

Short Communication

Effect of Deposition Pressure on the Microstructure and Corrosion Resistance of Diamond-Like Carbon Films Prepared by Plasma Enhanced Chemical Vapor Deposition

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To improve the corrosion resistance of biomedical stainless steel in bodily fluids, a diamond-like carbon (DLC) film deposited on steel has been developed by plasma enhanced chemical vapor deposition (PECVD) technology using methane and argon as gas sources. Through adjusting the deposition pressure, DLC films with different microstructure can be obtained. Upon an increase in pressure from 0.6 to 3 Pa, the degree of graphitization of the DLC film first increases and then decreases. The formation of small graphite clusters releases internal stress in the material and increases the density of the DLC film. Meanwhile, the increase in density prevents electrolyte diffusion to the substrate surface, which increases corrosion resistance. At a pressure of 1 Pa, the degree of graphitization is relatively high with an ID/IG value of 0.6, and a more dense DLC film is obtained. From the electrochemical impedance spectroscopic (EIS) fitting results, the charge transfer resistance in 0.9 wt.% NaCl solution is higher than $6 \times 10^8 \Omega \cdot \text{cm}^2$, i.e. the corrosion of the substrate is very slow. At a deposition pressure of around 1 Pa, the DLC film shows obvious protection of the stainless steel substrate.

Keywords: PECVD, DLC film, deposition pressure, microstructure, graphitization degree, corrosion resistance

1. INTRODUCTION

Due to the improvement in medical treatments, there is a need to develop advanced human implant materials. Biomedical grade stainless steel is widely used in biomedical applications due to its many outstanding advantages, such as good mechanical properties and corrosion resistance, considerable biocompatibility and low price [1]. However, human implant materials need to be able to function in corrosive environments with a high chloride ion content, so local corrosion of the materials in the form

of crack and pitting corrosion often occurs [2–4]. Therefore, improving corrosion resistance in bodily fluids is a challenge. To this aim, an effective approach is coating the surface of biomedical stainless steel with a suitable film.

Diamond-like carbon (DLC) film is thought to be an ideal coating for human implants made of biomedical stainless steel due to its hardness, low friction coefficient, considerable corrosion resistance and biocompatibility [5]. The structure of this film is made up of a three-dimensional cross-network, formed by the sp^3 hybrid bonds of the diamond phase and sp^2 hybrid bonds of the graphite phase [6–8]. The microstructure of the DLC film is decided on the graphite and diamond phase content, that is, the degree of graphitization. To meet the requirements of DLC film that can be used to coat biomedical stainless steel, the study of the material corrosion resistance in simulated body fluid is valuable [9]. The corrosion resistance of the DLC film is related to its density [10, 12]. In general, improving the degree of graphitization releases internal stress in the material and increases the density of the DLC film [9–11]. In recent years, plasma enhanced chemical vapor deposition (PECVD) has been widely used to prepare DLC films on biomedical stainless steel. During the PECVD method, the degree of graphitization of the DLC film depends on two factors: the energy and concentration of hydrocarbon free radicals in the plasma. X. Ling, S. R. Yu and J. Y. Zhang studied the influence of hydrocarbon free radical energy on the degree of graphitization of DLC film by increasing the pressure of PECVD from 7 to 15 Pa [13]. With an increase in the pressure, the energy of the hydrocarbon free radicals decreased and the degree of graphitization of the DLC film was reduced. However, at low pressure, the concentration of hydrocarbon free radicals obviously changes. The effect of pressure on the microstructure of DLC film is therefore worth studying. So, to investigate the co-effects of the concentration and energy of hydrocarbon free radicals on the microstructure of DLC film, the deposition should be carried out at a lower pressure.

In this study, PECVD technology has been used to prepare DLC film on the surface of 316L stainless steel, and the influence of the deposition pressure on the microstructure and corrosion resistance of the DLC film were explored by adjusting the deposition pressure from 0.6 to 3 Pa.

