Functionality of Amorphous Hydrogenated Carbon (a-C:H) Film Coatings for an Artificial Heart

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(Received 31 January 2005; accepted 15 April 2005)

Key words: a-C:H film coatings, rf plasma CVD method, hemispheric polyurethane diaphragm of artificial heart system

Amorphous hydrogenated carbon (a-C:H) film coatings are used for passivation, for example, wear resistant surfaces, corrosion protection, and vapor transport barriers. In addition, a-C:H films have good properties as biomaterials. In this study, a-C:H film coatings were applied to the hemispheric polyurethane diaphragm of an artificial heart. The purpose of such coatings is to prevent penetration of hydraulic silicone oil and blood through the diaphragm. The a-C:H film was produced on the hemispheric polyurethane diaphragms using radio frequency (rf) plasma chemical vapor deposition (CVD) with a hemispheric electrode. This electrode has been developed to fabricate a-C:H film uniformly. In estimating the uniformity of the a-C:H film, the film thickness was measured using scanning electron microscopy (SEM). Additionally, the structure of the film was evaluated with infrared spectroscopy (IR) and Raman spectroscopy (Raman). The amount of silicone oil penetrating the diaphragm was measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A pulsation on test the diaphragm was carried out for 20 days. The a-C:H film reduced the amount of silicon oil penetrating the diaphragm to 1/3 the amount in the absence of the film. Moreover, it was observed that the a-CH film had good stability during the pulsation of the diaphragm. The use of a-C:H film coatings on diaphragms for artificial hearts is expected.

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1. Introduction

Amorphous hydrogenated carbon films (a-C:H) have been the focus of considerable research effort because of their electrical, mechanical, and chemical properties.\(^{(1-6)}\) The combination of these properties makes many applications possible. For example, a-C:H film coatings are used for wear-resistant surfaces, corrosion protection, and heat transfer layers in electronic devices.\(^{(2,5)}\) The characteristics of a-C:H films depend strongly on carbon-hydrogen bonds. These bonds involve sp\(^3\)-carbons, sp\(^2\)-carbons, and even sp\(^1\)-carbons, all of which are present in a disordered network.\(^{(7)}\) The ratio of sp\(^3\) to sp\(^2\) hybridized carbons and the hydrogen content determines the properties of a-C:H films. In a-C:H film deposition, radio frequency (rf) plasma chemical vapor deposition (CVD) is useful because it enables fabrication of a film on most substrates behaving as conductors and/or insulators at low temperatures.\(^{(1,8,9)}\) Furthermore, very smooth films can be uniformly deposited over wide areas on many substrates. In recent studies, a-C:H films have been deposited on polymeric materials used as biomaterials. A large number of reports have suggested biomedical applications of a-C:H films, and the films are expected to be suitable for use in new biomedical applications.\(^{(4,8)}\)

In terms of artificial organs, electrohydraulic total artificial hearts (EHTAH) are currently being developed.\(^{(10)}\) The EHTAH system consists of two hemispheric diaphragm blood pumps, an energy converter, and several electronic units (Fig. 1(a)). The diaphragm, made of polyurethane elastomer, separates blood and silicone oil in the chamber (Fig. 1(b)).

![Fig. 1. (a) Schematic diagram of electrohydraulic total artificial heart (EHTAH). (b) Hemispheric polyurethane diaphragm blood pump.](image-url)
In this artificial heart system, two diaphragms pulse alternately using silicone oil to carry out blood circulation. However, penetration of the silicone oil through the diaphragms could pose problems in the long-term use of this system. It might result in the accumulation of silicone oil in the recipient’s body, which could cause toxicity, or it could compromise the device’s hydraulic function.

In this study, an a-C:H film coating has been applied to a hemispheric diaphragm. The purpose of this coating is to prevent the penetration of silicone oil and blood through the diaphragm; a-C:H films are excellent as fluid and vapor transport barriers. Since the diaphragm must continuously pulsate to carry out long-term blood circulation (approximately 100,000 pulses per day), it is necessary for the a-C:H film to be evaluated in regard to its adaptability to the diaphragm. Although many reports have appeared suggesting that a-C:H films have the possibility of being applied as new biomaterials, it is most important to investigate the durability of a-C:H films in each potential environment. It has been estimated that the functionality and stability of a-C:H film is sufficient for the dynamic transformations of the diaphragm accompanying pulsation and to prevent penetration of silicone oil through the diaphragm.

