Deposition of DLC Films onto Oxynitriding-Treated V4E High Vanadium Tool Steel through DC-Pulsed PECVD Process

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In this work, DLC films are prepared by DC-pulsed PECVD after the oxynitriding treatment of V4E high vanadium tool steel. The experimental design includes various power densities (200, 400, 600 and 800 mW·cm⁻²) with an unbalanced bipolar-pulsed voltage. The deposition time is 90 min, and the CH₄ gas flow is maintained at 5 sccm, respectively. The experimental results show the duplex coating layers to have better properties when the DLC films are treated by an appropriate power density (400 mW·cm⁻²). These films also possess the lowest wear loss volume (for loads of 2 N and 5 N of 6.23×10^{-3} mm³ and 1.19×10^{-2} mm³, respectively), the lowest corrosion current (4.09×10^{-4} A·cm⁻²) and the highest polarization resistance (258.83 Ω·cm²) after the 3.5 mass% NaCl corrosion test. This study confirms that the wear and corrosion resistance of V4E tool steel can be effectively improved through the DLC/oxynitriding duplex treatment. [doi:10.2320/matertrans.M2016375]

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1. Introduction

Since the tool steels are used in very different operating environments and conditions, steel must meet a wide variety of requirements, where ultra-high strength with high wear resistance and good toughness is required. To obtain the best steel properties, proper heat treatments including hardening and tempering are required. Currently, numerical methods are increasingly often used in modelling of technological processes.^{1,2} Vanadis 4 Extra (V4E) tool steel is a Cr-Mo-V alloyed steel which possess the good ductility, high wear resistance and compressive strength, and excellent temper-back resistance.³ Moreover, V4E is especially suitable for applications where adhesive wear and/or chipping are the dominant failure mechanisms. In addition, it also very suitable for blanking and forming of advanced high strength steels.^{3,4}

In order to further extend V4E applications, surface modification is necessary to improve its properties, including corrosion resistance and surface hardness etc. It was reported that nitriding and oxynitriding processes are the widely used surface modification techniques.⁵ Nitriding is a thermochemical process that is typically used to diffuse nitrogen into ferrous materials. This treatment can improve the surface hardness, fatigue strength, wear and corrosion resistance of nitride components.^{6,7} The previous studies indicated that oxygen addition can increase the efficiency of gas nitriding, thus the cycle time can be shortened and the energy consumption can be reduced. Oxynitriding processes use air or steam at the end of the nitriding stage, while the complex oxide layer with Fe₂O₃ and Fe₃O₄ structures are formed on the surface. Actually, better properties including higher surface hardness and better corrosion resistance, can be obtained by oxynitriding than those traditional nitriding, due to the oxides of Fe₃O₄ and little Fe₂O₃.^{5,8}

Furthermore, diamond-like carbon (DLC) coatings can be

used in order to improve the surface properties of steel molds because they combine unique mechanical, tribological and chemical properties. DLC films are metastable amorphous carbon (sp³ and sp² bonds) materials with superior tribological characteristics. They have high surface hardness, a low friction coefficient, reduced material adhesion, and they offer high protection against abrasive wear and corrosive attacks.^{9,10} However, the poor adhesion of DLC films on ferrous alloys reduces a wide range of industrial applications. Because the carbon diffuses into the metals delaying the DLC nucleation. Secondly, the thermal expansion coefficients of the coatings and the steels are not compatible, causing poor adhesion and high residual stresses.^{9,11} Therefore, many studies of the intermediate layers of DLC coatings have been frequently reported.^{12,13}

On the other hand, a number of different techniques have been used for depositing DLC films such as PVD, RF magnetron sputtering, PECVD, ion beam deposition and cathodic micro-arc discharge. Among them, the most common deposition technique used is plasma-enhanced chemical vapor deposition (PECVD). Moreover, the DC-pulsed PECVD is a novel method, because it is simpler and can be used in industrial scale with lower cost.¹⁴⁻¹⁶ As mentioned previously, an oxynitride layer can significantly improve the adhesion and properties of DLC films. Therefore, this research utilized DC-pulsed PECVD and DLC/oxynitriding duplex treatments to study the characteristics of DLC films, as well as to increase the tool life of V4E high vanadium tool steel.

