Study of bias voltage effect on the performance of ta-C coating prepared by high power impulse magnetron sputtering

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Abstract The mechanical and frictional properties of ta-C coatings deposited on the substrate surface affect applications in the field of cutting tools and wear-resistant components. In this paper, the effect of bias parameters on the performance of ta-C coatings was investigated based on high power impulse magnetron sputtering (HiPIMS) technology. The results show that bias voltage has a significant effect on the deposition rate, structure, and wear resistance of the coating. In the range of bias voltage −50 V to −200 V, the ta-C coating performance was the best under bias voltage −150 V. The thickness reached 530.4 nm, the hardness value reached 35.996 GPa, and the bonding force increased to 14.2 N. The maximum sp^3 bond content was 59.53% at this condition.

Key words bias voltage, magnetron sputtering, deposition rate, wear resistance

0 Introduction

Diamond-like coatings having the advantages of high hardness, good wear resistance, high thermal conductivity, low thermal expansion coefficient, low friction coefficient, and chemical inertness[1 − 4], are widely used in aerospace, aviation, military, biomedical science, and mechanical engineering fields[4 − 6]. Diamond-like coatings are mainly composed of diamond structure sp^3 carbon atoms and graphite structure sp^2 carbon atoms mixed with each other, and their hardness, elastic modulus, lubricity and chemical inertness can be further enhanced when the percentage of sp^3 hybrid bonds in the coating exceeds 50%[7], which is also called tetrahedral amorphous carbon coating (ta-C for short).

Tetrahedral amorphous carbon coatings (ta-C) were first proposed by Mckenzie et al.[8] in 1991. Since then, methods and research tools for preparing ta-C have been developed, and in 1998, Kalish et al.[9] prepared ta-C coatings by mass separated ion beam method (MSIB) with increasing sp^3 bond content by increasing graphitization temperature. Bonelli et al.[10] prepared ta-C coatings with high sp^3 hybrid bond content at room temperature using a pulsed laser deposition technique at a wavelength of 248 nm, but thickness of the coating was not uniform. In foreign research, Inkin et al. used pulsed cathodic arc technique to deposit Ti transition layer before depositing ta-C and obtained ta-C coatings with good bonding[11]. In contrast, domestic research on ta-C coatings started late. Han et al.[12] prepared ta-C thin coatings with more than 80% sp^3 bonding content and got a defect free coating surface by double-bending filtered cathodic arc technique. Wang et al.[13] studied the deposition of ta-C:N coatings under different N_2 partial pressures, and the results showed that the N and C binding mode was C-N bonding, and the N content increased with the increase of N_2 partial pressure, but the sp^3 bonding con-

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tent decreased. With the in-depth study of ta-C coatings, there are still some problems, such as the contamination of large particles in ta-C coatings deposited by cathodic arc technique, which reduces various properties of the coatings; excessive internal stress during the deposition process will reduce the coating base bonding force and lead to coating delamination low target erosion rate and low deposition rate. Based on this, high power impulse magnetron sputtering (HiPIMS) technology is proposed in this paper for the preparation of ta-C thin coatings.

HiPIMS is a magnetron sputtering technique that uses higher peak pulse power and lower pulse duty cycle to obtain high sputtering metal ionization rate. This technique was first proposed by Kouznetsov and his team in 1999[14] and successfully deposited Cu coatings. Due to the short pulse duration time, the peak power of HiPIMS, about 1 000−3 000 W/cm^2 is 100 times higher than that of conventional magnetron sputtering, and the plasma density can reach 10^{18} m^{-3} order of magnitude, with high ionization rate and dense coatings generated with excellent performance. However, HiPIMS technology can cause excessive stress by too strong ions bombardment and adhesion problem is still a concern to researchers. It has been reported that the substrate bias can effectively improve the coating layer adhesion problem[15]. Based on this, this paper aims to investigate the performance of ta-C based on HiPIMS technique, which is deposited with different bias voltage, and to make effort to reduce the internal stress in the coating layer and its effect to the sp^3 bonding properties of the coating.