2. EXPERIMENTAL

2.1 Preparation of the DLC films

DLC films were deposition using the PECVD method at different deposition pressures. The substrates used for each deposition were 316L stainless steel (15 mm×15 mm×1 mm) and (100) Si wafers (15 mm×10 mm×0.5 mm). The major chemical composition of 316L stainless steel are Fe 69.43 wt.%, Cr 17.09 wt.%, Ni 9.65 wt.%, Mo 2.58 wt.% and Mn 1.25 wt.%. Prior to deposition, the stainless steel sheets were burnished, cleaned ultrasonically in ethanol and deionized water, and then dried with nitrogen. The substrates were placed in a PECVD chamber, and then the chamber was pumped down to a base pressure (5.0×10^{-4} Pa). The DLC films were synthesized in a methane/argon mixture with flow rates of 8/10 sccm at room temperature with a constant applied radio-frequency power of 100W for 1 hour. The deposition pressure was varied from 0.6 Pa to 3 Pa.

2.2 General characterization

The thicknesses of the DLC films were measured using a step profiler DEKTAK 150. The morphologies of the deposited films were characterized by scanning electron microscopy (SEM, Model S-4800). Atomic force microscopy (AFM, afm5500) was used to analyze the roughness of the surfaces of the coatings surface. Images with an area of $5\ \mu\text{m}\times 5\ \mu\text{m}$ were recorded for in each surface. Raman spectroscopy (inVia reflex) was used to determine the microstructure, chemical composition and chemical bonding states of the deposited DLC films with an incident Ar⁺ beam at a wavelength of 532 nm, recorded in the range 1200-1800 cm^{-1} .

2.3 Corrosion testing

The open circuit potential (OCP) and electrochemical impedance spectra (EIS) were measured using a conventional three-electrode cell, consisting of a saturated calomel electrode (SCE, 0.241 V versus a standard hydrogen electrode) as the reference electrode, a Pt sheet as the counter electrode and a sample with a $0.8\ \text{cm}^2$ exposed area as the working electrode, to evaluate the corrosion resistance of the DLC coating in a corrosive solution. The electrolyte used simulates bodily fluid (0.9 wt.% NaCl, pH 7.4) and during the tests it was kept at a constant temperature of 37 °C in a water bath. Before testing, the sample was immersed in the electrolyte for 1 h to achieve a stable OCP. The frequency of the electrochemical impedance spectroscopy was 10^{-2} – 10^5 Hz, and the perturbation potential was 10 mV.

3. RESULTS AND DISCUSSION

3.1 Growth rate of the DLC film

Fig. 1 shows the growth rate of the DLC film as a function of pressure. With an increase in the pressure from 0.6 to 1 Pa, the growth rate gradually increased. Upon a further increase in pressure from 1 to 3 Pa, the growth rate decreased gradually with an increase in pressure. When the pressure was 3 Pa, the growth was as low as 5 nm/min. The reason for this is that when the deposition pressure is lower than 1 Pa, the growth rate of the film is mainly controlled by the concentration of hydrocarbon free radicals. A higher pressure increases the amount of hydrocarbon free radicals, resulting in a high growth rate. However, as the pressure increases further, the probability of the collision of ions is improved during movement, leading to a decrease in the energy of the hydrocarbon free radicals. The average adsorption time on the substrate surface and the diffusion ability decreases, which then finally leads to a reduction in the growth rate.

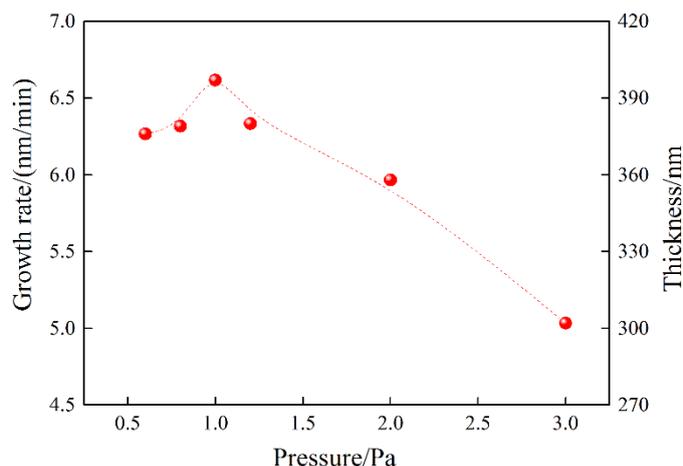


Figure 1. Growth rate of the DLC films versus pressure

3.2 Microstructure analysis

Fig. 2 shows SEM images of the surface morphologies of the DLC films. All of the samples have smooth surfaces, without any delamination, meaning that the films show good adhesion. As the pressure increased from 0.6 to 1 Pa, the surface gradually became smoother. Upon a further increase in the pressure to 3 Pa, the surface appeared granular and the film density decreased.