2. Experimental Procedure

V4E high vanadium tool steel possesses superior mechanical properties, which combine high wear resistance, high toughness and good stability, making it suitable for cold work tools. In the present research, V4E tool steel was chosen as the substrate material to undergo a homogeneous heat treatment: it was quenched at 1100°C, and tempered at 525 and

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570°C for 2 h, respectively. Hence, the hardness value reached 62 ± 1 HRC. Furthermore, a typical microstructure was obtained through the heat treatment, comprising the structure of tempered martensite and various metallic carbides. The chemical compositions (mass%) of V4E tool steel are as follows: 4.7% Cr, 3.5% Mo, 3.7% V, 1.4% C, 0.4% Si, 0.4% Mn, and 85.9% Fe. The oxynitriding-treated specimens of V4E tool steel were nitriding-treated for 8 h at 550°C and oxidized *via* steam for 60 min at 525°C.

In this study, the DC-pulsed PECVD utilized an unbalanced bipolar-pulsed voltage. In order to study the effects of different duty cycles of the bipolar-pulsed PECVD process, the negative-pulsed duty cycle was maintained at $-15\%+10\%$, with power densities of 200, 400, 600 and 800 $\text{mW}\cdot\text{cm}^{-2}$, respectively. Simultaneously, the coating times of the DC-pulsed PECVD was maintained at 90 min; the pulsed voltage and frequency were kept at -1.5 kV and 10 kHz, respectively. Moreover, CH_4 gas (5 sccm) was added to the chamber at less than 1.33 Pa and continued for 90 min, followed by depositing of the DLC films.

Investigation of the properties of DLC films for DLC/oxynitriding treated V4E tool steel by different power densities of the DC-pulsed PECVD, the Raman spectroscopy analysis (MOF-iHR550), wear test (POD-FM800-25NT), indentation test (Indentec-8150LK),¹⁷⁾ scratch test (ASTM C1624-5, JLST022 Scratch Tester J & L Tech. Co., Korea) 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 $\varnothing 36 \times \text{D}5$ mm, diameter of WC ball (HRA 90 ± 1) was 6 mm, disk rotation was 200 rpm and total rotation was 10,000 revolutions, axial load was 2 N and 5 N, and sliding speed of $0.25 \text{ m}\cdot\text{s}^{-1}$, respectively.

Additionally, corrosion potential analysis uses three electrodes method and follows by ASTM G59-97: the reference electrode is a saturated of silver-silver chloride electrode, auxiliary electrode uses a platinum electrode, and the working electrode is connected to the test specimens^{10,13)} The contact area of the specimen was 2.01 cm^2 . The corrosive solvent used 3.5 mass% NaCl was maintained at room temperature. A scanning speed of 0.01 Vs^{-1} , 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 V4E specimens.

3. Results and Discussion

Figure 1 shows the XRD patterns and surface hardness profile of the oxynitriding-treated V4E tool steel. Significantly, the primary phases and structures of the oxynitride layer were Fe_3O_4 and Fe_3N (ϵ phase), as shown in Fig. 1(a). While α -Fe was the main element of the matrix for the V4E tool steel, it also appeared in the XRD patterns. In this study, neither a hard, brittle nor dense structure of the δ - Fe_2N phase was found. It was speculated that the wear properties would be significantly improved in the subsequent wear tests. Moreover, a complex oxide layer of Fe_3O_4 and Fe_3N structures was successfully formed on the surface. In fact, the oxynitride

Fig. 1 XRD patterns and hardness test results of the oxynitriding treated V4E specimens.

layer not only improved the wear and corrosion resistance, but, as the intermediate layer, it was advantageous to the adhesive strength. This result confirmed that the V4E tool steel was successfully nitride-treated at 550°C for 8 h and oxide-treated at 525°C for 60 min, and possessed a well-oxidized layer and stable crystal structures.