1 Experimental method

1.1 Materials

In this paper, YG6 tungsten-cobalt cemented carbide, widely used in cutting tool industry with the advantages of high strength and good impact toughness, high wear resistance, etc. is selected as the test material. The size of the substrate material is 19 mm × 19 mm × 5.5 mm rectangular sample, the average hardness is HRA89.5. the chemical composition (by mass fraction) of WC and other alloy components content are 94.0%, Co content 6.0% respectively. The selected equipment is QPlex type magnetron sputtering system of Shanghai New- Arc Coating Technology Co., Ltd. The QPlex magnetron sputtering equipment is installed with four target positions and uses a closed unbalanced magnetic field (UMF) layout as shown in Fig. 1. In this experiment, graphite target and Cr target are installed at target positions 1 and 4, respectively. The process conditions: process gas Ar flow 150 mL/min, deposition temperature 90−100 ℃, process pressure between 0.2−0.3 Pa, input power 5 kW, fixed pulse frequency 4 000 Hz, fixed pulse width 50 μs. Based on above conditions, the effect of substrate bias on the ta-C coating properties deposited on the WC carbide surface is investigated. The specific process steps from the beginning to the end are: heating and pumping; ion etching; cleaning of the targets; deposition of transition layer (CrN layer + CrC layer); ta-C deposition (substrate bias voltage of −50 V, −100 V, −150 V, −200 V).

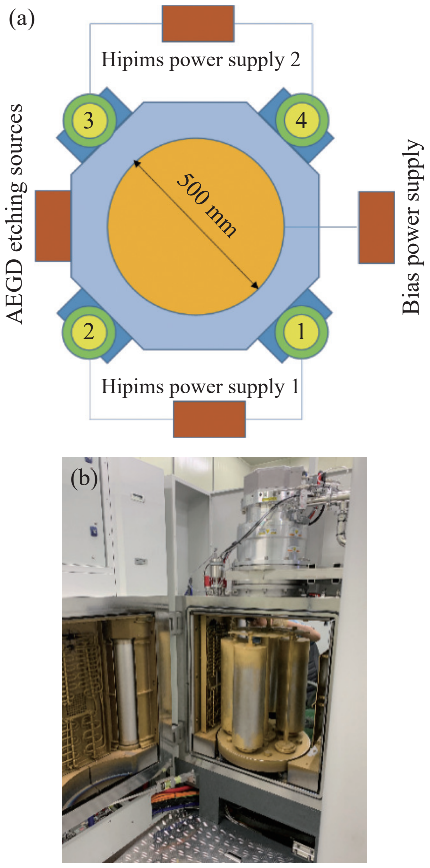

Fig. 1 Layout and appearance of equipment (a) layout (b) appearance

1.2 Characterization

In this experiment, the surface cross-sectional morphology of ta-C thin coatings was observed using a ZEISS Gemini 300 field emission scanning electron microscope from Germany. The bonding condition in the ta-C coatings was analyzed using a Horiba LabRAM HR Evolution laser Raman spectrometer from Japan. 514 nm was chosen as the laser wavelength, and the spectral measurement range was set from 700 cm^{-1} to 2 000 cm^{-1} with a scan step of 2 cm^{-1}. Gaussian fitting of the Raman spectra allowed the characterization of the sp^2 and sp^3 bond ratios. A K-Alpha multifunctional X-ray photoelectron spectrometer from Thermo Fisher, USA, was used to analyze the surface structure of the coatings, operating at a vacuum of about 3 × 10^{-7} torr, with an X-ray source of monochromatic Al Kα source (Mono Al Kα), energy 1 486.6 eV, 6 mA × 12 kV, beam spot size: 400 μm. The nano-indenter can precisely control the indentation depth and load to avoid the influence of the substrate on the coating, and is commonly used to measure the hardness and elastic modulus of thin coating materials. The Nano Indenter G200 from Agilent, USA, equipped with a Berkovich indenter, was used to measure the mechanical properties of the coatings. The Poisson's ratio of the coating was set to 0.25 before testing, and each sample was randomly indented five times to ensure reproducibility, while a static load mode was selected with a constant indentation load and a maximum load setting of 8 mN held for 10 s to avoid the effects of surface roughness and soft substrates.

