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Optimization of DLC films on oxynitriding-treated Vanadis 10 tool steel through the various duty cycles of DC-pulsed plasma-enhanced CVD

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Abstract

In this study, DLC films were coated on oxynitriding-treated Vanadis 10 tool steel using the DC-pulsed plasma CVD technique. The experimental parameters included different duty cycles (9, 13, 17, and 21 %) with asymmetric bipolar-pulsed voltages of –3 kV, a gas flow of CH_4 maintained at 15 sccm, and a deposition time of 90 min. Meanwhile, the properties of DLC films were measured by Raman spectroscopy, Rockwell indentation, wear tests, FT-IR, corrosion tests, water contact angle tests, and four-point probes analysis. The experimental results showed that the optimum properties of DLC films occurred at a duty cycle of 17 %. It had the lowest wear volume loss for loads 2 N and 5 N were 3.49×10^{-3} mm^3 and 4.08×10^{-3} mm^3, respectively. Moreover, the optimal DLC films possessed the lowest corrosion current ($I_{\mathrm{corr}} = 7.91 \times 10^{-5}$ A cm^{-2}) and highest polarization resistance ($R_{\mathrm{p}} = 1185.21$ Ω cm^2) in 3.5 wt.% NaCl solutions. The FT-IR spectrum analysis also found that the characteristic peaks of DLC films were generated at positions of 2852 and 2921 cm^{-1}, and the water contact angle tests showed that the DLC films had great hydrophobicity (78.33°). Consequently, the results confirmed that the duplex surface treatment effectively improved the coating properties of Vanadis 10 tool steel.

Key words: diamond-like carbon (DLC), oxynitriding, Vanadis 10 tool steel, DC-pulsed plasma-enhanced CVD, wear, corrosion, water contact angle

1. Introduction

Vanadis tool steels are a trademark of Uddeholm Company which are high vanadium content (along with chromium and molybdenum) steels with unique mechanical properties, such as very high wear resistance along with good machinability, dimensional stability, and grind ability [1]. Among them, Vanadis 10 (also known as V10, the subsequent content is called V10) is a high vanadium alloyed powder metallurgy tool steel offering a unique combination of excellent abrasive wear resistance in combination with a good chipping resistance. Therefore, it is widely used in blanking, stamping, deep drawing, and cutting molds [1, 2].

Oxynitriding is the process that includes gas nitriding and post-oxidizing treatments, which use steam at the end of the nitriding step [3]. Generally speaking, the oxynitriding process can form several kinds of nitride (Fe_2N, Fe_3N, and Fe_4N) and oxides (Fe_2O_3 and Fe_3O_4). Particularly, the Fe_3O_4 layer of oxidation treatment can effectively protect and improve steels' erosion and corrosion resistance. Our previous studies showed that the oxynitriding layer could form the passive oxidative film, which improved the adhesive strength as an intermedi-

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ate layer during the duplex coating treatments [3–5].

Diamond-like carbon (DLC) thin films have attracted much interest due to their unique properties such as high hardness, low friction, good wear resistance, and high chemical inertness. Besides, DLC is a metastable form of amorphous carbon that contains a significant fraction of sp^3 bonds. The ratio of sp^2/sp^3 carbon atoms is one of the most important factors of the DLC films [6–8]. Several different techniques have been used for depositing DLC films, such as PVD, RF magnetron sputtering, plasma enhanced chemical vapor deposition (CVD), and ion beam deposition in recent years. Among them, the most common deposition technique of DLC films is plasma-enhanced CVD [5]. It is worth mentioning that the DC-pulsed plasma-enhanced CVD is a novel method because it is simpler and can be used on an industrial scale at a lower cost [9–12].

DLC coatings can improve the surface properties of steel molds because they combine unique mechanical, tribological, and chemical properties [11, 12]. However, a significant factor determining the quality of DLC coatings is their adhesion to substrates. It has been found that using intermediate layers between the DLC film and the substrate can increase the adhesion strength of the film [13, 14]. As studied previously, the oxynitriding layer improves the corrosion properties and the adhesive strength as an interlayer [3–5]. Therefore, this research utilized DC-pulsed plasma-enhanced CVD and DLC/oxynitriding duplex treatments to study the characteristics of DLC films and improve the coating properties of V10 tool steel.

2. Experimental procedures

V10 tool steel is a high vanadium alloy steel with great strength, hardness, and wear resistance after appropriate heat treatment. The chemical compositions (mass %) of V10 tool steel are as follows: 2.9 C, 0.5 Si, 0.5 Mn, 8.0 Cr, 1.5 Mo, 9.8 V, and a balance of Fe. In this experiment, V10 tool steel was utilized as the substrate material to undergo a series of homogeneous heat treatments: the specimen was quenched at 1020 ℃ and tempered at 525 ℃ for 3 h. This process was repeated 3 times to reach a hardness of 62 ± 1 HRC. The heat-treated V10 tool steel was then subjected to various surface treatments, including oxynitriding and a DLC coating after oxynitriding. In this study, the oxynitriding-treated specimens of V10 tool steel were nitriding treated at 480 ℃ for 8 h and then oxidized via steam at 480 ℃ for 30 min.

Since the oxynitriding layer can improve the hardness and the adhesive strength as an interlayer, this study employed the duplex surface treatment (DLC/oxynitriding) technique on V10 tool steel. The duplex surface treatments involved depositing DLC films onto oxynitride-treated V10 tool steels. In this work, DLC coating utilized the asymmetric bipolar-pulsed plasma-enhanced CVD technology. The 5 % duty cycle of the bipolar-pulsed plasma-enhanced CVD meant that the plasma deposition time was only 5 µs during 100 µs. Meanwhile, the T_{on}^{+} (or T_{on}^{-}) of the positive-pulsed duty cycle was kept at 10 µs, and the T_{off}^{+} (or T_{off}^{-}) was 40 µs [4]. To evaluate the effects of different duty cycles of the DC-pulsed plasma-enhanced CVD process on the DLC films, the positive-pulsed duty cycle was maintained at 10 %, and the negative-pulsed duty cycles were 9, 13, 17, and 21 %. The different duty cycles are designated as 9, 13, 17, and 21 %, hereafter. Simultaneously, the coating time was maintained at 90 min; the frequency was 10 kHz; the bipolar-pulsed voltage was kept at –3 kV. Moreover, CH$_4$ gas (15 sccm) was continued for 90 min, and followed by depositing the DLC films.