The surface hardness was measured at an applied load of 0.49 N (approximately equal to 50 g, expressed as $HV_{0.05}$ in this study, and tested at least three times) along the cross section of the test pieces through the micro-hardness tester (VMT-XT). As a result, the depth profile of the micro-hardness of the oxynitriding-treated V4E tool steel was obtained, as shown in Fig. 1(b). In addition, owing to the oxynitriding treatment, the specimen's surface generated several types of nitrides and oxides. When the specimen's surface possessed a higher concentration of oxide and nitrogen ions, a significant hardening effect of the atomic lattice resulted. As a result, the surface hardness of the oxynitriding-treated specimen was elevated to a high of $HV_{0.05}$ 1429. When the depth of the hardened layer was less than 20 μm , the hardness value was more than $HV_{0.05}$ 1200. Moreover, when the depth of the diffusion layer was 20–70 μm , the hardness value was about $HV_{0.05}$ 900–1100. However, with an increase in the diffusion depth, the oxide and nitrogen concentrations were obviously reduced, which led to a decrease in hardness. The hardness reverted to the original hardness of the substrate (about $HV_{0.05}$ 772.5) after a depth of 70 μm , as seen in Fig. 1(b). Clearly, stable oxide (Fe_3O_4) and nitride layers (Fe_3N) were successfully formed on the surface of the V4E tool steel by the oxynitriding treatments, which led to an increase in the surface

hardness of the specimen.

Figure 2 shows the SEM cross-sectional observations of the DLC films for the different power densities of the DC-pulsed PECVD. Significantly, the DLC films possessed a mixed diamond (sp^3) and graphite (sp^2) amorphous structure. Furthermore, the thickness of the DLC films displayed a similar level after each of the different power densities of the DC-pulsed PECVD treatments of about $2.8\ \mu\text{m}$. Apparently, the thickness of the DLC films was not affected by the power density. The adhesion layer between the steel substrate and the DLC thin films is usually referred to as the interlayer or intermediate layer. Previous literature¹¹⁾ showing the cross-section images of DLC/interlayer/substrate systems give no evidence as to the existence and/or function of the two interfaces that constitute the interlayer. In this work, the intermediate layer of the V4E steel and the DLC films was the oxynitride layer. As shown in Figs. 2(a)–2(d), the DLC films possessed good adhesion, while the SEM images showed no micro-cracks in the DLC films (Fig. 2). Clearly, the oxynitride layer had a significant effect on the adhesion of DLC films.

Previous literature has shown that the mechanical properties of DLC films are strongly affected by the hydrogen content, because hydrogen is monovalent and it acts to terminate potential carbon-carbon bonds.¹⁸⁾ Moreover, other literature has indicated that a larger supply of hydrocarbon in the plasma contributes to film growth. The DLC films' hydrogenation presented few variations when each system was analyzed separately.¹⁹⁾ In this study, the thickness of the DLC films displayed a similar level after each of the different power densities of DC-pulsed PECVD treatments. It is reasonable to suggest that the hydrogen content of the specimens would show insignificant variations. An important potential benefit is that carbon clusters play a significant role in the growth of DLC films or crystalline diamond. In general, Gaussian function dismantling and synthesis are used to calculate the results of the integration area ratio (I_D/I_G) and the offset of the G-peak for the different power densities of DC-pulsed PECVD. The previous literature have indicated that a relationship between the G-peak position, I_D/I_G , and sp^3 content.²⁰⁾ The Raman spectrum of graphitic carbon consists of two peak: the G peak

centered on $1550\ \text{cm}^{-1}$ is the zone center E_{2g} mode of the perfect graphite crystal and the D peak centered on $1350\ \text{cm}^{-1}$ is a zone edge A_{1g} mode which is activated by disorder. The D mode is a common feature of all disordered graphitic carbons whose intensity related to the G peak has been shown to vary inversely with the size of the graphite crystallites.^{21,22)} The I_D/I_G ratio is often used to derive an sp^2 correlation length for a-C(:H). Both I_D/I_G and the optical gap depend on L_a , and according to the following equation²¹⁾:

$$I_D/I_G = k/L_a$$

Where k depends on factors such as the electrode areas, and L_a is the length of a-C(:H). It suggested that the I_D/I_G increased with increasing bias voltage for plasma-deposited a-C:H, implying that L_a falls with increasing bias from above equation. In this study, we seriously consider the evolution of G-peak position and I_D/I_G ratio. The offset of the G-peak can also reveal the relative performance of the carbon films. For all specimens, a bulge in the Raman band occurred at $1550\ \text{cm}^{-1}$, as shown in Fig. 3(a). However, the main difference was not apparent. It was necessary to further analyze the synthesized peak decomposition to obtain the value of I_D/I_G and the offset of the G-peak position.