2 Results and discussion

2.1 Effect of bias voltage on ta-C coating performance

The growth process of thin coating deposition is a more complex physicochemical process, and many factors directly affect the deposition efficiency and structural properties of thin coatings[16]. In order to improve the ta-C coating deposition efficiency, only argon gas flow was introduced into the chamber and the pulse frequency was kept 4 000 Hz, pulse width was kept 50 μs, the target power was set to 5 kW, and on the basis of this coating condition, the effect of different bias voltage during ta-C coating deposition was investigated , and its effect on the ta-C coating interface morphology is shown in Fig. 2. It can be seen that there is a clear interface between the coating layers , as well as between coating and the WC substrate. The coating has three layers, which are CrN layer, CrC layer and ta-C coating, and there is also a clear interface between the transition layer and ta-C. The thickness of the transition layer (CrN + CrC) is around 1 100 nm. The thickness of ta-C coating increases firstly and decreases lately with the increase of bias voltage. Under the bias voltage of −50 V, −100 V, −150 V, and −200 V, the thickness of ta-C coating layer varies as follows: 514.5 nm, 519.4 nm, 530.4 nm, and 488.9 nm, respectively. The thickness of ta-C increases with bias voltage. It can be understood that more created ions are attracted by higher substrate bias voltage. While the bias voltage increases from −150 V to −200 V, the thickness of the ta-C coating layer first increases and then decreases, which may be analyzed because of there-sputtering effect. When the substrate bias voltage is too high, the deposited particles on the substrate will be sputtered away by the coming particles again, which can cause a reduction in the thickness of the coating.

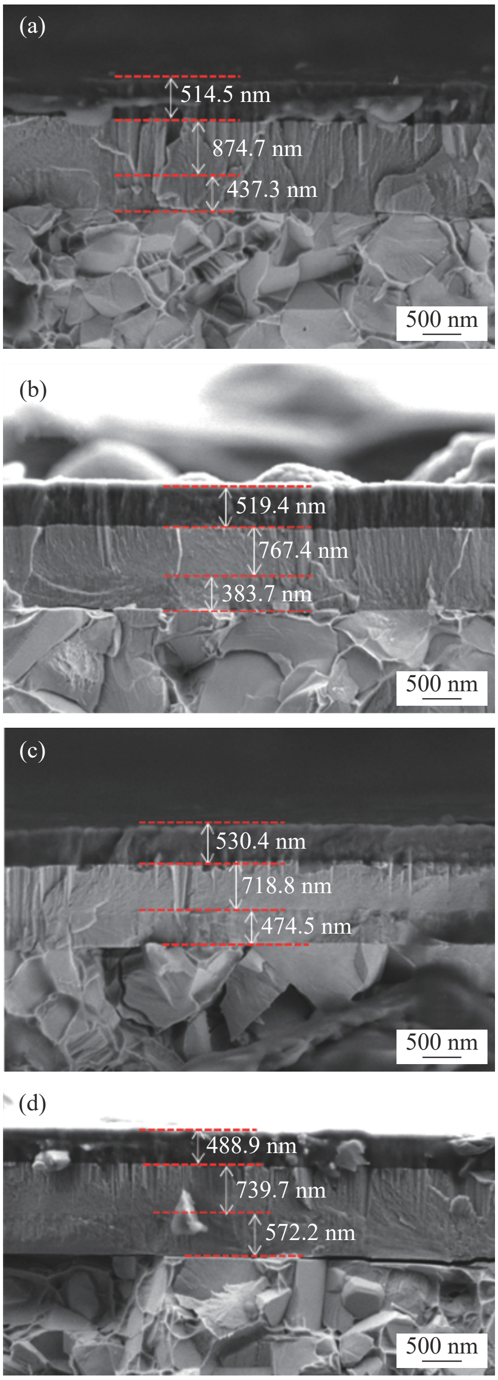

Fig. 2 Effects of different bias voltage on deposition thickness of ta-C coatings (a) −50 V (b) −100 V (c) −150 V (d) −200 V

