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Duplex diamond-like carbon film fabricated on 2Cr13 martensite stainless steel using inner surface ion implantation and deposition

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Abstract

A duplex plasma immersion ion implantation and deposition (PIIID) process, involving carbon ion implantation and diamond-like carbon (DLC) film deposition, is proposed to treat the inner surface of a tube. Samples of 2Cr13 martensite stainless steel were placed inside the tube to investigate the performance of the films. Carbon ion implantation was finished by biasing the tube with a high voltage, and the DLC film deposition was obtained by biasing the tube with a medium voltage. Raman spectrum, ball-on-disc, indentation and scratch tests were used to investigate the structure, tribological property and adhesion strength of the as-deposited films. The Raman spectrum shows that the sp^3 bonding is formed in the as-synthesized film. Tribological and scratch test results reveal that the duplex DLC coating with the implantation time of 1 h has the largest adhesion strength and the best wear resistance.

Keywords: Diamond-like carbon; Plasma immersion ion implantation and deposition; Duplex treatment; Inner surface; 2Cr13

1. Introduction

2Cr13 martensite stainless steel is commonly used as a structural material for mechanical components operated under high loading and corrosive environment. The service life of these components depends mainly on its wear and corrosion resistances. Hence, surface strengthening is usually used to prolong the service life of these components. However, the inner surface of a cylinder-like component, like piston barrel in petroleum industries, is difficult to be strengthened by a common surface modification technique because of its irregular shape.

Diamond-like carbon (DLC) film is a metastable form of amorphous carbon with significant sp^3 bonding. Since it posses a high mechanical hardness and chemical inertness, it has a widespread application as a protective coating [1,2]. For a cylinder-like component, plasma immersion ion implantation and deposition (PIIID) is often used to modify its inner surface. Malik et al. [3] developed a PIIID technique to deposit DLC film on the inner surface of a tube. Baba [4] inserted a microwave antenna into the tube, and placed an electromagnetic coil outside the tube. By moving the coil and introducing C_2H_2 gas into the tube, the C_2H_2 plasma can be generated inside the tube. In addition, when applying a high voltage on the tube, the DLC film deposition was accomplished. Ronghua Wei [5] proposed a novel inner surface modification method called plasma immersion ion deposition (PIID). Using this method, the plasma can be generated inside the tube by applying a negative pulsed voltage, and the DLC film could be fabricated in the inner surface of the tube using CH_4 or C_2H_2 as the feeding gas. The setup of this method is simple and a number of tubes can be deposited simultaneously. In addition, to enhance the plasma density inside the tube, a magnetic field can be applied in the tube. However, because of lacking implantation, this method cannot get a DLC film with high adhesion strength.

Researches have found that a duplex process employing a carbon or silicon ion implantation before DLC deposition can improve the adhesion strength significantly, which can be ascribed to the formation of the multilayer interface [6–8].

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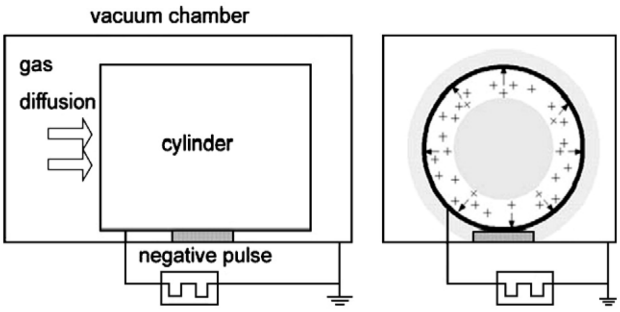

Fig. 1. The schematic of the experimental setup.

However, since the ion implantation in the inner surface of a tube is difficult, the method for fabricating a duplex DLC coating in the inner surface of a tube is still a hard task. In this work, we proposed a simple method to form a duplex DLC layer in the inner surface. The influences of the processing parameters on the wear resistance were investigated and the optimum parameters for a duplex DLC film fabrication were proposed.

2. Experimental details

The schematic of the experimental setup is shown in Fig. 1. A tube was set in a vacuum chamber and the tube was biased with a series of negative pulsed voltage. The inner diameter, length and thickness of the tube were 42, 100 and 4 mm, respectively. To evaluate the performances of the coating, samples of 2Cr13 martensite stainless steel (hardness of HV 280 and composition listed in Table 1) with the diameter of 6 mm and the thickness of 0.5 mm were set on the inner surface of the tube. The samples received a final polish to a surface roughness, Ra, of 0.04 μm, and were cleaned ultrasonically in acetone and ethanol. During the experiment, C_2H_2 gas was introduced into the chamber, and the C_2H_2 plasma was generated by the pulsed bias. The samples underwent a duplex treatment of carbon ion implantation and DLC film deposition. Carbon ion implantation was finished by a large magnitude pulsed bias (several tens kV) and the DLC film deposition was obtained by a medium bias (several kV). The high voltage pulse is generated by a power supply based on hard-tube technology, and the medium voltage pulse is obtained by a power source based on serials IGBTs technology.

