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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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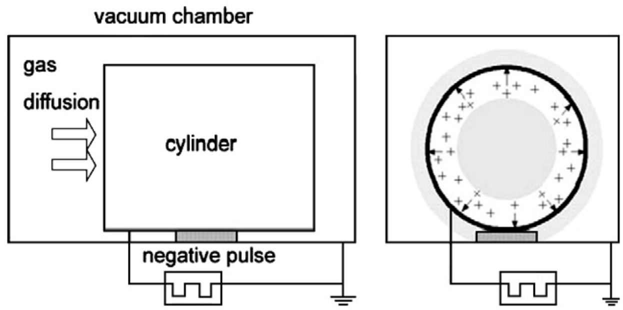


Fig. 1. The schematic of the experimental setup.

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 |

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=$6\times10^{-1}$ 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 |

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

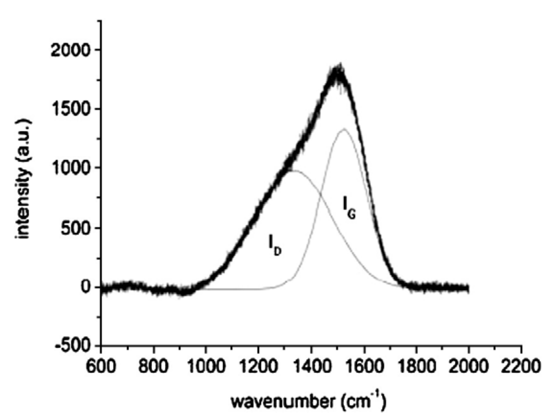


Fig. 2. Raman spectrum of the sample S1.