DLC deposition inside tubes using hollow cathode discharge plasma immersion ion implantation and deposition

X.B. Tian a,b,⁎, H.F. Jiang a, C.Z. Gong a, S.Q. Yang a, R.K.Y. Fu b, Paul K. Chu b

a State Key Laboratory of Advanced Welding Production and Technology, Harbin Institute of Technology, 150001 Harbin, China
b Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong

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A B S T R A C T

Plasma immersion ion implantation and deposition into the inner wall of a small diameter tube has gained more interest. A custom-designed plasma source based on hollow cathode discharge excited by radio-frequency (RF) is utilized to deposit a DLC film inside the slender tube. The internal cathode nozzle (shielded by an external grounded electrode) is made of stainless steel 6 mm in inner diameter and, 10 mm in outer diameter whereas the inner diameter of the tube to be treated ranges from 20 to 40 mm. The discharge is ignited and sustained in tubes with inner diameter of 20 mm and lengths of 140 mm and 500 mm. The DLC films with similar I0/Ig value and G-band position can be fabricated on the inner wall of the entire tube. The film thickness increases from the bottom to the upper parts and the tube diameter also has a critical influence on the deposition rate and film thickness uniformity. This can be attributed to the special discharge behavior in the hybrid hardware system composed of the internal hollow cathode and tube itself. Better film thickness uniformity can be readily achieved by moving the tube. The custom-designed hollow cathode discharge system is demonstrated to be an effective tool to treat the inner wall of small diameter tubes.

1. Introduction

Tube-like components are widely used components in traditional industry as well as specialized industry such as aerospace [1] and biomedical engineering [2,3]. These tubes which comprise both outer and inner surfaces are often treated to obtain better surface properties and longer service lifetime. Surface enhancement of the inner wall of tubes has been reported. For instance, Ensinger has developed ion- and carbon coatings. Therefore we pay more attention on the small diameter tubes.

2. Experimental details

The schematic of the custom-designed RF hollow cathode discharge system for implantation of the inner wall of small diameter tubes is depicted in Fig. 1(a). The cylindrical hollow stainless steel nozzle (10 mm in outer diameter and 6 mm in inner diameter) is connected to the RF generator. A cylindrical grounded shielding electrode 15 mm in outer diameter and 13 mm in inner diameter is installed outside the hollow cathode to stabilize the hollow cathode discharge. The high voltage applied to the tube frequently extinguishes the RF discharge if the external shielding electrode is not in place. An electromotor is employed to move the tube for more uniform treatment.

Stainless steel tubes with inner diameters of 20 to 40 mm and length of 140 mm were implanted and samples with dimensions of 10 mm × 1 mm × 140 mm were affixed on the inner wall of the tubes. The deposited films from five sites were measured to evaluate the uniformity of film thickness and microstructure as shown in Fig. 1(b). The base pressure in the vacuum chamber was 2 × 10⁻² Pa. The samples were ultrasonically cleaned before loading into the vacuum chamber into which high-purity (99.99%) argon and C2H2 gases were bled. Prior to DLC deposition, the samples were sputtered by argon ions for 30 min at a bias voltage of −2 kV with the discharge sustained at a pressure of 0.8 Pa and RF power of 400 W. Subsequently, DLC films were produced by using a mixture of Ar (15 sccm)
and C₂H₂ (25 sccm) at a total pressure of 0.8 Pa. Film production lasted for 100 min during which the RF power was kept at 200 W. During the process, the tube was moved up and down by a motor for more uniform deposition of DLC films onto the inner wall of the tubes.

Raman spectra were obtained on a Jobin-Yvon HR800 spectrometer equipped with a 20-mW green argon laser (458 nm). The spectra were recorded from 800 to 2000 cm⁻¹ and fitted by two Gaussian peaks. The integral intensity I_d/I_g ratios were calculated from the areas of the D-band and G-band to estimate the sp³/sp² ratios in the films. The film thickness at different axial locations was determined by scanning electron microscopy (SEM).

3. Results

3.1. Internal discharge

Fig. 2 shows the hollow cathode discharge ignited in a tube with a diameter of 20 mm. The instrumental parameters are: (i) Ar gas flow rate = 15 sccm and C₂H₂ gas flow rate = 25 sccm, (ii) RF power = 400 W, (iii) gas pressure = 0.8 Pa, and (iv) bias applied to the tube = −2 kV. A bright glow discharge is sustained in the small diameter tube indicating the hollow cathode plasma source is adequate in treating the inner wall of the slender tube. The coaxial shielding grounded electrode is critical to sustaining the stable discharge in this hardware configuration as the discharge frequently extinguishes without the grounded electrode outside the hollow cathode.