As shown in Fig. 3, the G peak shifts toward the high wave number band as the bias voltage changes. This indicates that the increase of the bias voltage drives the change of the structure of the coating. From the Gaussian fit plot, it can be seen that the D peak and G peak of the Raman spectrum of the ta-C coating at −50 V are at 1 381.9 cm^{-1} and 1 552.3 cm^{-1}, respectively; the D peak and G peak at −100 V are at 1 369.4 cm^{-1} and 1 555.1 cm^{-1}, respectively;

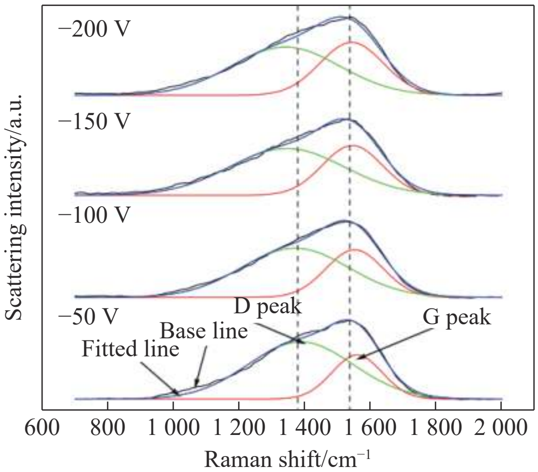

Fig. 3 **Gaussian fit of ta-C coatings with different bias voltages**

the D peak and G peak at −150 V are at 1 387.4 cm^{-1} and 1 559.2 cm^{-1}, respectively; the D peak and G peak at −200 V are at 1 401.6 cm^{-1} and 1 565.8 cm^{-1}, respectively. As shown in Table 1, with the increase of bias voltage, the ratio of I_D and I_G first decreases and then increases, which indicates that the content of sp^3 bond in ta-C coatings first increases and then decreases with the increase of bias voltage. The commonly accepted mechanism for the formation of sp^3 bonds in ta-C coating is the sub-surface injection model. This model suggests that the carbon plasma moves to the surface of the substrate with a certain kinetic energy and injects into the subsurface layer, forming sp^3 bonds under a large compressive stress, but if the energy is small, it can only be attached to the superficial layer and cannot generate sp^3 bonds. When the energy of the incident ion is high, it is more favorable to form sp^3 bonds. Under certain other conditions, the initial kinetic energy of the ion is equal, and the greater the bias voltage, the greater the attraction to the ion. The higher the kinetic energy when incident to the substrate, the greater the likelihood of successful bonding, according to the sub-injection model, with the increase of bias voltage, there are more high-energy carbon ions generated by the injection effect of sp^3 bonds, from −50 V to −150 V in line with this law. However, as the bias voltage continues to increase, the ion energy continues to increase and the continued bombardment of the coatings will produce more heat, resulting in the intensification of the thermal peak. Relaxation occurs around the implanted carbon atoms, converting part of the sp^3 bonds to sp^2 bonds, and the content of sp^3 bond decreases with increasing bias voltage.

Table 1 **Raman spectral Gaussian fitting of ta-C coatings with different bias voltages**

Bias voltage/V	D peak/cm^{-1}	D FWHM/cm^{-1}	G peak/cm^{-1}	G FWHM/cm^{-1}	I_D/I_G
−50	1 381.9	374.7	1 552.3	137.8	1.79
−100	1 369.4	401.5	1 555.1	204.9	1.39
−150	1 387.4	375.8	1 559.2	179.8	1.27
−200	1 401.6	364.6	1 565.8	161.6	1.31