2. Materials and Methods

2.1 Plasma states of hemispheric electrode

Since the most common system of rf plasma CVD processing consists of two planar electrodes (the normal process), it is difficult to adapt to insulator surfaces with a three-dimensional shape. In order to deposit a-C:H films on a hemispheric diaphragm surface uniformly, we have developed a hemispheric electrode that can hold the entire hemispheric polyurethane diaphragm of the blood pump (Nihon Miractran, Miractran E980). Before deposition of a-C:H films on the diaphragm using the hemispheric electrode, it is necessary to study the conditions of plasma deposition in the hemispheric electrode process.

A schematic diagram process of using a hemispheric electrode is shown in Fig. 2. This system consists of a hemispheric electrode (aluminum-magnesium alloy: A5052) that is electrically connected to an rf side electrode, an anode side electrode, an rf generator (Fuji Electronic Industrial, SS-301AAE), a matching box (Tokyo Hy-power Labs., HC-2000), and a vacuum pump (Sargent-Welch Scientific, 1397). As for the hemispheric electrode process, plasma measurements were carried out for helium (He) plasma and an rf power of 13.56 MHz and 100 W. Helium gas pressures were kept at 10, 50, and 100 Pa. Because the electrode surfaces and the electrostatic probe tip could always be kept clean and without any contamination, He gas was used to estimate plasma states (profiles of electron temperature $T_e$ and electron number density $N_e$). These measurements were carried out at three different positions (from the center position to the edge) on the hemispheric electrode surface using the double-probe method. The double-probe data analysis system consists of two Langmuir probes (platinum wires 200 μm in diameter) and a power supply for the probes (Advantest Corporation, R6243). The two probes were positioned parallel to each other 10 mm apart, and the outside of the probes was shielded with glass.
2.2 Production of a-C:H film on a hemispheric polyurethane diaphragm

The hemispheric electrode process deposited a-C:H film on the hemispheric polyurethane diaphragm of the EHTAH. The 13.56 MHz plasma at an electrical power of 100 W decomposed hydrocarbon gas (CH₄) and deposited a-C:H film on the diaphragm under the following conditions: CH₄ gas pressure of 50 Pa with a deposition time of 30 min. Distributions of the film thickness and hardness were measured using the cross section of scanning electron microscopy (SEM: JEOL, JSM-5310LVB) images and a micro-hardness tester (Shimazu, HMV-2000), respectively. Additionally, using an infrared spectrometer (IR: JASCO, FT/IR-620) and an Ar-laser Raman spectrometer (Raman: JASCO, NRS-2100), the structure of the a-C:H film was investigated. Properties of a-C:H films are determined by measuring the hybridization of the carbon atoms and the relative concentration of different kinds of bonds. Due to the importance of the ratio of sp³ to sp² hybridized carbon and the hydrogen content in determining the properties of a-C:H films, it is of primary interest to characterize these two properties. IR and Raman analyses are most often used to study a-C:H film structure.⁴

In order to estimate the structure of an a-C:H film satisfactorily, in this experiment the a-C:H film was deposited on silicon {100} substrates that were attached at three different locations on the diaphragm surface.

2.3 Penetration through an a-C:H film-coated diaphragm during pulsation

A schematic of the pulsating operating system for the penetration test is shown in Fig. 3. This in-vitro test system featuring mock circulation consists of a blood pump, a flexible stainless-steel conduit, and a hydraulic actuator. These units are used in the EHTAH system.¹⁰ The a-C:H film-coated diaphragm was put between the blood chamber of the pump and the hydraulic oil chamber. Then, the a-C:H film-coated surface was set to the side
of the oil chamber. The hydraulic oil chamber was filled with silicone oil (Toray Silicon, SH-200) to a volume of 250 ml. The blood pump was connected to the receiver circulation circuit, which was filled with 2500 ml of physiological saline.

