribological behaviors of Si interlayer/Si doping diamond-like carbon film developed on nitrile butadiene rubber, *Diam. Relat. Mater.* 92 (2019) 208–218, <https://doi.org/10.1016/J.DIAMOND.2019.01.005>.
- [6] M. Lubwama, B. Corcoran, K.A. McDonnell, D. Dowling, J.B. Kirabira, A. Sebbit, K. Sayers, Flexibility and frictional behaviour of DLC and Si-DLC films deposited on nitrile rubber, *Surf. Coatings Technol.* 239 (2014) 84–94, <https://doi.org/10.1016/J.SURFCOAT.2013.11.023>.
- [7] R. Gahlin, M. Larsson, P. Hedenqvist, ME-C:H coatings in motor vehicles, *Wear* 249 (2001) 302–309, [https://doi.org/10.1016/S0043-1648\(01\)00565-8](https://doi.org/10.1016/S0043-1648(01)00565-8).
- [8] S. Thirumalai, A. Hausberger, J.M. Lackner, W. Waldhauser, T. Schwarz, Effect of the type of elastomeric substrate on the microstructural, surface and tribological characteristics of diamond-like carbon (DLC) coatings, *Surf. Coatings Technol.* 302 (2016) 244–254, <https://doi.org/10.1016/J.SURFCOAT.2016.06.021>.
- [9] M. Lubwama, B. Corcoran, K. Sayers, J.B. Kirabira, A. Sebbit, K.A. McDonnell, D. Dowling, Adhesion and composite micro-hardness of DLC and Si-DLC films deposited on nitrile rubber, *Surf. Coatings Technol.* 206 (2012) 4881–4886, <https://doi.org/10.1016/J.SURFCOAT.2012.05.079>.
- [10] X.L. Bui, Y.T. Pei, E.D.G. Mulder, J.T.M. De Hosson, Adhesion improvement of hydrogenated diamond-like carbon thin films by pre-deposition plasma treatment of rubber substrate, *Surf. Coatings Technol.* 203 (2009) 1964–1970, <https://doi.org/10.1016/J.SURFCOAT.2009.01.027>.
- [11] Y.T. Pei, X.L. Bui, X.B. Zhou, J.T.M. De Hosson, Tribological behavior of W-DLC coated rubber seals, *Surf. Coatings Technol.* 202 (2008) 1869–1875, <https://doi.org/10.1016/J.SURFCOAT.2007.08.013>.
- [12] J.Q. Liu, L.J. Li, B. Wei, F. Wen, H.T. Cao, Y.T. Pei, Effect of sputtering pressure on the surface topography, structure, wettability and tribological performance of DLC films coated on rubber by magnetron sputtering, *Surf. Coatings Technol.* 365 (2019) 33–40, <https://doi.org/10.1016/J.SURFCOAT.2018.05.012>.
- [13] G. Ma, S. Gong, G. Lin, L. Zhang, G. Sun, A study of structure and properties of Ti-doped DLC film by reactive magnetron sputtering with ion implantation, *Appl. Surf. Sci.* 258 (2012) 3045–3050, <https://doi.org/10.1016/J.APSUSC.2011.11.034>.
- [14] A. Vereschaka, A. Aksenenko, N. Sitnikov, M. Migranov, S. Shevchenko, C. Sotova, A. Batak, N. Andreev, Effect of adhesion and tribological properties of modified composite nano-structured multi-layer nitride coatings on WC-Co tools life, *Tribol. Int.* 128 (2018) 313–327, <https://doi.org/10.1016/J.TRIBOINT.2018.07.039>.
- [15] I. Masami, M. Haruho, M. Tatsuya, C. Junho, Low temperature Si-DLC coatings on fluoro rubber by a bipolar pulse type PBI system, *Surf. Coatings Technol.* 206 (2011) 999–1002, <https://doi.org/10.1016/J.SURFCOAT.2011.04.011>.
- [16] M. Azzi, P. Amirault, M. Paquette, J.E. Klemberg-Sapieha, L. Martinu, Corrosion performance and mechanical stability of 316L/DLC coating system: role of interlayers, *Surf. Coatings Technol.* 204 (2010) 3986–3994, <https://doi.org/10.1016/J.SURFCOAT.2010.05.004>.