Figure 3(b) shows that at the power density of $200\ \text{mW}\cdot\text{cm}^{-2}$ the highest I_D/I_G value (0.95) and the smallest offset amount of G-peak ($1563\ \text{cm}^{-1}$) were obtained. Upon increasing the power density ($200 \rightarrow 400 \rightarrow 600 \rightarrow 800\ \text{mW}\cdot\text{cm}^{-2}$) of the DC-pulsed PECVD, both the I_D/I_G value and the position of the G-peak showed an obvious decline, and then rapidly rose, respectively. Based on the relationship between I_D/I_G and the size of the graphite planes, values of I_D/I_G greater than unity

Fig. 2 SEM cross-sectional observations of the DLC films by the different power densities of DC-pulsed PECVD: (a) 200, (b) 400, (c) 600, and (d) $800\ \text{mW}\cdot\text{cm}^{-2}$.

Fig. 3 Comparison of the (a) original Raman spectrum, and (b) I_D/I_G and G-peak of Raman analysis by the different power densities of DC-pulsed PECVD.

are often found in a-C and a-C:H. The presence of a large D component suggests that the sp^2 cluster model is basically correct.²¹⁾ It is reasonable to suggest that increasing the I_D/I_G value resulted in the size of the graphite planes decreased. Thus, as shown in Fig. 3(b), it is possible to say that increasing the power density from 200 to 400 $W\cdot cm^{-2}$ (the I_D/I_G value decline), the size of the graphite planes increases. However, increasing the power density from 400 to 800 $W\cdot cm^{-2}$ (the I_D/I_G value rose), the size of the graphite planes decreases. In addition, the 400 $mW\cdot cm^{-2}$ specimen had the lowest I_D/I_G value (0.86) and a relatively greater offset amount of the G-peak (1556 cm^{-1}). In the present research, the power density of 200 $mW\cdot cm^{-2}$ of the DLC film had a relatively lower plasma energy, which likely resulted in the greater sp^2 bond and the higher I_D/I_G value. As the power density increased ($200 \rightarrow 400\text{ mW}\cdot cm^{-2}$), the plasma bombardment energy was obviously enhanced, which easily allowed for the sp^2 to transform to an sp^3 bond. The experimental results showed that the 400 $mW\cdot cm^{-2}$ specimen produced more stable sp^3 bonds (I_D/I_G of 0.86 and G-peak offset of 1556 cm^{-1}), with presumably better mechanical properties.

Our previous study³⁾ also showed 250 and 300 $mW\cdot cm^{-2}$ to have more off-time, sufficient to release the charge accumulation; thus, the power density of the energy and the gas dissociation rate were relatively lower, which resulted in the poor properties of the DLC films. Conversely, the higher ion energy of the plasma bombardment (over 600 $mW\cdot cm^{-2}$) easily caused the high increase in the specimen's surface energy and, thus, the generation of unstable structures. This led to the likelihood of the sp^3 structure of the DLC films transforming to sp^2 and further affecting the film's characteristics, so that the DLC films gradually approached graphitization. Consequently, the 600 and 800 $mW\cdot cm^{-2}$ specimens possessed a relatively higher value of I_D/I_G and smaller G-peak offset (compared to the 400 $mW\cdot cm^{-2}$ specimen).