To investigate the properties of DLC films for DLC/oxynitriding treated V10 specimens by different duty cycles of the DC-pulsed plasma-enhanced CVD, Raman spectroscopy analysis (MOF-iHR550), wear test (POD-FM800-25NT), indentation test (Indentec-8150LK) [15], FT-IR test (PerkinElmer FT-IR Spectrometer), water contact angle analysis (Sindatek Model 100SB Contact Angle Goniometer, and followed by ASTM D-5725), Four-point Probes (LRS4-TG2), XRD (D2 PHASER) and SEM (Hitachi-S4700) microstructure inspections were performed. The wear resistance of the specimens was evaluated in a ball-on-disk test (ASTM G99). The wear test parameters were as follows: the specimen size was ø 36 × 5 mm^2, the diameter of WC ball (HRA 90 ± 1) was 6 mm, disk rotation was 200 rpm, and total rotation was 10,000 revolutions, the axial load was 2 and 5 N, and sliding speed was 0.25 m s^{-1}.

Furthermore, corrosion potential analysis used three electrodes method and was followed by ASTM G59-97. The contact area of the specimen was 2.01 cm^2. The corrosive solvent used 3.5 wt.% NaCl was maintained at room temperature. The scanning speed of 0.01 V s^{-1}, the initial potential of –2.0 V, and the final potential of 2.0 V were controlled. The polarization curve was obtained by Corr-View software to analyze and compare the corrosion potential (E_{corr}), corrosion current (I_{corr}), and polarization resistance (R_{p}) of DLC/oxynitriding-treated V10 tool steel specimens.

3. Results and discussion

Figure 1 shows the XRD patterns and surface hardness profile of oxynitriding-treated V10 specimens. The primary phases and structures of the oxynitride layer were Fe$_3$O$_4$ and Fe$_3$N (ε phase), as shown in

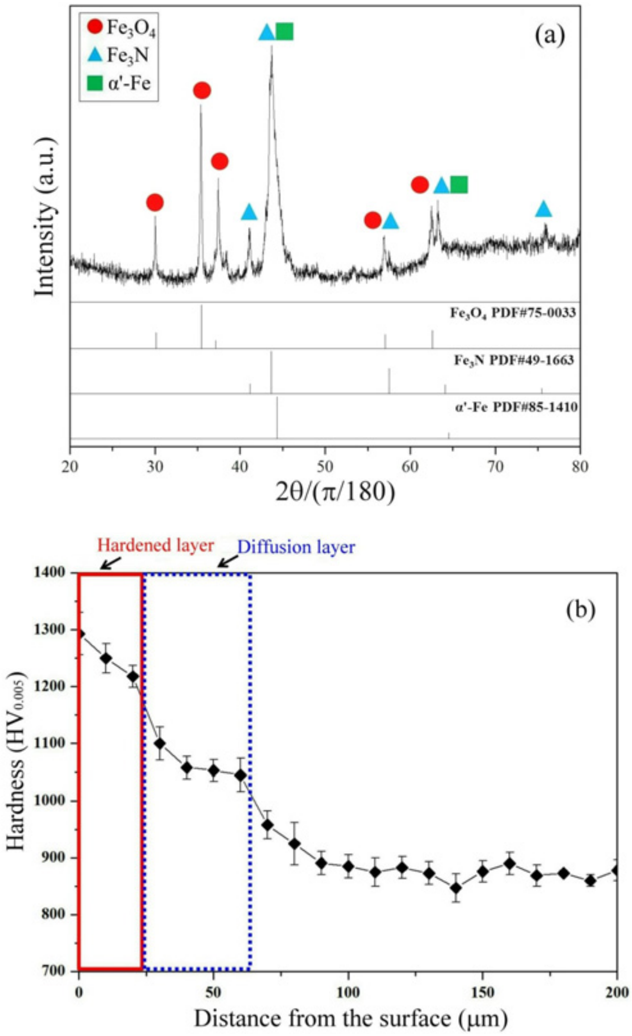

Fig. 1. XRD patterns and microhardness test results of the oxynitriding-treated V10 tool steel: (a) XRD patterns and (b) microhardness.

Fig. 1a. Because α'-Fe was the main element of the matrix for V10 tool steel, it also appeared in the XRD patterns. As mentioned previously, the oxynitride layer improved not only wear and corrosion resistance but also the intermediate layer. Previous studies indicated that an oxynitride layer could increase DLC films' adhesive strength since passive oxide film (Fe_3O_4) can be used to decrease the microporous structure during the nitriding process [4, 5]. In the study, hard and brittle δ-Fe_2N phases were not found; therefore, the surface brittleness of the oxynitriding layer could be significantly improved. Complex Fe_3O_4 and Fe_3N structures were successfully formed on the specimen's surface. The XRD analysis results confirmed that V10 tool steel possessed a well-oxynitrided layer and stable crystal structures.

Figure 1b shows the surface microhardness and depth profile test results of the oxynitriding-treated V10 specimens. The specimen's surface generated several types of nitrides and oxides after the oxynitriding treatment. It possessed a higher concentration of oxide and nitrogen ions, resulting in a significant hardening effect of the atomic lattice. Figure 1b displays that the surface hardness of the oxynitriding-treated specimen was elevated to $1293\,HV_{0.05}$. When the depth of the hardened layer was less than 25 μm, the hardness value was more than $1150\,HV_{0.05}$. The concentration of nitrogen and oxygen atoms gradually decreased, and the diffusion rate was relatively slow. As a result, the depth of the diffusion layer was about $25 \sim 68$ μm, and the hardness value declined to about $1050\,HV_{0.05}$. It is reasonable to suggest that with an increase in the diffusion depth, the nitrogen and oxygen concentrations were reduced, which led to a decrease in hardness. Thus, the hardness reverted to the original hardness of the substrate (about $890\,HV_{0.05}$) after the depth of 68 μm. The microhardness tests confirmed that stable oxynitride layers were successfully formed on the surface of the V10 tool steel by oxynitriding treatments, which led to an increase in the surface hardness of the specimen.