Typical parameters for the carbon ion implantation are: pulse width=60 μs, C_2H_2 gas flow=40 sccm, working pressure=6×10^{-1} Pa, pulse frequency=350 Hz. The implantation voltage and time varied from 20 to 30 kV and 0.5 to 2.0 h, respectively. And the pulse current was increased from 0.4 to 0.6 A when the implantation voltage was added from 20 to 30 kV. The parameters for the DLC film deposition are: pulse width=20 μs, C_2H_2 gas flow=80 sccm, working pressure=2 Pa, pulse frequency=8 kHz, deposition time=2 h, and the magnitude of the bias was varied from 2 to 4 kV. In addition, the pulse current was increased from 0.03 to 0.05 A when the implantation voltage was added from 2 to 4 kV. The processing parameters for each sample are listed in Table 2.

Table 1
Chemical composition of 2Cr13 martensite stainless steel

Element	C	Si	Mn	Cr	S	P	Fe
Composition (wt.%)	0.16	≤0.60	≤0.80	12~14	≤0.030	≤0.035	Rest

Table 2
Processing parameters of each sample

Sample no.	Implantation voltage	Implantation time (h)	Deposition voltage (kV)
S1	0	0	4
S2	0	0	2
S3	20	1.0	4
S4	30	0.5	4
S5	30	1.0	4
S6	30	1.5	4
S7	30	2.0	4

Structural analysis of the as-deposited DLC layers was performed by Raman spectrum. The static load bearing capacity of the duplex treated samples was evaluated using an indentation method with a Brinell hardness tester, and the applied load is 60 kgf. The dynamical load bearing capacity of the duplex treated sample was evaluated by employing a scratch tester, and testing parameters are: scratching speed=2 mm/min, loading rate=40 N/min, and maximum load=80 N. The tribological properties of DLC films were evaluated using a ball-on-disc friction tester at a linear velocity of 0.05 m/s. The tests were carried out under dry running condition with a Si_3N_4 ball of 6.3 mm and a wear diameter of 3 mm. The load used in the test includes 100 and 400 g, which generated a contact stress of 500 and 800 MPa inside the sample, respectively. The cut-through number, which is defined as the wear number where the friction coefficient increases rapidly, is used to characterize the wear resistance. In addition, the wear and scratch tracks as well as the indentation were observed by an optical microscope.

3. Results and discussion

Raman spectrum is often used to prove the existence of the diamond structure. According to the shape of the Ramon spectrum and the ratio of I_D/I_G, the sp^3 ratio of the DLC film

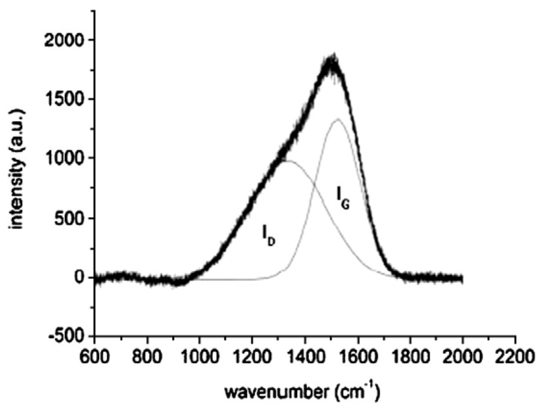

Fig. 2. Raman spectrum of the sample S1.