- [17] V.Y. Kulikovskiy, F. Fendrych, L. Jastrabik, D. Chvostova, Study of formation and some properties of Ti-C:H films prepared by d.c. magnetron sputtering, *Surf. Coatings Technol.* 91 (1997) 122–130, [https://doi.org/10.1016/S0257-8972\(96\)03146-5](https://doi.org/10.1016/S0257-8972(96)03146-5).
- [18] P.C. Tsai, Y.F. Hwang, J.Y. Chiang, W.J. Chen, The effects of deposition parameters on the structure and properties of titanium-containing DLC films synthesized by cathodic arc plasma evaporation, *Surf. Coatings Technol.* 202 (2008) 5350–5355, <https://doi.org/10.1016/J.surcoat.2008.06.073>.
- [19] Y.T. Pei, D. Galvan, J.T.M. De Hosson, C. Strondil, Advanced TiC/a-C:H nanocomposite coatings deposited by magnetron sputtering, *J. Eur. Ceram. Soc.* 26 (2006) 565–570, <https://doi.org/10.1016/J.JEURCERAMSOC.2005.06.023>.
- [20] A.P. Mousinho, R.D. Mansano, M.C. Salvadori, Influence of substrate surface topography in the deposition of nanostructured diamond-like carbon films by high density plasma chemical vapor deposition, *Surf. Coatings Technol.* 203 (2009) 1193–1198, <https://doi.org/10.1016/J.SURFCOAT.2008.10.025>.
- [21] Y. Jeon, Y. Seob Park, J. Kim, B. Hong, W.S. Choi, Tribological properties of ultrathin DLC films with and without metal interlayers, 51 (2007) 1124–1128, <https://doi.org/10.3938/jkps.51.1124>.
- [22] P. Vasconcelos, J. Alves, R. Neto, P. Henrique, Contribution of the phase-matrix interface to the behaviour of aluminium filled epoxies, 455–456 (2004) 635–638, <https://doi.org/10.4028/www.scientific.net/MSF.455-456.635>.
- [23] V.E. Basin, Advances in understanding the adhesion between solid substrates and organic coatings, *Prog. Org. Coatings* 12 (1984) 213–250, [https://doi.org/10.1016/0033-0655\(84\)80010-2](https://doi.org/10.1016/0033-0655(84)80010-2).
- [24] V. Singh, V. Palshin, R.C. Tittsworth, E.I. Meletis, Local structure of composite Cr-containing diamond-like carbon thin films, *Carbon N. Y.* 44 (2006) 1280–1286, <https://doi.org/10.1016/J.CARBON.2005.10.048>.
- [25] K. Polychronopoulou, C. Rebholz, M.A. Baker, L. Theodorou, N.G. Demas, S.J. Hinder, A.A. Polycarpou, C.C. Doumanidis, K. Böbel, Nanostructure, mechanical and tribological properties of reactive magnetron sputtered TiC_x coatings, *Diam. Relat. Mater.* 17 (2008) 2054–2061, <https://doi.org/10.1016/J.DIAMOND.2008.07.007>.
- [26] F. Santerre, M.A. El Khakani, M. Chaker, J.P. Dodelet, Properties of TiC thin films grown by pulsed laser deposition, *Appl. Surf. Sci.* 148 (1999) 24–33, [https://doi.org/10.1016/S0169-4332\(99\)00139-7](https://doi.org/10.1016/S0169-4332(99)00139-7).
- [27] A. Lebugle, U. Axelsson, R. Nyholm, N. Mårtensson, Experimental L and M core level binding energies for the metals 22Ti to 30Zn, 23 (5A) (2007) 825, <https://doi.org/10.1088/0031-8949/23/5A/013>.
- [28] J. Robertson, Diamond-like amorphous carbon, *Mater. Sci. Eng. R Reports* 37 (2002) 129–281, [https://doi.org/10.1016/S0927-796X\(02\)00005-0](https://doi.org/10.1016/S0927-796X(02)00005-0).