Figure 4 shows the SEM images of the loading impact tests (Rockwell C scale indentation) for various power densities of the DC-pulsed PECVD process. All specimens had similar surface features after the loading impact test. There were radial cracks on the substrate, but no significant peeling-off phenomenon was generated, as seen in Figs. 4(a)–4(d). The DLC coatings for the 200 and 800 $mW\cdot cm^{-2}$ power densities

evidenced more obvious radial cracks, as shown in Figs. 4(a) and 4(d). Actually, the radial cracks did not result from fractures of the DLC films, but were caused by the compressive stress on the specimen's surface from the oxynitriding process. Generally speaking, the adhesion strength of DLC films on steel is poor¹⁰⁾ and adhesion-enhancing materials have been used directly as intermediate layers. In this work, the oxynitriding process used pre-treated V4E tool steel as an intermediate layer. The nitrogen and oxide atoms entered the interstices of the lattice *via* atomic diffusion, and easily resulted in the lattice deformation and surface hardening. Furthermore, the lower plasma bombardment (200 $mW\cdot cm^{-2}$) readily produced the loose sp^2 bond, while the higher plasma bombardment (800 $mW\cdot cm^{-2}$) led to greater internal stress and more uneven sp^3 and sp^2 structures. The VDI 3198 indentation test¹⁷⁾ showed the adhesion strength of the power densities of 400 and 600 $mW\cdot cm^{-2}$ DLC film treatments to be the HF 1 grade and the 200 and 800 $mW\cdot cm^{-2}$ the HF 1~2 grade.

Figure 5 shows the surface morphology observations of the scratch tests after the different power densities of the DC-pulsed PECVD process. For the scratch test, the load was gradually increased from 0 to 100 N, and the total traveling distance was 5 mm. All specimens showed no significant ruptures on the DLC films after the scratch tests. Even at a maximum load of 100 N, a good bonding strength of the DLC films was retained. Significantly, all specimens were better able to resist rupture and the adhesion strength of the DLC films remained fairly stable. The poor adhesion of DLC films on ferrous alloys limits the range of industrial applications.¹¹⁾ Interlayers are commonly employed in an attempt to improve DLC adhesion on metallic alloys. In these experiments, with the oxynitride layer as an interlayer between the DLC films and V4E tool steel, the adhesion strength of DLC films was effectively improved. Further observation of the specimens' appearance after the scratch tests (as seen in Figs. 5(a)–5(d)) confirmed that all specimens possessed good DLC coating adhesion as a result of the good interlayer. This result also agreed with our finding in the foregoing indentation test result (Fig. 4).

As already noted, DLC films possess superior tribological characteristics correlated to the fraction of sp^3 bonds in the films, such as a low friction coefficient and high wear resistance. Generally, the volume loss of the wear tests allows the wear rate of the material to be calculated. Figure 6 shows the

Fig. 4 SEM images of the loading impact test by the different power densities of DC-pulsed PECVD: (a) 200, (b) 400, (c) 600, and (d) 800 $mW\cdot cm^{-2}$.

Fig. 5 Surface morphology observations of scratch test by the different power densities of DC-pulsed PECVD: (a) 200, (b) 400, (c) 600, and (d) 800 $mW\cdot cm^{-2}$.

wear loss volume and specific wear rate for the different power densities of the DC-pulsed PECVD. Figure 6(a) reveals that the wear loss volume showed an obvious decrease and then an increase as the power density was enhanced. The highest wear volume value ($1.72 \times 10^{-2} \text{ mm}^3$) occurred at the power density of $200 \text{ mW}\cdot\text{cm}^{-2}$ after the lower load (2 N) of the wear tests. The DLC films at a power density of $200 \text{ mW}\cdot\text{cm}^{-2}$ exhibited an unstable sp^3/sp^2 structure, which showed in the wear test results. The lowest wear loss volume ($6.23 \times 10^{-3} \text{ mm}^3$) occurred at a power density of $400 \text{ mW}\cdot\text{cm}^{-2}$ (2 N). As the axial load increased (2 $\rightarrow$ 5 N), the wear loss volume of all specimens at the different power densities dramatically increased, as also shown in Fig. 6(a). The lowest wear loss volume ($1.21 \times 10^{-2} \text{ mm}^3$) occurred at the power density of $400 \text{ mW}\cdot\text{cm}^{-2}$ at a higher load (5 N), while the highest value of wear loss volume ($2.27 \times 10^{-2} \text{ mm}^3$) was at a power density of $200 \text{ mW}\cdot\text{cm}^{-2}$ after the wear test (5 N). Clearly, the $400 \text{ mW}\cdot\text{cm}^{-2}$ specimen possessed the optimal wear resistance under the different loads of the wear tests.