3.2. Film thickness

Fig. 3 depicts the typical cross-sectional SEM images of the films at different locations along the 30 mm diameter tube. These films have not obvious defects and bond well to the substrate. However, some thickness non-uniformity is observed. Thicker films are found near the bottom compared to the upper end. Fig. 4 displays the dependence of the thickness of the DLC films axially on the tube diameter. The film thickness decreases with increasing tube diameter from 20 to 40 mm at a given axial location. The film thickness uniformity is also affected by tube diameter. The uniformity can be estimated by the relationship: n = d_min/d_max, where d_min is the minimum thickness and d_max is the maximum thickness [7]. Consequently, a 40 mm diameter tube yields a value of about 0.25 while a small diameter tube (20 mm diameter) gives a value of 0.4.

3.3. Film structure

Fig. 5 displays the typical Raman spectra of the DLC films obtained from the 30 mm diameter tube. All the spectra show two peaks, the G (graphite) peak at around 1590 cm⁻¹ and D (disorder) peak at around 1370 cm⁻¹. The G peak originates from the symmetric E₂g vibrational mode in graphite-like materials, whereas the D peak arises from the limitations in the graphite domain size induced by grain boundaries or imperfections such as sp³ carbon or other impurities [8].
It has been reported that the position of the G-band is related to the bond-angle disorder or $sp^3$ bonding content, and the $I_d/I_g$ value is related to the ratio of $sp^3/sp^2$ bonds [9]. The variations in the G peak position and $I_d/I_g$ value for different axial position along the 30 mm diameter tube are shown in Fig. 6. The G-band position varies slightly between 1590 and 1593 cm$^{-1}$. Furthermore, the films at different axial positions have similar $I_d/I_g$ values of 1.5–2.0. This may be attributed to a little higher sample temperature caused by the local intensive RF discharge. In fact $I_d/I_g$ value has been reported to change from 0.2 to 3.5 dependent on gas pressure, plasma density, bias voltage, sample temperature, etc [10,11]. In practical applications the instrumental parameters have to be optimized to achieve excellent surface properties, e.g., higher hardness, lower wear rate, etc. Our results indicate that the DLC films fabricated on different locations have a fairly similar structure although the film thickness can vary quite significantly.

4. Discussion

Our experiments demonstrate that hollow cathode discharge is very suitable for surface enhancement of the inner wall of small diameter tubes. The film thickness is found to gradually increase upwards axially. It may be due to the configuration of the hollow cathode discharge system. On the one hand, the local discharge can be regarded as a plasma jet composed of a high density plasma, atoms, and radicals depending on the gas species and conditions [12]. The plasma jet is generally very bright and has a certain length [13,14]. The length of the plasma jet created by the RF source depends mainly on the RF power, gas species, and gas pressure. Barankova, et al. have reported that a hollow cathode plasma source may generate more than a 15 cm long argon plasma jet at a microwave power of 500 W [15,16]. Consequently, the upper part of the tube is more frequently covered by the plasma jet. In contrast, the lower part of the tube contacts the plasmas only when the cathode nozzle moves to the bottom of tube. Most of the particles excited within the tube exit through the upper part since the bottom part in the tube is filled with the hollow cathode hardware. This leads to more radicals on the inner wall of the upper part of the tube. These two factors are believed to give rise to the film thickness non-uniformity. However, this does not pose a big problem because better uniformity can easily be accomplished by adjusting the rotation speed of the motor for different parts. The film thickness is observed to decrease with increasing tube diameter due to the decreased plasma density in a larger diameter tube for a given RF discharge power.

5. Conclusion

DLC films have been fabricated onto the inner wall of small diameter tubes by means of internal hollow cathode discharge. The internal discharge varies slightly with the tube length. The films at different axial locations possess a similar structure as indicated by the similar $I_d/I_g$ value and G-band position. The film thickness is not uniform in spite of the tube movement. This may be attributed to the discharge behavior in a small tube. In practice, better uniformity can be accomplished by controlling the speed of the motor. All in all, our results demonstrate that internal hollow cathode discharge is an effective means to treat the inner surface of long tubes with a small diameter.

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