Fig. 4 shows the XPS analysis of ta-C coatings deposited at different bias voltages. There are four orbital peaks of C1s, N1s, O1s and Ar2p in the sample. The peak of C for the sample is fitted by XPSPEAK41 software. According to the peak type and binding energy position, the C1s orbital in the sample can be divided into sp^2, sp^3, C-O and C=O, with binding energies at 284.60 eV, 284.56 eV, 286.43 eV and 288.80 eV, respectively. According to the XPS analysis, the specific content of C1s chemical bonds can be obtained, as shown in Table 2. It can be seen that when the bias voltage is −150 V, the sp^3 C content is higher, indicating that when the initial kinetic energy of the ions is equal, the greater the bias voltage, the greater the attraction to the ions, and the more high-energy carbon ions are generated, which is consistent with the summary of I_D/I_G ratio of Raman fitting . The results show that ta-C coatings at bias voltage −150 V are closer to diamond coatings with excellent performance and desirable hardness values.

Fig. 5 shows the nanoindentation of bias voltage −150 V and −50 V. It can be seen that the indentation depth reaches a maximum of 111.3 nm at bias voltage −150 V and 120.1 nm at bias voltage −50 V when the indenter reaches a maximum load of 8 mN. Based on the nanoindentation results, the hardness of the ta-C coating was about 35.996 GPa at bias voltage −150 V and about 31.786 GPa at bias voltage −50 V. At the same load, the indentation depth was shallower and the hardness values were higher at bias voltage −150 V, indicating that the mechanical properties of the coatings prepared at bias voltage −150 V were better. Meanwhile, there is no fracture type increase in the graph, which can indicate that the toughness of the coating is better at this parameter.

Fig. 6 shows the ta-C scratch diagram prepared at different bias voltage. When the ta-C coating was prepared at a

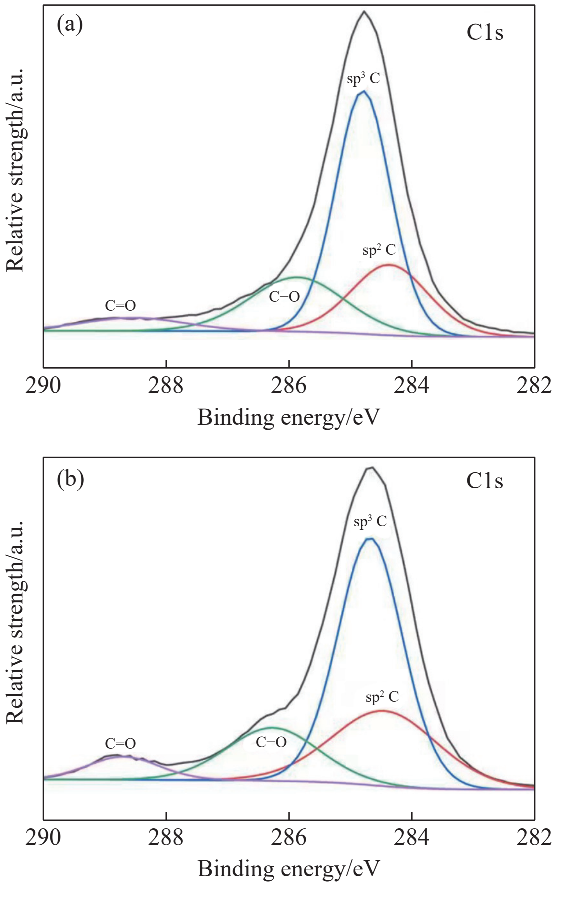

Fig. 4 C1s peak fitting of XPS for ta-C coatings with different bias voltages (a) −50 V (b) −150 V

Table 2 Relative content of C1s chemical bond in ta-C coating (at.%)

Bias voltage/V	sp^2 C	sp^3 C	C-O	C=O
−150	20.08	59.53	14.98	5.41
−50	23.17	50.54	17.30	5.21