Previous literature indicated that the Raman spectra of DLC samples were first treated with linear background removal and then fitted with two Gaussian peaks simulating the D peak and G peak [16]. Figure 2 shows the Raman spectrum fitted with two Gaussian peaks after background removal by different duty cycles of DC-pulsed plasma-enhanced CVD. As seen in Fig. 2, an apparent G peak and D peak appeared on the Raman spectra. The Raman spectrum of a typical DLC structure generally shows a broad asymmetrical peak around $1500\,cm^{-1}$, whereas the G peak and D peak appeared around 1580 and $1350\,cm^{-1}$, respectively. In this work, the duty cycle was mainly determined by the time that the negative-pulse turned on, which can be regarded as the time when the plasma bombarded the specimen's surface. Thus, increasing the duty cycles and enhancing the efficiency of plasma bombardment resulted in DLC film being deposited on the substrate more quickly. Significantly, almost all the G peaks and D peaks had the same variation as a typical DLC structure. It is reasonable to surmise that all specimens possessed the typical characteristics of DLC films.

Figure 3a shows an original Raman spectrum of DLC films with different duty cycles by DC-pulsed plasma-enhanced CVD. The Raman spectrum of different duty cycles did not show any apparent variations, only slightly different intensity values. Hence, it was necessary to analyze the synthesized peak decompositions further to obtain the G peak position's offset and the value of I_D/I_G. On the other hand, the full width at half maximum (FWHM) of the G peak analysis could be evaluated. In this study, Gaussian function dismantling and synthesis were used to cal-

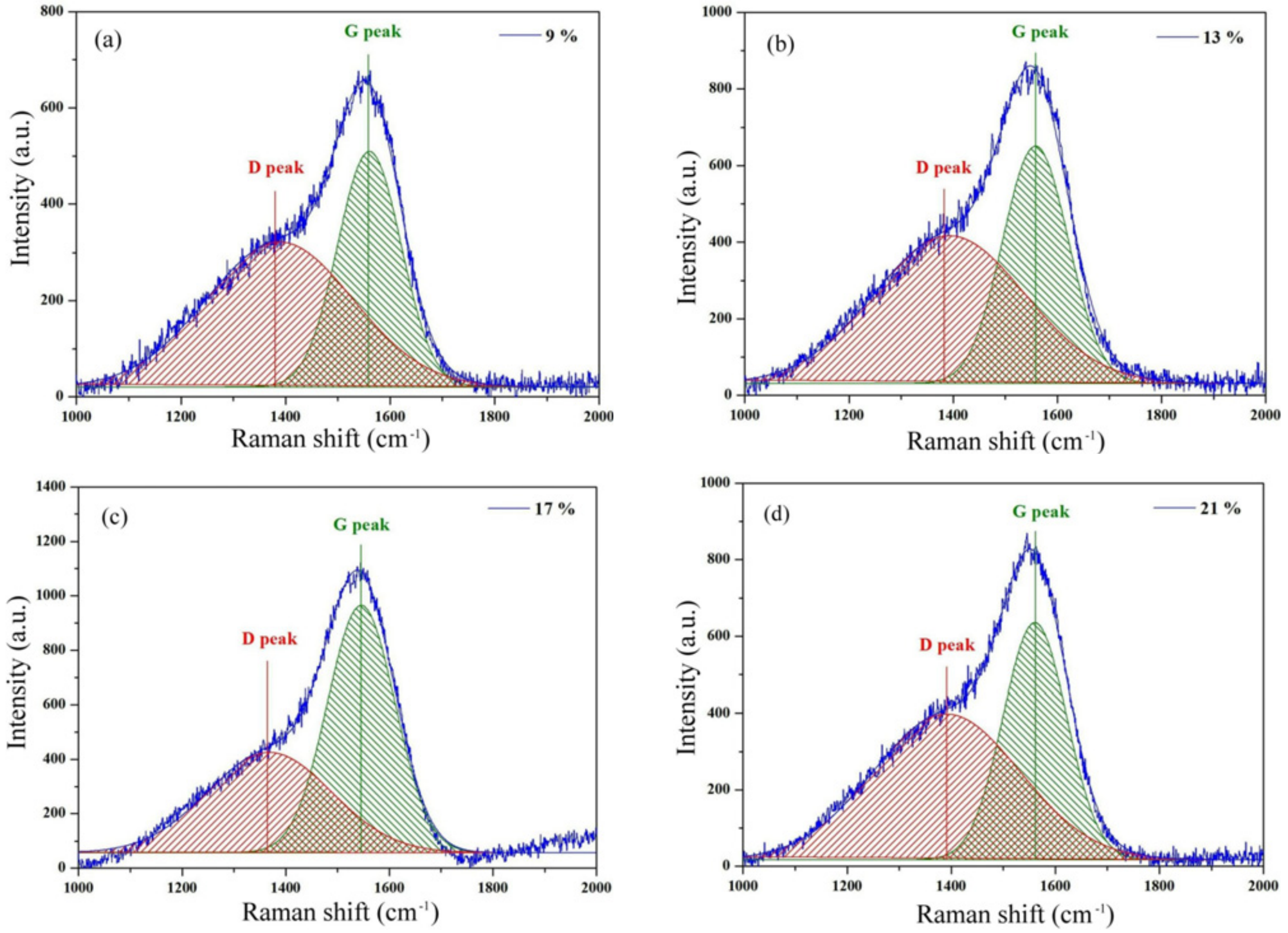

Fig. 2. Raman spectra of DLC fitted with double Gaussian peaks by different duty cycles of DC-pulsed plasma enhanced CVD. (The blue lines show the total fits, the red and green lines show the Gaussian peaks corresponding to the D peak and G peak, respectively): (a) 9 %, (b) 13 %, (c) 17 %, and (d) 21 %.

