POTENTIAL OF IMPROVING BLOOD COMPATIBILITY OF BIOMATERIALS BY COATING DIAMOND-LIKE CARBON FILM

Huang Nan[1], Yang Ping[1], Leng Yongxiang[1], Chen Junying[1], Sun Hong[1], Wang Jin[1] Wan Guojiang[1], Paul K Chu[2], Leng Yang[3]*

1.*Institute of Biomaterials and Surface modification, Department of Materials Engineering, Southwest Jiaotong University, Chengdu, 610031, China*

2.*Plasma Laboratory, Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China*

3.*Department of Mechanic Engineering, Hong Kong University of Science and Technology, Clear water Bay, Kowloon, Hong Kong*

Introduction

Blood compatibility is a critical property of blood contacting biomaterials. Improving the surface characteristics of materials toward to modify the behavior of anticoagulation of the materials has been developed since last decade. Diamond-like carbon (DLC) films have received much attention owing to their properties such as higher hardness, good thermal conductivity, excellent corrosion resistance against chemicals, abrasion resistance and good biocompatibility. Some attempts have been made to adopt DLC films as coating material for improving blood compatibility of biomaterials, and which even has been expected as 21 century's blood contacting material [1]. But up to now some problems have not be entirely solved. The first is the lower adhesion strength between DLC film and the matrix material. The traditional applied biomaterials such as titanium, stainless steel and TiNi alloy etc. possess higher thermal expansion coefficient (α), and for DLC films the value of α is much lower, thermal mismatch as well as intrinsic stress easily cause the DLC film be peeled from metal matrix [2]. So some conventional synthesis methods such as plasma enhanced vapor deposition (PECVD) shown lower adhesion ability of DLC film on metal materials. The second is that the potential of blood compatibility of the DLC films is still not very clear, in many case authors compared the blood compatibility of their synthesized DLC films with titanium and declared that the films were better than titanium in some extent. Few of papers compared blood compatibility of the DLC films with low temperature isotropic pyrolytic carbon LTIC which have been regarded as the clinic applied best blood contacting material for artificial heart valves. The last decade developed film synthesis process such as ion beam enhanced deposition (IBED), filtered arc deposition (FAD) and plasma immersion ion implantation and deposition (PIIID) have improved the binding strength of the films on matrix materials due to higher energy of the deposition ions or particles about from several ten eV to several ten thousands eV, while in the case of traditional PECVD process the energy of the deposition particles is only several eV. But IBED process is not very suitable for deposition films on medical device because of the line -of- sight feature. It is proved that higher hardness and higher sp3 bonds content can be achieved with ions energy about 100 eV in FAD process[3]. But in this case the intrinsic stress is higher and the film thickness has to be limited lower than several hundred nm, and the film is still easily peeled. PIIID process has combined the advantage of IBED of a large variable energy range and macro particle free of FAD, it should represent one of the most advanced DLC fabrication technique for deposition on biomaterials.

Experimental

In our earlier work, we had deposited DLC films using IBED method and it shown that the blood compatibility of the films was lower than LTIC [4]. In the present work, DLC films were synthesized using PIII process. Carbon plasma was ignited from graphite cathode by pulsed triggering and transported through a curved magnetic duct and deposited on the sample surface, macro-particles were eliminated by the curved magnetic filter duct. Pulsed voltage from 100 to several ten thousands voltage was applied on the sample stage to control the film structure and the binding strength of the films on titanium surface. To obtain better adhesion strength of the films, 20 and 5 thousands voltage with the frequency of 10000 Hz and pulse wide of 20 μs was in turn applied to the sample stage during the first 10 minutes and then the pulse voltage was decreased to 100 V. The DLC film with the thickness of about 400 nm measured by profile meter was obtained. For comparing, DLC film deposited without high voltage applied on the samples was also performed. The base pressure of synthesis was 9×10^{4} Pa Structure of the films and surface roughness were investigated by a laser raman spectroscopy and alpha step profile meter. The adhesion strength was estimated by immersing the DLC coated samples into liquid CO2 and liquid nitrogen for three times and by nano-scratch tester. Interaction of blood with DLC film was evaluated by Platelet adhesion experiment. Human platelet rich plasma (PRP) was obtained from human whole blood and the samples were immersed into PRP up to 3 hours. The statistics and the morphology of platelet adherent on DLC film was observed by optical microscopy and scanning electron microscopy by statistic account of the number of platelet in twenty fields of 3200μm^2 in radon . LTIC and TiNi alloy samples were also used as comparing.