In investigating whether the a-C:H films had sufficient stability for the dynamic transformations of the diaphragm accompanying pulsation and to prevent penetration of silicone oil through the diaphragm, the \textit{in-vitro} test system was operated for 20 days. The experimental conditions for the pulsating operation are listed in Table 1. The amount of silicone oil that had penetrated the diaphragm was measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES: Nippon Jarrell-Ash, ICAP-757).

3. Results and Discussion

3.1 \textit{Plasma states of hemispheric electrode}

Using the hemispheric electrode process, plasma states (electron temperatures and electron number densities) were measured at 10, 50, and 100 Pa of He gas pressure. In the case of the hemispheric electrode process, dc self-bias ($V_b$) was generated at the hemispheric electrode. At the same time, the diaphragm was completely surrounded with an ion sheath of uniform thickness by the generation of $V_b$. The $V_b$ enabled ion bombardment of the entire diaphragm.

The lateral profiles of electron temperatures ($T_e$) at 10, 50, and 100 Pa gas pressure are shown in Fig. 4. It was observed that $T_e$ decreased as gas pressure increased. The profiles of $T_e$ were lower in the center and increased towards the edges of the hemispheric electrode surface. Moreover, the plasma density profiles of electron number densities ($N_e$) were also measured in the lateral direction (Fig. 5). In contrast to the $T_e$ distributions, the lateral profiles of $N_e$ were higher in the center than at the edges of the hemispheric electrode surface. The profiles of $N_e$ were the antithesis of the $T_e$. In common rf plasma using normal parallel electrodes, it is well known that such profiles can be attributed to the magnetic cup fields,
which confine electrons in the plasma region. This means that characteristics of the plasma are maintained in the same states even if the form of the plasma is controlled using a hemispheric electrode. Therefore, the lateral profiles of $T_e$ and $N_e$ are not peculiar to the hemispheric electrode process.

Table 1
Experimental conditions for the pulsation test.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsation test</td>
<td></td>
</tr>
<tr>
<td>Pre-load</td>
<td>10 mmHg</td>
</tr>
<tr>
<td>After-load</td>
<td>20 mmHg</td>
</tr>
<tr>
<td>Pulsation speed</td>
<td>70 pulse/min</td>
</tr>
<tr>
<td>Experimental term</td>
<td>20 days</td>
</tr>
<tr>
<td>Diaphragm</td>
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</tr>
<tr>
<td>Material</td>
<td>Polyurethane elastomer</td>
</tr>
<tr>
<td>Surface area</td>
<td>85 cm$^2$</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.3 mm</td>
</tr>
<tr>
<td>Silicone oil</td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>310</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.853</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.5 cSt</td>
</tr>
</tbody>
</table>

Fig. 4. Lateral direction of $T_e$ profiles of the He plasma generated using the hemispheric electrode process.
3.2 Production of a-C:H film on a hemispheric polyurethane diaphragm

Figures 6(a) and 6(b) show the thickness of the a-C:H film fabricated on the polyurethane diaphragm. Using the hemispheric electrode process, the a-C:H film was deposited uniformly at a thickness of approximately 300 nm. On the other hand, when the normal electrode process was applied to the diaphragm, it was impossible to fabricate the film uniformly due to the ion sheath between the plasma and surrounding the diaphragm surface. The deposition rate of an a-C:H film depends strongly on the production of the ion sheath. Moreover, the a-C:H films grown within the ion sheath region were hard (approximately 13 GPa of Vickers hardness).

The structure of the a-C:H film was investigated with IR and Raman spectroscopy. The IR spectra are shown in Fig. 7. These spectra were compared to the structure of the a-C:H film deposited at each position (the center position, the middle-edge position, and the edge position) on the diaphragm surface. The main peak in all the spectra is the absorption around 2920 cm\(^{-1}\), and the \(sp^3\) and \(sp^2\) carbon-hydrogen peaks were observed at approximately 2855–3000 cm\(^{-1}\). The IR spectra at the three different positions were similar; moreover, the ratios of \(sp^3/sp^2\) were all approximately 3.4 ± 0.2 (Fig. 7). This IR analysis establishes that the hemispheric electrode process produced uniformity in a-C:H film deposition.