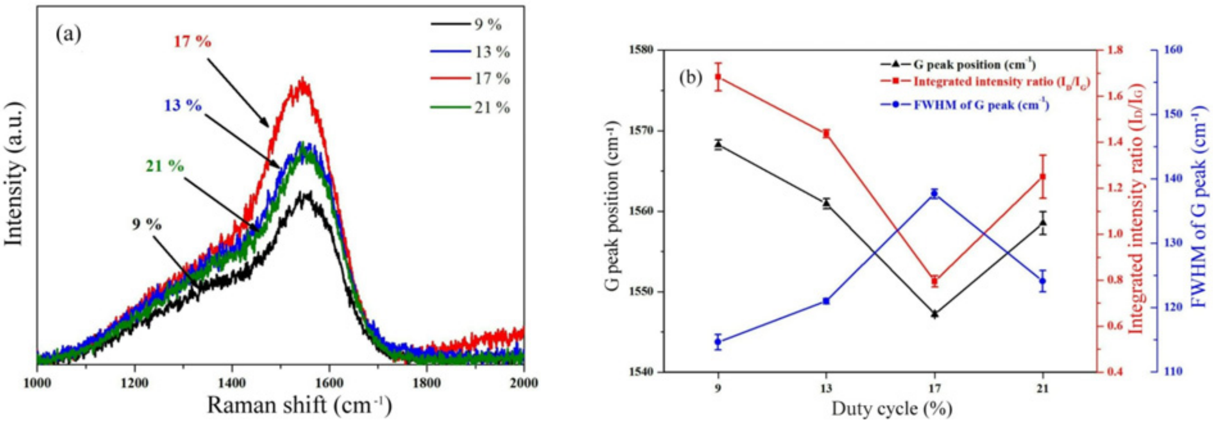

Fig. 3. Comparison of the (a) original Raman spectrum and (b) G-peak position, I_D/I_G and FWHM of G-peak analysis of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD.

culate the integration area ratio (I_D/I_G) results and the offset of the G peak for different duty cycles of DC-pulsed plasma enhanced CVD.

Figure 3b represents the increase in the duty cycle of DC-pulsed plasma enhanced CVD; both the value of I_D/I_G and the G peak position obviously declined and then rose rapidly. Conversely, the FWHM of the G peak was enhanced and then significantly decreased as the duty cycle increased. When the duty cycle was at 9 %, the plasma bombardment time was too short.

DLC film is easy to grow with sp^2 bonding, resulting in a larger I_D/I_G value. As the duty cycle increased (9 → 13 → 17 %), the plasma bombardment time increased, which produced more sp^3 bonds and resulted in the decline in the I_D/I_G value. The 17 % duty cycle specimen possesses the lowest value of the I_D/I_G ratio (0.79), the highest downshift of the G peak to 1547.22 cm^{-1}, and the highest FWHM of the G peak (137.67 cm^{-1}). In other words, the 17 % duty cycle specimen possesses the most sp^3 bonds of DLC films, leading to the lowest ratio value for I_D/I_G.

Furthermore, the I_D/I_G ratio is often used to derive an sp^2 correlation length for a-C(:H) [3]. This means that increasing the I_D/I_G value resulted in a decrease in the diamond-like carbon film size. Thus, it is reasonable to speculate that with the increase in the duty cycle from 9 to 17 % (the I_D/I_G value decline), the sp^2 correlation length of the DLC film decreased.

Although increasing the duty cycle can effectively increase plasma bombardment efficiency and lead to the quick production of DLC film, an excess of plasma bombardment easily causes many scattered carbon atoms [17]. As a result, increasing the duty cycle by more than 17 % is not conducive to the formation of DLC films. This leads to a likelihood that the sp^3 structure of DLC films transforms to an sp^2 structure. Consequently, the 21 % duty cycle possesses a higher value of I_D/I_G and a higher offset amount of the G peak, which is disadvantageous to DLC films' properties. According to the above experimental results, it was found that an appropriate duty cycle usually increases the efficiency of plasma bombardment and can effectively help in reducing the I_D/I_G value. Therefore, the G peak shifts to lower wavenumbers, and the sp^3 content tends to increase. These results are consistent with our previous research [3, 4]. Significantly, the 17 % duty cycle specimen relatively produced more stable sp^3 bonds (lowest value of I_D/I_G, the highest offset amount of G-peak and FWHM of G-peak), with presumably better mechanical properties.

In the present research, FT-IR was used to judge DLC films' functional group and composition bond. Figure 4 shows the FT-IR spectrum of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD. It can be seen that the DLC films possess obvious C-H vibration absorption peaks between wavenumbers of 2800–3000 cm^{-1} after undergoing different duty cycles. The main reason is related to C-H vibration absorption [9], indicating that the DLC film has a -CH_n compound and high hydrogen content. Further analysis of the FT-IR spectrum of each DLC film reveals that characteristic peaks are generated at positions of 2852 and 2921 cm^{-1}. According to our previous study, the peak at wavenumber 2852 cm^{-1} corresponds to the symmetry of sp^3-CH_2, and the peak at wavenumber 2921 cm^{-1} corresponds to sp^3-CH and the asymmetry of sp^3-CH_2 [3]. Generally speaking, the C-H vibration absorption peaks are all below 3000 cm^{-1}, proving that the carbon atoms in the DLC film are all saturated. As the duty cycle gradually increases (9 → 13 → 17 → 21 %), the plasma bombardment energy dramatically increases (2.63 → 3.80 → 4.97 → 6.14 W cm^{-2}). However, the high-speed plasma bombardment of the film surface (21 %) will produce a sputtering effect, resulting in a metastable sp^3 transfer to the sp^2 bond. As a result, the sp^2 bond content is relatively increased. This result is consistent with previous literature [18]. Consequently, the 17 % duty cycle specimen has the strongest absorption peak, indicating that it may have the highest sp^3 bond. This agrees with the trend of previous Raman analysis in this study.