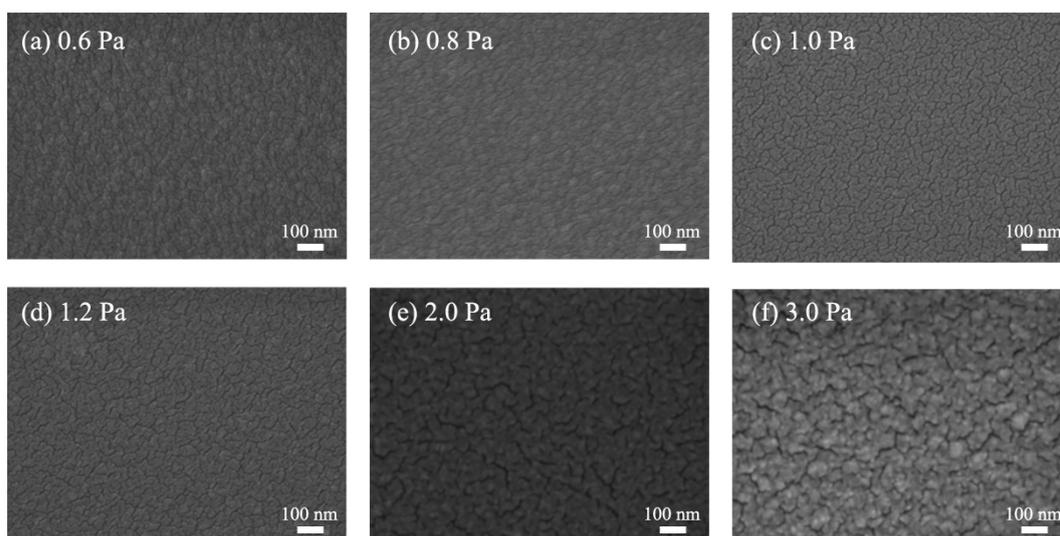


Figure 2. SEM images of the DLC films prepared at different pressures

To further analyze the surface morphology, AFM was used to measure the surface roughness of the DLC films. From Fig. 3, it can be seen that low surface roughness was obtained at different deposition pressures (<5 nm), while the surface roughness decreased slightly on going from 0.6 to 1 Pa and increased slightly from 1 to 3 Pa. When the pressure was 1 Pa, a smooth DLC film with low surface roughness was prepared. By utilizing high-energy plasma, the PECVD method produces a high proportion of activated free radicals at a low temperature, and the free radicals conduct chemical

reactions on the substrate surface to promote the growth of the films, so DLC films with smooth surfaces can be obtained. When the pressure is low, upon an increase in the pressure, the concentration of the hydrocarbon free radicals increases, which is beneficial for increasing the continuity and compactness of the film. When the pressure is higher than 1 Pa, the diffusion capacity of the ions on the surface of the film decreases, which is not conducive to the formation of dense film.