The specific wear rate is defined as the wear volume loss per unit distance per unit load. In this research, all the specific wear rates under a high axial load (5 N) were lower than that for under a low axial load (2 N) for the different power densities, as shown in Fig. 6(b). The previous literature showed that higher thermal energy caused the DLC structure to be transformed into the graphite structure.²³ In this study, the specimen's surface generated a higher energy under a high axial load of the wear process, which easily resulted in the

graphitization phenomenon of the DLC film, and caused the sp^3 transform to a sp^2 bond. As a result, the wear resistance was obviously improved by the self-lubricating effect of the graphite. In other words, the high axial load specimens possessed a relatively lower specific wear rate. Besides, the specific wear rate generated a significant declining trend under a high axial load wear process. This result confirmed the relationship between the high energy and graphitization phenomenon of the DLC films. The lowest specific wear rate of $4.86 \times 10^{-3} \text{ mm}^3\text{m}^{-1}\cdot\text{N}^{-1}$ (5 N) appeared at a power density of $400 \text{ mW}\cdot\text{cm}^{-2}$. Conversely, the highest specific wear rate of $1.75 \times 10^{-2} \text{ (2 N) mm}^3\text{m}^{-1}\cdot\text{N}^{-1}$ appeared at a power density of $200 \text{ mW}\cdot\text{cm}^{-2}$. According to the above discussion and results, we were able to confirm that at a power density of $400 \text{ mW}\cdot\text{cm}^{-2}$ the DC-pulsed PECVD resulted in DLC films with the ideal adhesion strength and optimal wear resistance.

Figure 7 shows the SEM surface morphology of the wear test under a load of 5 N and a sliding speed of $0.25 \text{ m}\cdot\text{s}^{-1}$ for the different power densities of the DC-pulsed PECVD. Figures 7(a) and 7(d) reveal the relatively wide and deep wear tracks, while Figs. 7(b) and 7(c) show a significantly shallower wear track. Particularly, the surface morphology showed almost no abrasion damage at a power density of $400 \text{ mW}\cdot\text{cm}^{-2}$, as shown in Fig. 7(b). In addition, the power density of $600 \text{ mW}\cdot\text{cm}^{-2}$ generated a slight spalling phenomenon between the DLC films and the V4E substrate and displayed a wide but shallow wear track, as shown in Fig. 7(c). Conversely, the DLC films produced a dramatic peeling phenomenon and micro-cracks after the lowest and highest power densities of 200 and $800 \text{ mW}\cdot\text{cm}^{-2}$, as shown in Figs. 7(a) and 7(d). As mentioned, too-low and too-high power densities usually generated an unstable plasma energy, which easily caused a low content of both sp^3 carbon and hydrogen under a plasma atmosphere. Therefore, it was reasonable to suggest that the power densities of 400 and $600 \text{ mW}\cdot\text{cm}^{-2}$ with more sp^3 bonding and a stable DLC structure resulted in good adhesion strength and wear resistance. This also agreed with our previous finding.

Generally speaking, DLC films have many excellent properties, such as high hardness, low friction coefficient and high corrosion resistance; thus, the corrosion behavior of the DLC

Fig. 6 Comparison of the wear volume loss of various wear tests by the different power densities of DC-pulsed PECVD: (a) load 2 N, and (b) load 5 N and sliding speed $0.25 \text{ m}\cdot\text{s}^{-1}$, respectively.

Fig. 7 Surface morphology of wear test (sliding speed of $0.25 \text{ m}\cdot\text{s}^{-1}$ and load of 5 N) by the different power densities of DC-pulsed PECVD: (a) 200, (b) 400, (c) 600, and (d) $800 \text{ mW}\cdot\text{cm}^{-2}$.