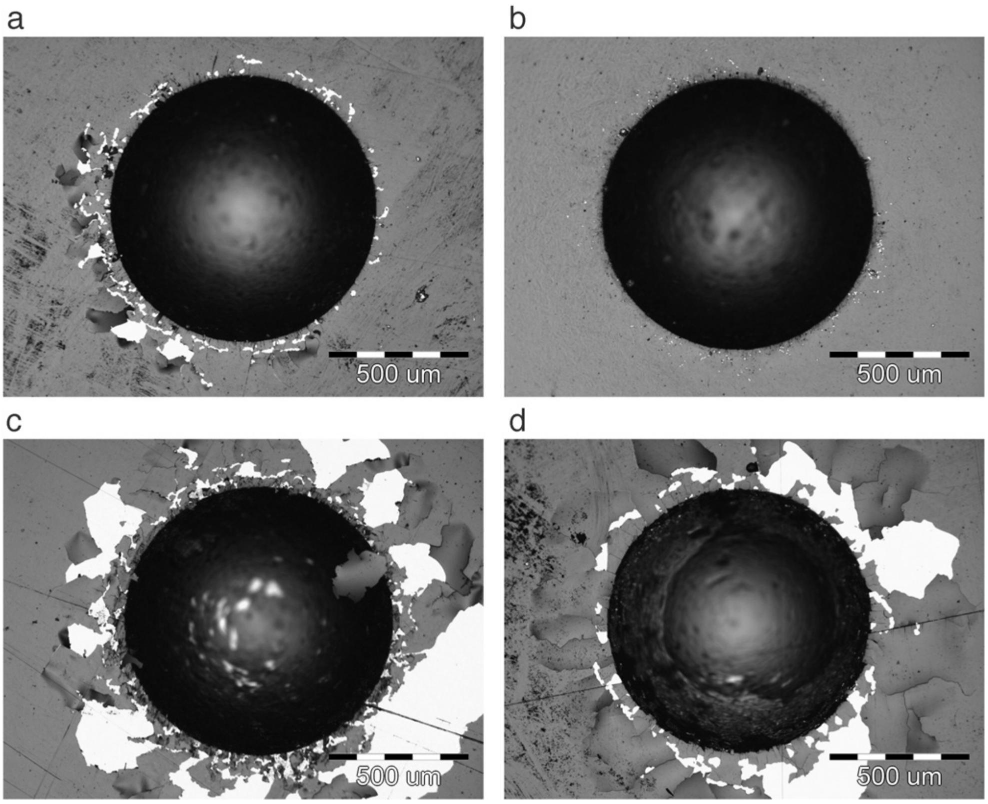

Fig. 3. Optical micrographs of the indentation in different samples a) S4 b) S5 c) S6 d) S7.

can be estimated [2]. The as-deposited films were characterized by this method. The results reveal that all samples have the similar Raman spectrum, and only the result of sample S1 is shown in Fig. 2. The peak with a shoulder in the range of 1300–1600 cm^{-1} insures the formation of a DLC structure. In addition, from the spectrum, we can obtain the value of I_D/I_G and the Raman shift of G peak, which have the value of 1.26 and 1530 cm^{-1}, respectively. Comparing with the testing results listed in literature [9], the ratio of sp^3 structure in the as-synthesized film is about 40%.

Because carbon ion implantation was employed before DLC film deposition, the load bearing capacity and adhesion strength should be improved obviously. Since the indentation method can be used to characterize the static load bearing capacity

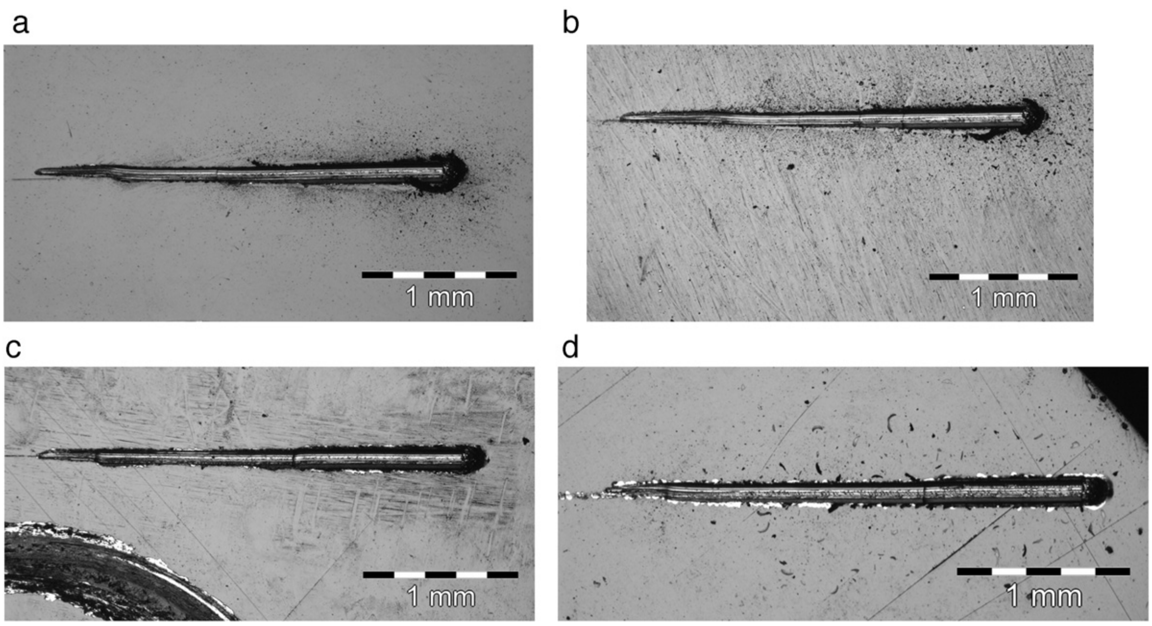

Fig. 4. Optical micrographs of the scratch track in different samples a) S4 b) S5 c) S6 d) S7.