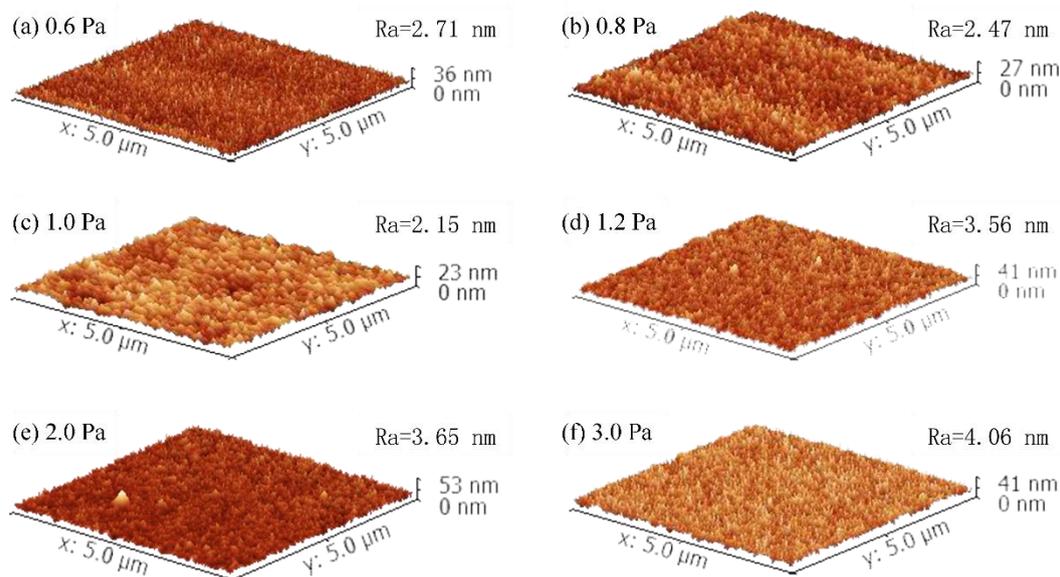


Figure 3. AFM images of DLC films prepared at different pressures

Fig. 4 (a) shows the Raman spectra of DLC films deposited at different pressures from 0.6 to 1 Pa, measure using visible light with a wavelength of 532 nm. All of the spectra exhibit a broad asymmetric Raman scattering band in the range of 1200–1700 cm^{-1} , mainly composed of a G band peak at around 1560 cm^{-1} , with a shoulder peak of the D band at around 1410 cm^{-1} , which are typical characteristics of a DLC film [14–16]. To further analyze the relationship between the pressure and microstructure of the DLC film, the Gaussian equation was used to separate the fused peak into two peaks. The D band peak at around 1410 cm^{-1} can be assigned to the breathing mode of A_{1g} symmetry only on the rings present in the film and the G band peak at around 1560 cm^{-1} can be ascribed to the in-plane bond-stretching motion of E_{2g} symmetry, which occurs for all of the $C\ sp^2$ atoms. So, according to the intensity ratio, I_D/I_G , of the two peaks, the sp^2 hybrid bond content in the film can be analyzed. A high I_D/I_G value indicates a high sp^2 content, and a high degree of graphitization. The position of the G band peak is related to the internal stress of the DLC film, where a blueshift in the G band peak position indicates a decrease in the internal stress. Fig. 4 (b) shows the G band position and I_D/I_G ratio as a function of pressure. Upon increasing the pressure from 0.6 to 1 Pa, the I_D/I_G ratio increases from 0.4 to 0.5, and the position of the D band peak blueshifts from 1559 to 1563 cm^{-1} . Further increasing the pressure from 1 to 3 Pa, the I_D/I_G ratio decreases from 0.5 to 0.3, and the position of the D band peak

redshifts from 1563 to 1558 cm^{-1} . At 1 Pa pressure, both the ID/IG ratio and position of the G band peak are at their highest values. The degree of graphitization of the DLC film increases and a number of small graphite clusters are formed. Also, the internal stress in the DLC film is released, which leads to an increase in the density of the DLC film. In previous studies, by increasing the pressure of PECVD from 7 to 15 Pa, the degree of graphitization of the DLC film decreased because the energy of the hydrocarbon free radicals increased [13]. However, at low pressure, the concentration of the hydrocarbon free radicals shows obvious changes with pressure. When the pressure is lower than 1 Pa, the degree of graphitization of the film is mainly dependent on the concentration of the hydrocarbon free radicals. With an increase in pressure, there is an increase in the number of hydrocarbon free radicals and the degree of graphitization is enhanced. Upon a further increase in the pressure from 1 to 3 Pa, the degree of graphitization of the film is mainly dependent on the energy of the hydrocarbon free radicals, when their energy increases, there is a decrease in the degree of graphitization of the DLC film.