films was an important consideration. Figure 8 shows the Tafel slope results of the V4E specimens for the various power densities of the DC-pulsed PECVD after the 3.5 mass% NaCl corrosion test. All specimens possessed a significant passivation phenomenon. The passivation layer generated a protective effect. A comparison of the corrosion resistance for the different power densities of the DLC/oxynitriding-treated V4E specimens is shown in Table 1. The samples with a lower current density (I_{corr}) and higher potential (E_{corr} or polarization resistance R_p) evidenced better corrosion resistance.¹⁰⁾ Table 1 lists the corrosion resistance (I_{corr} , E_{corr} and R_p) of the different power densities of the DLC/oxynitriding-treated V4E specimens. The lowest corrosion current ($4.09 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$) and highest polarization resistance ($258.83 \Omega\cdot\text{cm}^2$) of the V4E specimens appeared at a power density of $400 \text{ mW}\cdot\text{cm}^{-2}$, while the $200 \text{ mW}\cdot\text{cm}^{-2}$ specimen possessed the highest corrosion current ($6.96 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$) and the lowest polarization resistance ($192.54 \Omega\cdot\text{cm}^2$). This result indicated that the $400 \text{ mW}\cdot\text{cm}^{-2}$ specimen had a relatively stable sp^3/sp^2 bonding structure, which helped for improving the corrosion resistance. However, increases in the power density led to increases in the residual stress and loose structures (sp^2). As the power density increased ($400 \rightarrow 600 \rightarrow 800 \text{ mW}\cdot\text{cm}^{-2}$), the corrosion current increased ($4.09 \rightarrow 5.99 \rightarrow 6.37 \text{ A}\cdot\text{cm}^{-2}$) and the polarization resistance declined slightly ($258.83 \rightarrow 239.08 \rightarrow 223.1 \Omega\cdot\text{cm}^2$), respectively.

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 the increased current density and reduced corrosion resistance. Only with more stable sp^3 bonding structures

Fig. 8 Tafel results of V4E specimens by the different power densities of DC-pulsed PECVD after 3.5 mass% NaCl corrosion test.

Table 1 Comparison of the corrosion resistance of V4E specimens by the different power densities of DC-pulsed PECVD after 3.5 mass% NaCl corrosion test.

Specimens ($\text{mW}\cdot\text{cm}^{-2}$)	$I_{\text{corr}} (\times 10^{-4} \text{ A}\cdot\text{cm}^{-2})$	E_{corr} (Volts)	$R_p (\Omega\cdot\text{cm}^2)$
200	6.96	-1.03	192.54
400	4.09	-1.00	258.83
600	5.99	-1.02	239.08
800	6.37	-1.03	223.10

could the DLC films possess good corrosion resistance. Moreover, oxidation-treated steel usually forms a passive film (Fe_3O_4 structures), which contributes to a better anti-corrosion property during the corrosion test. Therefore, the stable DLC structures and oxide layers of the DLC/oxynitrided films were essential to improve the corrosion resistance. Consequently, the $400 \text{ mW}\cdot\text{cm}^{-2}$ specimen of the DC-pulsed PECVD possessed the optimal corrosion resistance in a 3.5 mass% NaCl solution.

4. Conclusions

The experimental results showed that DLC thin films (about $2.8 \mu\text{m}$) were successfully obtained after V4E tool steel was treated using the DLC/oxynitriding duplex treatment. In this work, the optimal power density of the DC-pulsed PECVD for V4E tool steel was $400 \text{ mW}\cdot\text{cm}^{-2}$. Moreover, the increase in the plasma bombardment energy resulted from the increased power density. The excess plasma bombardment energy appeared at 600 and $800 \text{ mW}\cdot\text{cm}^{-2}$, which easily caused the likelihood of the sp^3 to convert to sp^2 bonds and the I_D/I_G values was increased. As the $400 \text{ mW}\cdot\text{cm}^{-2}$ specimen produced the more stable sp^3/sp^2 bonds and had better adhesion strength due to the suitable power density, it possessed the lowest I_D/I_G (0.86) and the greatest offset of the G-peak (1556 cm^{-1}).

In addition, the lowest wear loss volume of $6.23 \times 10^{-3} \text{ mm}^3$ (load of 2 N) occurred at a power density of $400 \text{ mW}\cdot\text{cm}^{-2}$, which also accounted for the lowest specific wear rate of $4.86 \times 10^{-3} \text{ mm}^3\text{m}^{-1}\cdot\text{N}^{-1}$ (load of 5 N). This specimen also had a relatively low corrosion current ($4.09 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$) and high polarization resistance ($258.83 \Omega\cdot\text{cm}^2$). Clearly, the power density of $400 \text{ mW}\cdot\text{cm}^{-2}$ specimens possess the stable sp^3/sp^2 bonding, better properties, as well as good adhesion strength and wear resistance. Consequently, this study confirmed that these ideal DLC films were effective in improving the tribological and corrosion properties of the DLC/oxynitriding-treated V4E tool steel.