- [29] F. Wen, N. Huang, Y.X. Leng, A.S. Zhao, F.J. Jing, Study on wettabilities and platelet adhesion behavior of C:H and C:N:H films prepared by DC-MFCVA, *Appl. Surf. Sci.* 255 (2008) 469–472, <https://doi.org/10.1016/J.apsusc.2008.06.071>.
- [30] A.C. Ferrari, Resonant Raman spectroscopy of disordered, amorphous, and diamond like carbon, 64 (7) (2001), <https://doi.org/10.1103/PhysRevB.64.075414>.
- [31] S. Lee, S.J. Park, S. Oh, W.M. Kim, J.H. Bae, B. Cheong, S.G. Kim, Optical and mechanical properties of amorphous CN films, *Thin Solid Films* 308–309 (1997) 135–140, [https://doi.org/10.1016/S0040-6090\(97\)00382-9](https://doi.org/10.1016/S0040-6090(97)00382-9).
- [32] I.H. Shin, T.D. Lee, Effect of nitrogen doping on field emission characteristics of patterned diamond-like carbon films prepared by pulsed laser deposition, 18 (2) (2000) 1027–1030, <https://doi.org/10.1116/1.591320>.
- [33] P.A. Steinmann, Y. Tardy, H.E. Hintermann, Adhesion testing by the scratch test method: the influence of intrinsic and extrinsic parameters on the critical load, *Thin Solid Films* 154 (1987) 333–349, [https://doi.org/10.1016/0040-6090\(87\)90377-4](https://doi.org/10.1016/0040-6090(87)90377-4).
- [34] J.E. Greene, J. Woodhouse, M. Pestes, A technique for detecting critical loads in the scratch test for thin film adhesion, 45 (6) (1974) 747–749, <https://doi.org/10.1063/1.1686727>.
- [35] J.W. Lee, S.K. Tien, Y.C. Kuo, C.M. Chen, The mechanical properties evaluation of the CrN coatings deposited by the pulsed DC reactive magnetron sputtering, *Surf. Coatings Technol.* 200 (2006) 3330–3335, <https://doi.org/10.1016/J.SURFCOAT.2005.07.047>.
- [36] Y. Pauleau, Residual Stresses in DLC Films and Adhesion to Various Substrates, (2008), https://doi.org/10.1007/978-0-387-49891-1_4.
- [37] L. Huang, J. Yuan, C. Li, D. Hong, Microstructure, tribological and cutting performance of Ti-DLC/a-C:H multilayer film on cemented carbide, *Surf. Coatings Technol.* 353 (2018) 163–170, <https://doi.org/10.1016/J.SURFCOAT.2018.08.076>.
- [38] Y.T. Pei, D. Martinez-Martinez, J.P. van der Pal, X.L. Bui, X.B. Zhou, J.T.M. De Hosson, Flexible diamond-like carbon films on rubber: friction and the effect of viscoelastic deformation of rubber substrates, *Acta Mater.* 60 (2012) 7216–7225,

- <https://doi.org/10.1016/J.ACTAMAT.2012.09.031>.
- [39] L. Cui, H. Zhou, K. Zhang, Z. Lu, X. Wang, Bias voltage dependence of superlubricity lifetime of hydrogenated amorphous carbon films in high vacuum, *Tribol. Int.* 117 (2018) 107–111, <https://doi.org/10.1016/J.TRIBOINT.2017.08.020>.
- [40] Y.T. Pei, X.L. Bui, J.P. van der Pal, D. Martinez-Martinez, X.B. Zhou, J.T.M. De Hosson, Flexible diamond-like carbon films on rubber: on the origin of self-acting segmentation and film flexibility, *Acta Mater.* 60 (2012) 5526–5535, <https://doi.org/10.1016/J.ACTAMAT.2012.07.017>.
- [41] Y. Liu, A. Erdemir, E.I. Meletis, A study of the wear mechanism of diamond-like carbon films, *Surf. Coatings Technol.* 82 (1996) 48–56, [https://doi.org/10.1016/0257-8972\(95\)02623-1](https://doi.org/10.1016/0257-8972(95)02623-1).