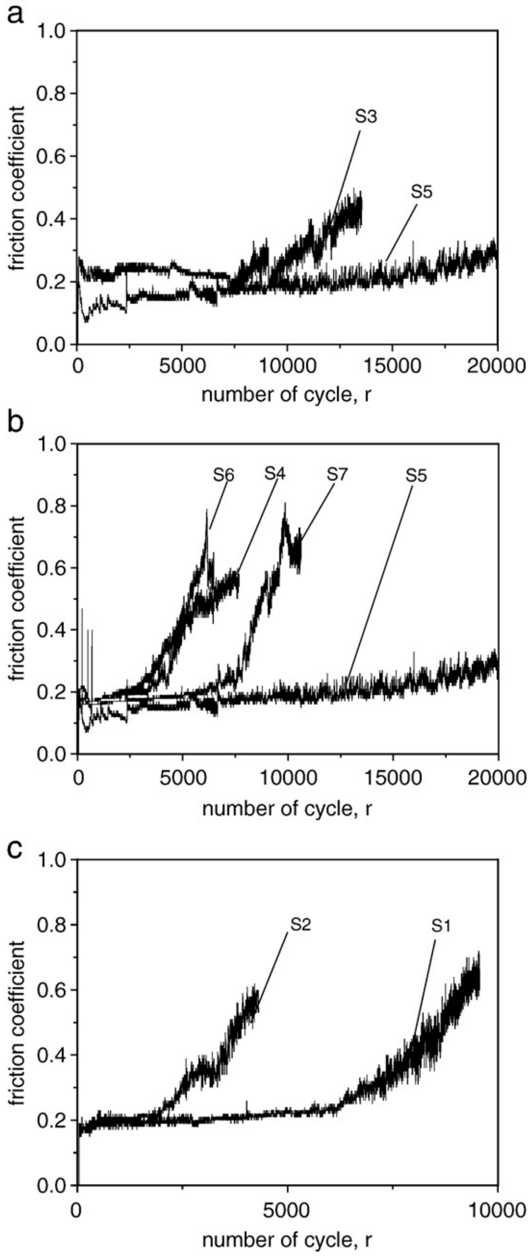

Fig. 5. Influences of processing parameters on the tribological property a) implantation voltage b) implantation time c) deposition voltage.

[9,10], the samples treated with variable implantation time were characterized by this method. The optical micrographs of the indentation in these samples are shown in Fig. 3a–d. In the indentation micrograph of sample S4 (the implantation time of 0.5 h), it can be seen that cracks spread out radially from the indentation margin and some peelings and spallings of the coating can be found around the indentation margin, as shown in Fig. 3a. However, for sample S5 (the implanting time of 1 h), except some slight cracks in the indentation margin, none peeling and spalling can be found. For the samples with the implantation time of 1.5 h (S6) and 2 h (S7), more serious peelings and spallings around the indentation margin were formed, which is similar to that of the un-implanted samples S1 and S2.

Scratch test can be used to evaluate the dynamic load bearing capacity of coatings under both normal and tangential forces [11,12]. Therefore the dynamic load bearing capacity has been assessed by the scratch test and verified by optical microscopy observation. Fig. 4a–d shows the scratch tracks in the duplex DLC film coated samples with the carbon implantation time varied from 0.5 to 2 h. It can be seen that few spalling occurs in the margin of the scratch track in the sample S5 (the carbon implantation time of 1 h), and the scratch track in the sample with the carbon implantation time of 0.5 h (S4) shows the similar phenomenon. However, in the scratch tracks in the samples with the carbon implantation time of 1.5 (S6) and 2 h (S7), serious spalling is easy to be found. Compared with the static load bearing capacity, it can be seen that the dynamic load bearing capacity of the sample with the variable implantation time shows the same trend.