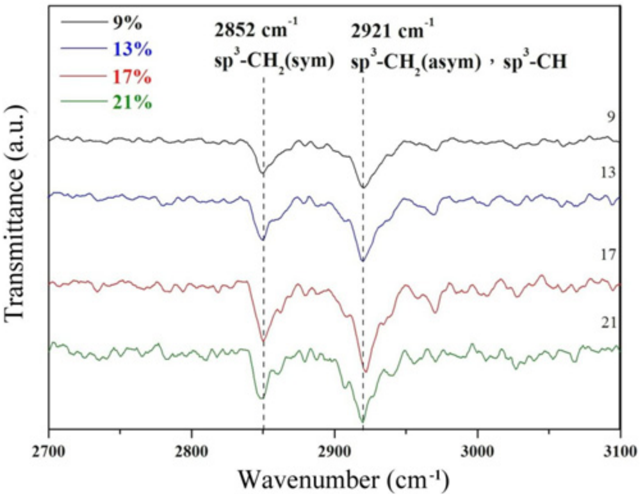

Fig. 4. Comparison of the FT-IR spectrum of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD.

Figure 5 shows the SEM images of the loading impact tests (Rockwell C scale indentation) for DLC films with different duty cycles by DC-pulsed plasma enhanced CVD. All the specimens have similar surface features after the loading impact test. There are radial cracks on the substrate, but no significant peeling-off phenomenon was generated, as seen in Figs. 5a–d. According to the VDI 3198 indentation test [15], the 9 % duty cycle specimen belongs to Grade 1 HF, while 13, 17, and 21 % duty cycles belong to grades 1–2 HF. In other words, all the DLC films have good adhesion after various duty cycles. As previously noted, the adhesion strength of DLC films on tool steel is poor, and adhesion-enhancing materials have been used directly as intermediate layers [3–5, 13, 14]. These results confirm that oxynitride layers (Fe_3N and Fe_3O_4) between the DLC films and the V10 tool steel can effectively improve the adhesion strength.

Although all specimens possessed good adhesion, the 21 % duty cycle specimen seems to have a little

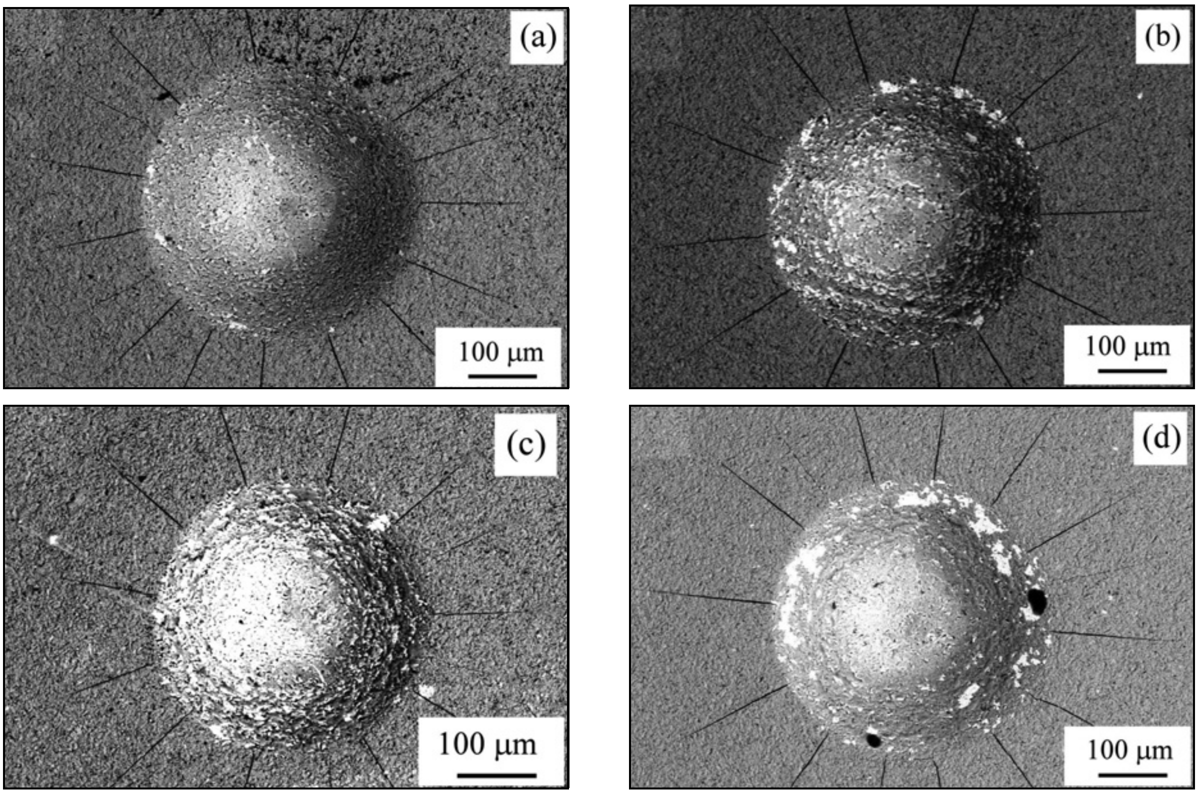

Fig. 5. SEM images of the loading impact test of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD: (a) 9 %, (b) 13 %, (c) 17 %, and (d) 21 %.