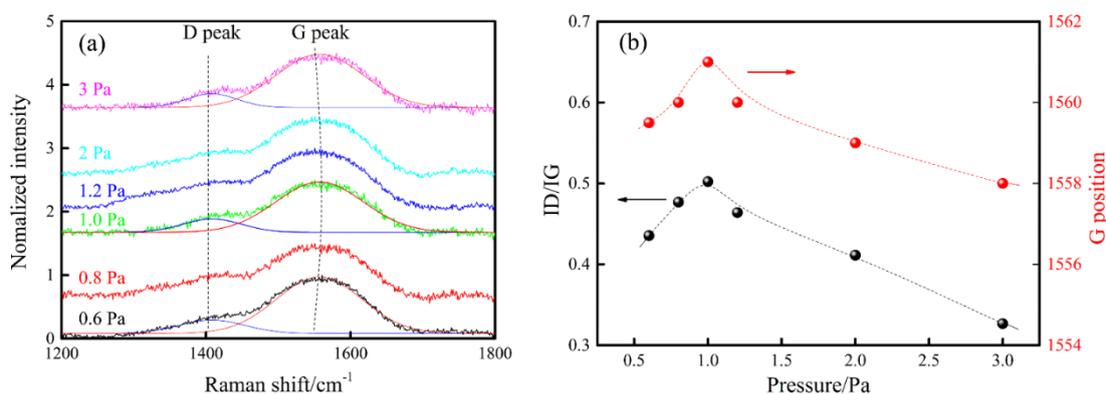


Figure 4. (a) Raman spectra of the DLC films under different pressures and (b) Results of Raman spectra of DLC films fitting by Gaussian

3.3 Corrosion resistance analysis

In order to achieve good materials for their use in biomedicine, corrosion resistance in the simulated bodily fluid should first be guaranteed. Therefore, the corrosion resistance of the DLC film was investigated in simulated bodily fluid (0.9 wt.% NaCl, pH 7.4). To qualitatively evaluate the tendency for surface corrosion, the OCP results of DLC films deposited at different pressures are shown in Fig. 5. To obtain a stable OCP value, the samples were immersed in simulated bodily fluid for 1h. Upon a pressure increase from 0.6 to 1 Pa, the OCP values of the samples gradually increased from -0.05 V to 0.27 V. At a pressure of 1 Pa, the value is as high as 0.27 V, where such a high OCP value reflects high electrochemical stability. Upon further increasing the pressure from 1 to 3 Pa, the OCP values gradually decreased. At 3 Pa, the OCP value is around -0.15 V, which is the same as the OCP of the 316L stainless steel substrate. Therefore, the DLC film deposited at 1 Pa can obviously improve the corrosion resistance of the substrate. However, when the pressure is lower or higher, the protective effect of the film on the substrate decreases.

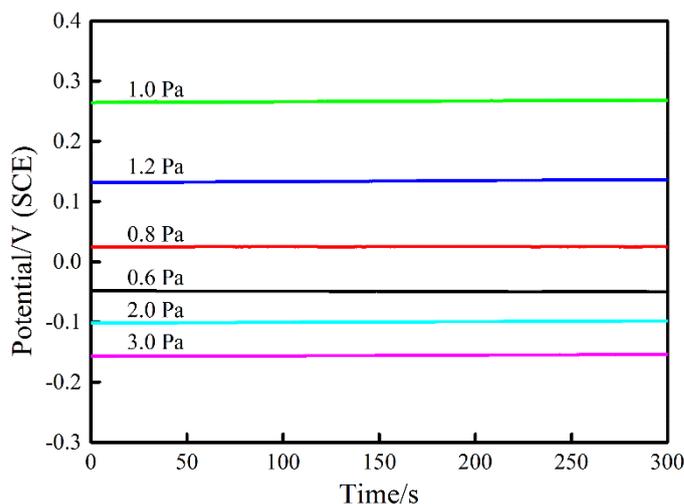


Figure 5. OCP results of the DLC films deposited under different pressures

Fig. 6 shows the Nyquist plots of the EIS tests. The Nyquist plots of all of the samples show one depressed semi-circle. A large diameter of the Nyquist plot represents higher corrosion resistance [17]. From the plots, at 1 Pa pressure, the largest arc radius reached was about $8 \times 10^7 \Omega \cdot \text{cm}^{-1}$, when the corrosion resistance of the DLC film is at its highest.