Because the carbon ion implantation can form a gradient structure between the substrate and the DLC film, according to the theory of electron density difference [13], the interfacial stress can be reduced by proper carbon ion implantation time. However, since there is a large internal stress in a DLC structure, and the DLC structures formed by high and medium bias are different, the internal stresses of these DLC structures are different [14]. Compared with other implantation time, 1 h may obtain a good stress matching between these different DLC structures. Therefore, the sample with the carbon implantation time of 1.0 h obtains a high adhesion strength and shows good static and dynamic load bearing capacities.

The influences of the implantation voltage and time as well as the deposition voltage on the tribological properties of the duplex DLC film were compared in Fig. 5. Fig. 5a shows that the cut-through number of sample S5 is larger than that of sample S3. It proves that the increase of the implantation voltage can improve the cut-through number, which may be attributed to the large adhesion strength between the DLC film and the substrate formed by the high energy ion implantation. As shown in Fig. 5c, the cut-through number of sample S1 is larger than that of sample S2, which exhibits that the increase of the deposition voltage also raises the wear resistance. Because increasing the magnitude of the bias voltage in high voltage glow discharge process can add the plasma density [15], a large

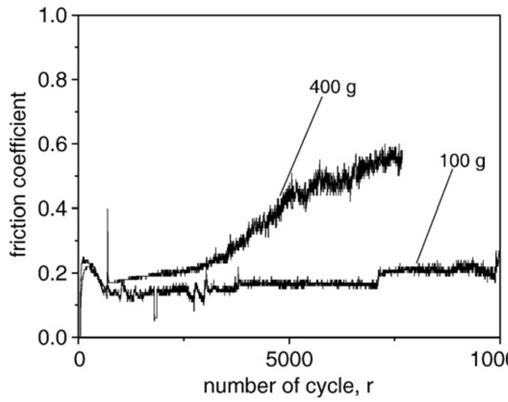

Fig. 6. The tribological behavior of sample S5 under different loads.

plasma density can improve ion impinging effect during the deposition. In addition, the influence of the implantation time on wear resistance has the same trend of that on the load bearing capacity. The sample with the implantation time of 1 h (S5) also shows the best wear resistance.

Fig. 6 compared the tribological behavior of sample S5 in different load. During the load of 100 g, the cut-through number is larger than 20,000 turns. However, when the load increases to 400 g, the cut-through number decreases to about 4000 turns. According to our previous study, the deposition rate is 0.5 μm/h, thus the thickness of the DLC layer is about 1.0 μm. Therefore, the DLC film of this sample with such a small thickness can not hold a large wear resistance under a high load.

4. Conclusions

Duplex DLC coatings involving carbon ion implantation and DLC deposition in a tube can be obtained by biasing the tube with a high and medium pulse voltage. The implantation time has a great influence on the static and dynamic load bearing capacities. In order to get a good load bearing capacity, the implantation time should be about 1 h. In addition, high magnitude of the implantation and deposition bias is benefit for the wear resistance.

Acknowledgments

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References

[1] Y. Lifshitz, Diam. Relat. Mater. 8 (1999) 1659.
[2] J. Robertson, Mat. Sci. Eng. R 37 (2002) 129.
[3] S.M. Malik, P.R. Fetherston, J.R. Conrad, J. Vac. Sci. Technol. A15 (1997) 2875.
[4] K. Baba, R. Hatada, Surf. Coat. Technol. 158 (2002) 741.
[5] R. Wei, C. Rincon, T.L. Booker, J.H. Arps, Surf. Coat. Technol. 188–189 (2004) 691.
[6] Y. Oka, M. Nishijima, K. Hiraga, M. Yatsuzuka, Surf. Coat. Technol. 201 (2007) 6647.
[7] P.W. Shum, Z.F. Zhou, K.Y. Li, Tribol. Int. 40 (2007) 313.
[8] Y. Oka, M. Nishijima, K. Hiraga, IEEE. T. Plasma. Sci. 34 (2006) 1183.
[9] J. Michler, E. Blank, Thin Solid Films 381 (2001) 119.
[10] X.Z. Hu, B.R. Lawn, Thin Solid Films 322 (1998) 225.
[11] Z.X. Zhang, H. Dong, T. Bell, Surf. Coat. Technol. 200 (2006) 5237.
[12] X.T. Zeng, S. Zhang, X.Z. Ding, D.G. Teer, Thin Solid Films 420 (2002) 366.
[13] K.J. Cheng, S.Y. Cheng, Prog. Nat. Sci. 8 (1998) 679.
[14] P. Wang, X. Wang, T. Xu, W.M. Liu, J.Y. Zhang, Thin Solid Films 515 (2007) 6899.
[15] R.K.Y. Fu, P.K. Chu, X.B. Tian, S.Q. Yang, Nucl. Instrum. Meth. B 242 (2006) 275.