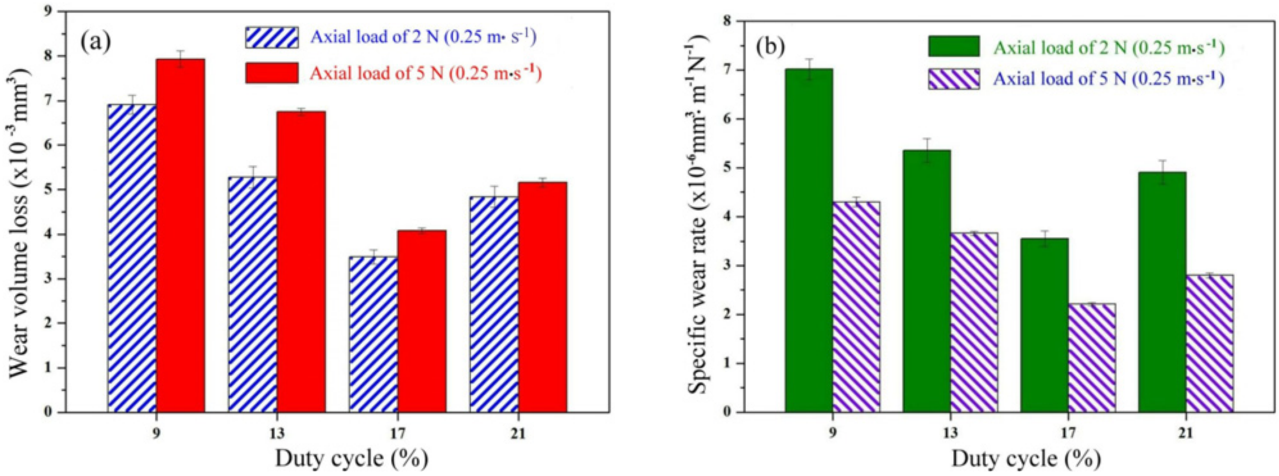

Fig. 6. Comparison of the (a) wear volume loss and (b) specific wear rate of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD.

peeling-off phenomenon, as shown in Fig. 5d. According to the previous definition, the 21 % duty cycle of DC-pulsed plasma enhanced CVD meant that the plasma deposition time was about 21 μs during 100 μs. Because the 21 % duty cycle specimen has a relatively long deposition time, it has higher bombardment energy ($6.14\,\mathrm{W\,cm^{-2}}$). It is reasonable to surmise that this is due to the excessive Ar ions' high-speed bombarding of the DLC films' surface. Moreover, the Ar gas easily dilutes methane (CH_4) in the plasma process [19]. Hence, the hydrogen content on the film's surface is easily sputtered out, and the relative content of sp^3-CH_3 in the DLC films is reduced. As a result, the proportion of sp^3 bonds decreases, and the proportion of sp^2 bonds increases, resulting in poor adhesion strength.

Figure 6 represents the wear volume loss and specific wear rate of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD. Figure 6a shows an obvious decrease and a slight increase in the wear volume loss as the duty cycle is enhanced. The lowest wear volume loss ($3.49 \times 10^{-3}\,\mathrm{mm}^3$) occurs at a gas flow with a 17 % duty cycle (2 N). As the axial load increases (2 → 5 N), all specimens' wear volume loss at different duty cycles increases obviously. The lowest wear volume loss ($4.08 \times 10^{-3}\,\mathrm{mm}^3$) similarly occurred at a 17 % duty cycle at a higher load (5 N), while the highest value of wear volume loss ($7.93 \times 10^{-3}\,\mathrm{mm}^3$) was at a 9 % duty cycle after the wear test (5 N). In addition, the average friction coefficients of 9, 13, 17, and 21 % duty cycles at a lower load (2 N) were 0.39, 0.35, 0.18, and 0.21, respectively. With an increase to a higher load (5 N), the average friction coefficients were 0.43, 0.43, 0.33, and 0.41. The 17 % duty cycle specimen had the lowest average friction coefficient of all the wear tests. The result could be further compared with that of the V10 tool steel. The wear volume loss and average friction coefficient of specimens without coating (V10) were $4.43 \times 10^{-3}\,\mathrm{mm}^3$ and 0.89 (wear test under a high load of 5 N). In other words, the wear resistance increased about 7.9 %, and the average friction coefficient decreased about 62.9 %. This result proves that it can indeed improve wear resistance by DLC/oxynitriding duplex surface treatment.

Since the 17 % duty cycle specimen possesses the lowest value of I_D/I_G and the strongest FT-IR absorption peak, it also has a relatively high adhesion strength and sp^3 bonding of DLC films. As a result, the DLC film of a 17 % duty cycle has a higher content of sp^3 bond. Moreover, the sp^3 bond of carbon can improve the hardness and increase the resistance to plastic deformation. Our previous study also found that the sp^3 bond was converted into a lower hardness of the sp^2 bond during the wear test. Still, the proper amount of sp^2 bond can generate a self-lubricating effect on the specimen's surface, thus improving the wear resistance. Consequently, the 17 % duty cycle specimen possessed the optimal wear resistance under different loads (2 and 5 N) for the wear tests.

The specific wear rate is defined as the wear volume loss per unit distance per unit load. Figure 6b shows that all specimens' specific wear rates under a high axial load (5 N) are lower than those under a low axial load (2 N). During the high load wear process, the surface of DLC films undergoes high-speed friction with the WC steel ball, which generates friction heat. Meanwhile, higher thermal energy caused the DLC structure to be transformed into a graphite structure [20]. Moreover, the produced thermal energy will drive the self-lubricating phenomenon of graphitization on the surface of the DLC films. As a result, the wear resistance was improved by the self-lubricating effect of the graphite. This was why the 17 % duty cycle specimen had the smallest specific wear rate (load 2 and 5 N is 3.55×10^{-6} and $2.21 \times 10^{-6}\,\mathrm{mm}^3\,\mathrm{m}^{-1}\,\mathrm{N}^{-1}$, respectively), indicating that it had better wear resistance. This result is consistent with the previous discussion in this study.