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REFERENCES

- 1) T. Domański and A. Bokota: *Int. J. Mech. Sci.* **96–97** (2015) 47–57.
- 2) H.G. Nanesa and M. Jahazi: *Mater. Sci. Eng. A* **634** (2015) 32–36.
- 3) “VANADIS 4 EXTRA SuperClean”. ASSAB Steel Website. <http://www.assab.com/media/ASSAB-Vanadis4ExtraSuperClean.pdf>, (accessed 2016-07-26)
- 4) “Uddeholm Vanadis® 4 Extra SuperClean”. Uddeholm Steel Website. http://www.uddeholm.com/files/PB_Uddeholm_vanadis_4_extra_english.pdf, (accessed 2016-07-26)
- 5) H. Liu, J.C. Li, Y.T. Chai, W. Wei and J. Hu: *Vac.* **121** (2015) 18–21.
- 6) A. Alsaran, H. Altun, M. Karakan and A. Çelik: *Surf. Coat. Technol.* **176** (2004) 344–348.
- 7) S. Kikuchi, T. Fukuoka, T. Sasaki, J. Komotori, K. Fukazawa, Y. Misaka and K. Kawasaki: *Mater. Trans.* **54** (2013) 344–349.

- 8) S.H. Chang, T.P. Tang, Y.C. Chen and J.K. Chen: *ISIJ Int.* **49** (2009) 421–424.
- 9) E.L. Dalibon, V. Trava-Airoldi, L.A. Pereira, A. Cabo and S.P. Brühl: *Surf. Coat. Tech.* **255** (2014) 22–27.
- 10) S.H. Chang, C.C. Yu, K.T. Huang and C.M. Liu: *ISIJ Int.* **55** (2015) 2631–2638.
- 11) F. Cemin, C.D. Boeira and C.A. Figueroa: *Tribol. Int.* **94** (2016) 464–469.
- 12) Z.Y. Xu, H. Sun, Y.X. Leng, X.Y. Li, W.M. Yang and N. Huang: *Appl. Surf. Sci.* **328** (2015) 319–324.
- 13) S.H. Chang, Y.K. Lin and K.T. Huang: *Surf. Coat. Tech.* **207** (2012) 571–578.
- 14) M. Ebrahimi, F. Mahboubi and M.R. Naimi-Jamal: *Diamond Related Materials* **52** (2015) 32–37.
- 15) G. Capote, E.J. Corat and V.J. Trava-Airoldi: *Surf. Coat. Tech.* **260** (2014) 133–138.
- 16) T. Morita, K. Andatsu, S. Hirota, T. Kumakiri, M. Ikenaga and C. Kaga-ya: *Mater. Trans.* **54** (2013) 732–737.
- 17) N. Vidakis, A. Antoniadis and N. Bilalis: *J. Mater. Process. Technol.* **143–144** (2003) 481–485.
- 18) M. Umeno, M. Noda, H. Uchida and H. Takeuchi: *Diamond Related Materials* **17** (2008) 684–687.
- 19) P.C.S. Silva, M.A.R. Ramos, E.J. Corat and V.J.T. Airoldi: *Mater. Res.* **19** (2016) 882–888.
- 20) A.C. Ferrari and J. Robertson: *Phys. Rev. B* **61** (2000) 14095–14107.
- 21) J. Robertson: *Surf. Coat. Tech.* **50** (1992) 185–203.
- 22) M.J. Paterson, K.G. Orrman-Rossiter, D.K. Sood and S.K. Bhargava: *Diamond Related Materials* **2** (1993) 1439–1444.
- 23) J.H. Wang, S. Zhang, H.L. Wang, K.E. Wong, Q.A. Zhou and Y.Z. Zhou: *Thin Films.* **517** (2009) 5202–5206.