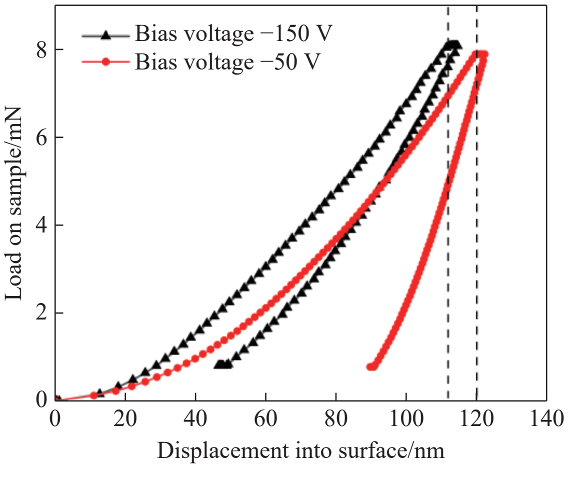

Fig. 5 Ta-C nanoindentation pattern with different bias voltages

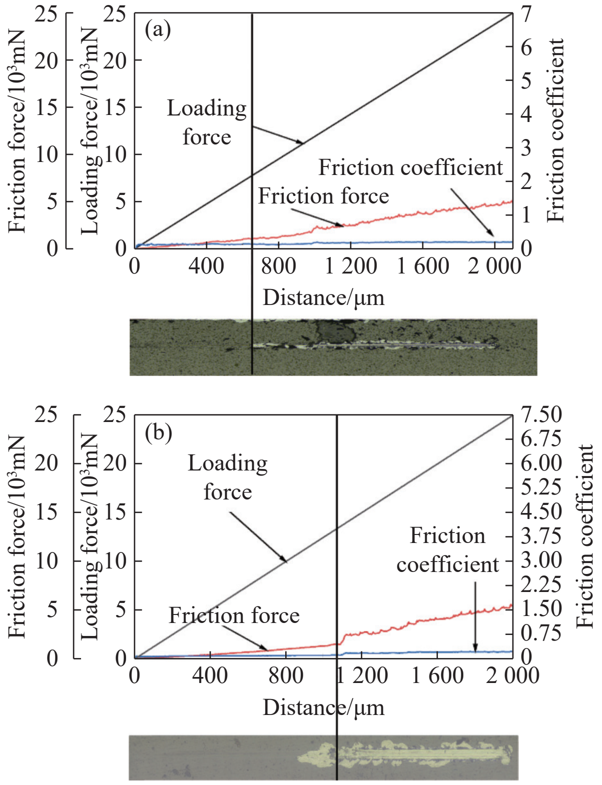

Fig. 6 Ta-C scratch diagram under different bias voltages (a) −50 V (b) −150 V

bias voltage of −50 V, the coating fractured at 680 μm and the loading force was 7 800 mN, i.e., the coating failed completely at 7 800 mN. It can be seen from the plot that the ta-C coating prepared at a bias voltage of −150 V fractured at 1 100 μm with a loading force of 14 200 mN, i.e., the coating failed completely at 14 200 mN. It can be seen from the topography that when the bias voltage increases, the area falling off of the coating surface also increases. This is because when the bias voltage is larger, the coating hardness is also larger, and the internal stress of the coating is also larger, so the surface is larger when the scratch passes.

3 Conclusions

(1) Changing the substrate bias voltage can improve the deposition rate of ta-C coatings to a certain extent. When the bias voltage is −150 V, the coating deposition rate is the fastest and the thickness of ta-C coating can be increased from 514.5 nm to 530.4 nm.

(2) The bias voltage has a significant effect on the structure of ta-C coating, and the I_D/I_G decreases and then increases with the increase of bias voltage, and the sp^3 bond content also shows the same trend according to XPS. At the bias voltage of −150 V, the sp^3 bond is higher in the ta-C

membrane.

(3) The bias voltage has some influence on the mechanical properties of ta-C coating. As the bias voltage increases, the hardness value of ta-C coating is increased from 31.786 GPa to 35.996 GPa, and the hardness is more excellent at the bias voltage of −150 V. The bonding force reaches 14.2 N.

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