The Raman spectra are shown in Fig. 8. As for the Raman spectra from all the positions on the diaphragm surface, each spectrum has the same form. Two broad peaks appear around 1530 cm\(^{-1}\) (\(G\)-peak) and 1260 cm\(^{-1}\) (\(D\)-peak). Raman spectroscopy is a standard nondestructive tool for the characterization of crystalline, nanocrystalline, and amorphous carbon. Generally, Raman spectra of disordered graphite show two rather sharp modes, the \(G\)-peak
Fig. 6. (a) Thickness of an a-C:H film fabricated on a polyurethane diaphragm using the hemispheric electrode process. (b) Thickness of an a-C:H film fabricated on the polyurethane diaphragm using the planar (normal) electrode process.

Fig. 7. IR spectra of the a-C:H film on the polyurethane diaphragm.
around 1540–1580 cm⁻¹ and the D-peak around 1350 cm⁻¹; the G-peak is assigned to the $E_{2g}$ symmetric vibration mode of graphite layers of microdomain in the films. \(^{(16,17)}\) Y. Taki et al. reported that movement of the G-peak and D-peak to lower wavenumbers depends on variations in substrate voltage. \(^{(17)}\) In this Raman spectra analysis (Fig. 8), taking Taki’s report into consideration, three spectra of a-C:H films are typical. Additionally, all the spectra of the a-C:H films on the diaphragm surface are similar. The ratios of $I_D/I_G$ that are the ratios of intensities of the G-peak to the D-peak are approximately 0.58. The IR analysis indicates that the cylindrical electrode process deposits the a-C:H films uniformly on the diaphragm.

The IR and Raman analyses proved that the structure of the deposited a-C:H film on the diaphragm was uniform. In a-C:H film deposition using the hemispheric electrode process, at the rf electrode side including the hemispheric electrode, $V_b$ of −150 V was generated. The hemispheric electrode process uniformly held the diaphragm at $V_b$. During film deposition, $V_b$ is important for film properties, and the average impact-energy of ion bombardment also depends on $V_b$. \(^{(18)}\) For this reason, the hemispheric electrode process deposited the a-C:H film uniformly on the diaphragm. As a result, the entire hemispheric polyurethane diaphragm was sufficiently bombarded with ions to deposit the a-C:H film. \(^{(15,19,20)}\)

### 3.3 Penetration through an a-C:H films-coated diaphragm during pulsation

The in-vitro test system of estimating penetration was operated for 20 days. The a-C:H film on the diaphragm surface was tested under pulsating operation. Figure 9 shows the amount of silicone oil in the receiver circuit (physiological saline side) that had penetrated the diaphragm. After running the experiment for 20 days, the amount of silicone oil penetrating the diaphragm had been reduced to 1/3 that of a normal diaphragm by the a-C:H.
film coating. In addition, Fig. 10 shows cross-sectional images of the a-C:H film-coated diaphragm before and after pulsation. The stability of the a-C:H film was sufficient for the dynamic transformations of the diaphragm during pulsation.

Penetration of silicone oil through the blood pump diaphragm is a possible problem with the long-term use of an EHTAH. The total flux for silicone oil through a normal diaphragm was 2.1 ml/year; this is the annual amount of penetration in an EHTAH. This problem might compromise the device’s hydraulic function, and it might result in an accumulation of silicone oil in the recipient’s body, which could exert toxic effects. It is feared that such penetration could also cause more serious problems. Hence, the a-C:H film coatings are quite applicable to solving the problem of silicone oil penetration through a blood pump diaphragm.

Fig. 9. Amount of silicone oil in the receiver circulation that penetrated the diaphragm.

Fig. 10. Cross sectional SEM images of the a-C:H film deposited on the diaphragm before and after pulsation. (a) Before the pulsation test. (b) After the pulsation test.
4. Conclusions

Using a hemispheric electrode process, a uniform a-C:H film was fabricated successfully on a hemispheric diaphragm surface of an EHTAH blood pump. In the in-vitro test, pulsation of the diaphragm and penetration of silicone oil were examined. The stability of a-C:H film was sufficient for the dynamic transformations of the diaphragm. The a-C:H film has also improved the penetrability of the diaphragm to silicone oil. Accordingly, a-C:H film coatings may be quite applicable to new biomaterials such as blood pump diaphragms.

Reference