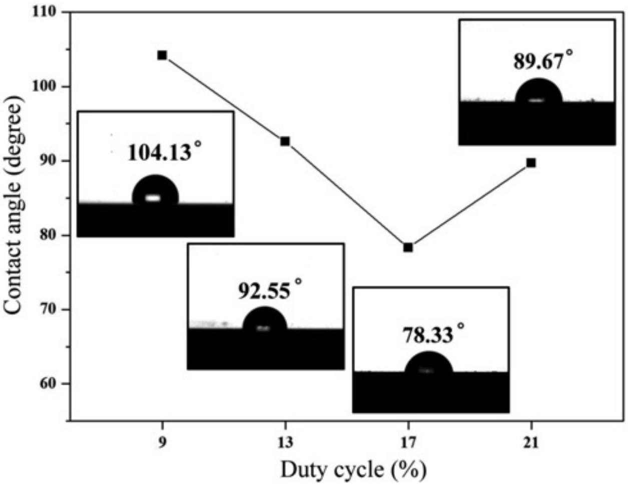

Fig. 7. Comparison of the water contact angle of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD.

The size of the water contact angle can be used to indicate the hydrophilic or hydrophobic properties of the material and understand changes in the composition of the material. Previous literature has proposed that a surface is hydrophilic when its contact angle (θ) is $< 90°$ and that it is hydrophobic when θ is $> 90°$ [7]. Figure 7 reveals the water contact angle of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD. It is found that the water contact angle shows an obvious decrease and then an increase as the duty cycle is enhanced. The maximum water contact angle is about 104.13° (9 % duty cycle), and the minimal contact angle is approximately 78.33° (17 % duty cycle). As previously discussed, the 17 % duty cycle possessed more stable sp^3 bonds, but the 9 % duty cycle produced more stable sp^2 bonds. Our previous study showed that sp^2 bonding has a higher water contact angle, and its hydrophobic properties increase as the sp^2 bond content of carbon increases [3]. Thus, the smallest water contact angle appeared at the 17 % duty cycle.

Also, the literature indicated that the surface energy of DLC film depends on the number of dangling bonds [21]. A smaller dangling bond usually has lower surface energy. The smaller the surface energy, the greater the water contact angle is. In general, the sp^2 bond of carbon has fewer dangling bonds than the sp^3 bond. Therefore, when the DLC film has a high content of sp^2 bond, its surface energy decreases, and the water contact angle increases. As a result, the maximum water contact angle appeared in the 9 % duty

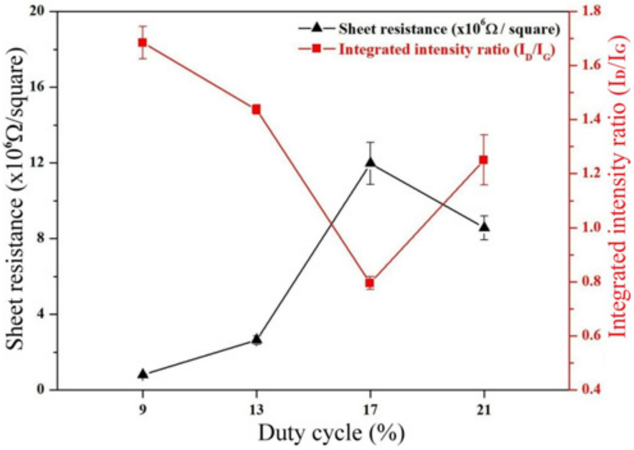

Fig. 8. Comparison of the sheet resistance and I_D/I_G of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD.

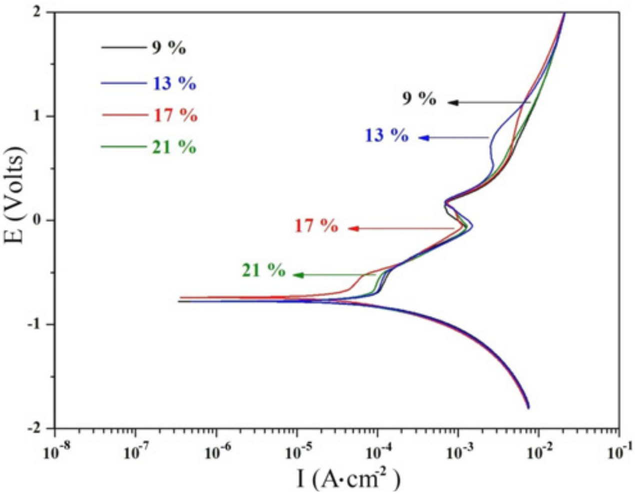

Fig. 9. Tafel results of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD after 3.5 wt.% NaCl corrosion test.

cycle specimen (with more stable sp^2 bonds and the highest I_D/I_G value (1.68)). Previous literature also showed that the water contact angle of amorphous hydrogen-containing DLC film was normally about 55°–70° [7]. In the present research, all the water contact angles of DLC films by different duty cycles were larger than stated in the literature. All of the DLC coatings in this study have certain hydrophobicity.

Figure 8 shows the sheet resistance of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD. As the duty cycle increases, the sheet resistance value increases and then decreases rapidly. The 17 % duty cycle specimen has the greatest sheet resistance value (1.19×10^7 Ω/square). The reason for this is related to the composition bonding of the DLC films. According to the literature, the electrical properties of DLC films are mainly determined by the sp^2 bonding content [22]. When the DLC film has a higher proportion of sp^2 bond, the sheet resistance value decreases (the conductivity increases). As mentioned previously, the 17 % duty cycle specimen possessed more stable sp^3 bonds, while the 9 % duty cycle had more stable sp^2 bonds. As a result, the 17 % duty cycle specimen has the largest sheet resistance value.