To analyze the corrosion behavior of the DLC film deposited at different pressures, the equivalent circuit $R(Q(R(QR)))$ in Fig. 7 was employed to fit the EIS results using the Zsim Demo software [18]. In the equivalent circuit, the meaning of the elements are as follows: the solution resistance is represented by R_s , the coating capacitance by CPE_f , the resistance of the micropores in the DLC films by R_{p0} , which is in parallel with CPE_f , the double layer capacitance is CPE_{dl} , for the formation of a double layer of charge at the substrate–electrolyte interface, and the charge transfer resistance is represented by R_i , which is the characterization of the substrate corrosion reaction [19].

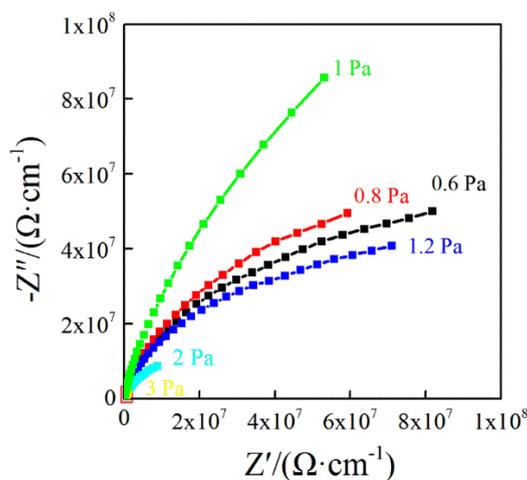


Figure 6. EIS results of the DLC films deposited under different pressures

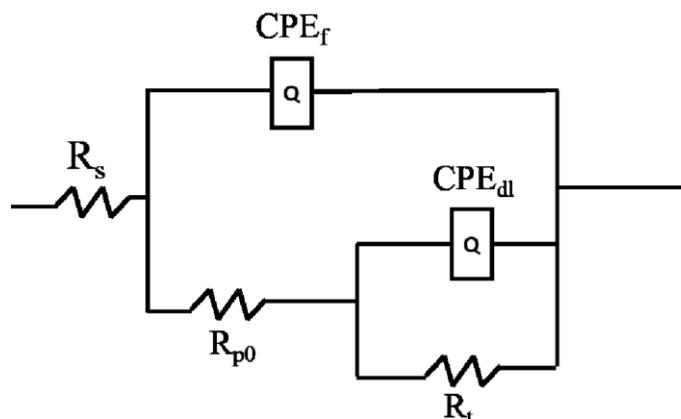


Figure 7. The equivalent electrical circuit model of the DLC films

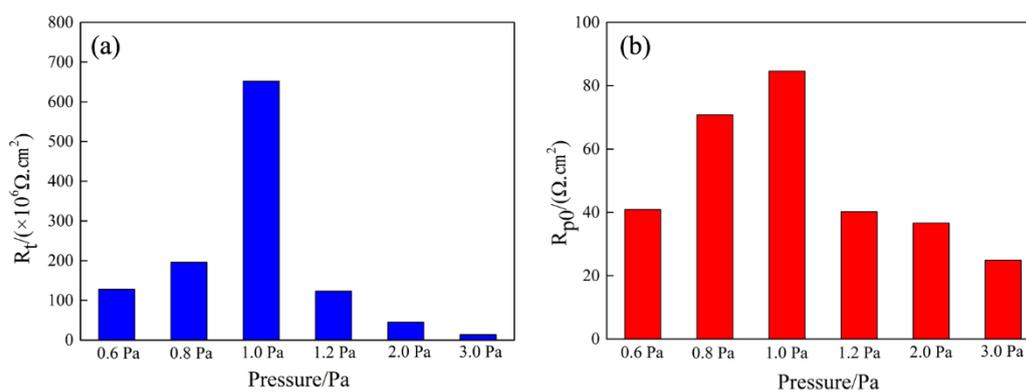


Figure 8. Fitting results of the EIS (a) Charge transfer resistance R_t and (b) resistance of the microporous in the DLC films R_{p0}

Fig. 8(a) and (b) show the fitting results of R_{p0} and R_t for DLC films deposited under different pressures. When the pressure is lower than 1 Pa, the R_{p0} and R_t increase gradually upon an increase in pressure, which indicates that the number of micropores in the DLC film decreases and the corrosion resistance of the DLC film increases. At a pressure of 1 Pa, the R_t value is higher than $6 \times 10^8 \Omega \cdot \text{cm}^2$, and the corrosion process of the stainless steel substrate is very slow. Under these conditions, the DLC film shows obvious protection of the substrate. Upon a further increase in the pressure from 1 to 3 Pa, the R_{p0} and R_t values decrease gradually with an increase in pressure. When the pressure is as high as 3 Pa, the R_t value decreases to $10^7 \Omega \cdot \text{cm}^2$ and the corrosion resistance of the DLC decreases significantly.