On the other hand, the trend of sheet resistance values of DLC films by different duty cycles changes conversely with the I_D/I_G value results. When the duty cycle is small (9 %), the DLC film has the smallest sheet resistance value (1.67×10^6 Ω/square) and the largest I_D/I_G value (1.68), indicating that it possesses the smallest sp^3/sp^2 bonds. As the duty cycle increases (9 → 13 → 17 %), the sheet resistance value of the DLC film increases, and the I_D/I_G value decreases, indicating that the sp^3/sp^2 bonding ratio gradually rises. However, when the duty cycle is too large (21 %), the sheet resistance value of the DLC film declines (8.57×10^6 Ω/square), and the I_D/I_G value increases (1.25). It is reasonable to suggest that the DLC film may gradually generate a graphitization phenomenon (sp^3/sp^2 bonding ratio decreases) after the treatment of a 21 % duty cycle. Hence, the electrical test results confirmed the relationship between the I_D/I_G value and the sp^3/sp^2 bonding ratio of DLC films.

In addition to a high hardness, high strength, and low friction coefficient, the corrosion resistance of DLC films is an important property. Figure 9 shows the Tafel slope results of DLC films with different duty cycles by DC-pulsed plasma enhanced CVD after the 3.5 wt.% NaCl corrosion test. All the specimens possessed a significant passivation phenomenon. A passivation layer will form on the material's surface, effectively protecting the interior material, thereby improving the corrosion resistance. A comparison of the corrosion resistance for the different duty cycles of DLC/oxynitriding treated V10 specimens is shown in Table 1. Our previous studies have shown that the samples with a lower current density (I_{corr}) and high polarization resistance (R_P) evidenced better corrosion resistance [4, 5]. In this study, the lowest corrosion current (7.9×10^{-5} A cm^{-2}) and highest polarization resistance (1185.21 Ω cm^2) of the V10 specimens appeared at the 17 % duty cycle. Conversely, the specimen for a 9 % duty cycle possessed the highest corrosion current (1.91×10^{-4} A cm^{-2}) and the lowest polarization resistance (506.87 Ω cm^2).

The test results above show that the 17 % duty cycle specimen possesses the best corrosion resistance. Increasing the duty cycle leads to an increase in the plasma bombardment efficiency and produces a stable sp^3/sp^2 bonding structure. As a result, as the duty cycle increased (9 → 13 →

Table 1. Comparison of the corrosion resistance of V10 specimens by various duty cycles of DC-pulsed plasma enhanced CVD after 3.5 wt.% NaCl corrosion test

Duty cycle (%)	I_{corr} ($\times 10^{-4}$ A cm^{-2})	E_{corr} (V)	R_{p} (Ω cm^2)
9	1.91	–0.78	506.87
13	1.85	–0.79	583.82
17	0.79	–0.74	1185.21
21	1.63	–0.78	687.71

17 %), the corrosion current declined ($1.91 \times 10^{-4} \rightarrow 1.85 \times 10^{-4} \rightarrow 7.9 \times 10^{-5}$ A cm^{-2}), and the polarization resistance was enhanced dramatically ($506.87 \rightarrow 583.82 \rightarrow 1185.21\,\Omega\,\mathrm{cm}^2$), respectively. However, excessive plasma bombardment easily generates an unstable sp^3/sp^2 bonding structure, resulting in reduced corrosion resistance. For the 21 % duty cycle specimen, the corrosion current increased, and the polarization resistance declined.

Although the DLC films possessed excellent chemical inertness, the sp^2 bonding generally accelerated the electro-migration between the substrate and etching solutions, which resulted in an increased current density and reduced corrosion resistance. Only the structures of the DLC films with more stable sp^3 bonding possessed good corrosion resistance. In the present research, oxynitriding-treated V10 specimens possessed a passive oxynitriding film (Fe_3O_4 and Fe_3N structures), which contributed to a better anti-corrosion property during the corrosion test. The stable DLC structures and oxide layers of the DLC/oxynitriding films were essential for improving corrosion resistance. Consequently, it is suitable to conclude that the DLC film treated by a 17 % duty cycle of DC-pulsed plasma enhanced CVD possessed good adhesion strength, optimal wear, and corrosion resistance. Simultaneously, the study results confirmed that the duplex surface treatment could effectively improve the coating properties of V10 tool steel.

4. Conclusions

The experimental results showed that V10 tool steel could form a stable oxynitriding layer (Fe_3O_4 and Fe_3N) with a thickness of about 68 μm after oxynitriding treatment. Meanwhile, the surface hardness increased to about 1293 HV$_{0.05}$. Furthermore, the optimal duty cycles of DC-pulsed plasma enhanced CVD for V10 tool steel is 17 %. An excess plasma bombardment appeared at a 21 % duty cycle, which caused the likelihood of the sp^3 to convert to sp^2 bonds, and the I_D/I_G values were increased. The 17 % duty cycle specimen possessed the most stable sp^3/sp^2 bonds and had better adhesion strength for DLC films.

FT-IR analysis reveals that the 17 % duty cycle specimen had the strongest absorption peak, indicating that it may have the highest sp^3 bond. Therefore, it possessed the lowest I_D/I_G (0.79), the highest offset amount (32.83 cm^{-1}), and an FWHM of the G-peak (137.67 cm^{-1}). The wear tests showed that the 17 % duty cycle specimen had the lowest wear volume loss for loads 2 N and 5 N were 3.49×10^{-3} mm^3 and 4.08×10^{-3} mm^3, respectively. Besides, it possessed the lowest corrosion current density ($I_{\mathrm{corr}} = 7.91 \times 10^{-5}$ A cm^{-2}) and highest polarization resistance ($R_{\mathrm{p}} = 1185.21\,\Omega\,\mathrm{cm}^2$) in the 3.5 wt.% NaCl solution corrosion tests. The water contact angle tests revealed that the 17 % duty cycle specimen had ideal hydrophobicity (78.33°). Moreover, it had the largest sheet resistance value ($1.19 \times 10^7\,\Omega$/square), indicating that it possessed the strongest sp^3/sp^2 bonds. Overall, the study results confirmed that an ideal duty cycle effectively improved the bonding structure and the tribological and corrosion properties of DLC/oxynitriding treated V10 tool steel.

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