4. CONCLUSION

The corrosion resistance of DLC film is mainly related to its density, and the deposition pressure affects the microstructure of the film. Increasing the pressure from 0.6 to 1 Pa, the degree of graphitization of the film increases, while when the deposition pressure is higher than 1 Pa, the degree of graphitization of the film increases with a decrease in the pressure. With a higher degree of graphitization, the formation of small graphite clusters reduces the internal stress and increases the

density of the DLC film. The formation of a denser DLC film prevents the diffusion of electrolyte to the substrate surface, increasing the corrosion resistance. When the deposition pressure is 1 Pa, the degree of graphitization is relatively high with an ID/IG value of 0.6. From the EIS fitting results, the charge transfer resistance in 0.9 wt.% NaCl solution is higher than $6 \times 10^8 \Omega \cdot \text{cm}^2$, meaning that the corrosion process of the substrate is very slow. Upon a further increase in the deposition pressure, the degree of graphitization decreases, the film density increases, and the corrosion resistance decreases. Therefore, the DLC film deposited at around 1 Pa shows obvious protection of the stainless steel substrate.

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References

1. D. Sivaraj and K. Vijayalakshmi, *J. Anal. Appl. Pyrolysis.*, 134(2018) 176
2. G. Hasan, *Biomater.*, 16(2004) 3325
3. R. L. L. Reclaru, P.-Y. Eschler, J.-M. Meyer, *Biomater.*, 3(2001) 269
4. S. Windecker, *Circulation*, 8(2001) 928
5. H. Zhou, L. Xu, A. Ogino and M. Nagatsu, *Diamond Relat. Mater.*, 17(2008) 1416
6. M. Cui, J. Pu, G. Zhang, L. Wang and Q. Xue, *RSC Adv.*, 6(2016) 28570
7. J. B. Pu, J. J. Wang, D. Q. He and S. H. Wan, *Surf Interface Anal*, 48(2016) 360
8. Y. M. Wu, S. G. Zhou, W. J. Zhao and L. Ouyang, *Chem. Phys. Lett.*, 705(2018) 50
9. D. Kek Merl, P. Panjan, M. Čekada, M. Kahn, W. Waldhauser, *ECS Trans.*, Electrochemical Society (2011), pennington, United States.
10. H. G. Kim, S. H. Ahn, J. G. Kim, S. J. Park and K. R. Lee, *Thin Solid Films*, 482(2005) 299
11. O. Sharifahmadian, F. Mahboubi and S. Yazdani, *Diamond Relat. Mater.*, 95(2019) 60
12. Y. Uematsu, T. Kakiuchi, T. Teratani, Y. Harada and K. Tokaji, *Surf. Coat. Tech.*, 205(2011) 2778
13. X. Ling, S. R. Yu and J. Y. Zhang, *Infrared. Laser Eng.*, 6 (2014) 1878
14. S. Takabayashi, R. Ješko, M. Shinohara, H. Hayashi, R. Sugimoto, S. Ogawa and Y. Takakuwa, *Surf. Sci.*, 668(2018) 29
15. S. Takabayashi, R. Ješko, M. Shinohara, H. Hayashi, R. Sugimoto, S. Ogawa and Y. Takakuwa, *Surf. Sci.*, 668(2018) 36
16. S. Takabayashi., H. Hayashi., M. Yang., R. Sugimoto., S. Ogawa. and Y. Takakuwa., *Diamond Relat. Mater.*, 81(2017) 16
17. M. J. K. Lodhi, K. M. Deen, M. C. Greenlee-Wacker and W. Haider, *Addit. Manuf.*, 27(2019) 8
18. P. Shuquan, *Int. J. Electrochem. Sci.*, 14(2019) 8611
19. Y. Liu, Z. Gao, X. Lu and L. Wang, *Int. J. Electrochem. Sci.*, 14(2019) 150