Results and discussion

After synthesis, it was observed that DLC film was peeled from sample surface if only -100 voltage was applied on samples during the synthesis process. While -20 and -5 kilo voltage were applied in turn on the sample stag at first 5 and second 5 minute the DLC film maintained tightly on titanium even the samples were immersed into liquid CO2 and liquid nitrogen. Nano-scratch test shown the adhesion strength was as high as 60 mN.

Alpha step profilemeter measurement shows that the roughness (Ra) of uncoated and DLC film coated titanium was 231 ± 77 nm and 240 ± 81nm respectively. After DLC film coating the surface roughness was almost unchanged .

Fig.1 shows the Raman spectra between 1000 cm^{-1} and 1800 cm^{-1} for DLC film , the Raman Spectra of amorphous hydrogen free DLC film exhibit a broad asymmetric peak. This peak can be approximated by two

Gaussians at about 1350 cm^{-1} and 1550 cm-1 (the so called D and G lines). It is typically Raman spectrum contain some fourfold coordinated bonds (sp^3) with disorder [5].

.]

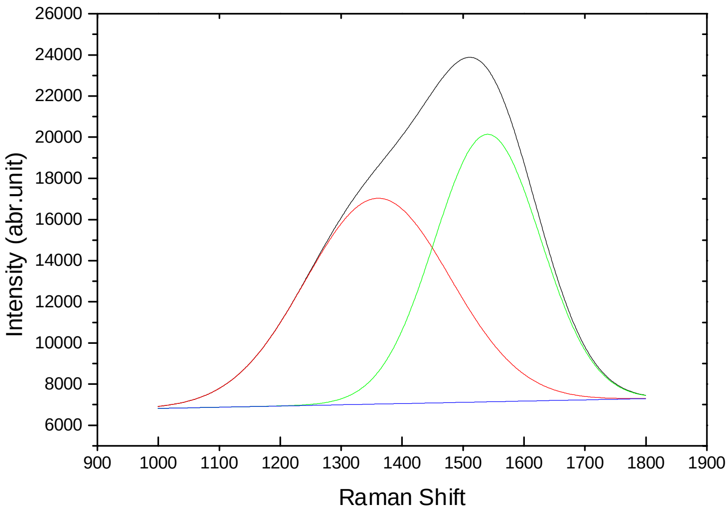

Fig.1 Raman spectroscope of DLC film synthesized by PIII process

Fig.2 shows the morphology of platelet adherent on NiTi alloy, LTIC and DLC film after 3 hour incubation. The platelets adherent on DLC film and on LTI carbon were maintained single layer, very few aggregation, the pseudopodium was slight. Comparing with DLC film, the aggregation, and pseudopodium of platelets on NiTi surface were very seriously, the platelets aggregated as three-dimension structure and connected by pseudopodium. The statistics analysis provided that the number of adherent platelets on DLC film and on LTI carbon were 158±43 and 141±68 on about 3200μm^2 area. The platelets adherent on NiTi alloy surface could not be account due to they stowed into three dimensional structure, in this case it could be estimated that the number of platelet on NiTi is over one order of that on DLC and LTI carbon. So the interaction of platelet of our synthesized DLC film is the same level as LTI carbon and is much better than TiNi alloy which has been adopted as bimaterial such as stents.

DLC film LTI carbon NiTi

Fig. 2 The morphology of platelet adherent on different materials. Incubation time 3 hours, human platelet rich plasma.

During the DLC synthesis process the higher negative pulse voltage applied on sample stage is very effectively to improve adhesion strength of the film on titanium. According to the calculation of projected range, carbon ions can be implanted in to titanium in the distance about 10 to 40 nm from surface when 5 to 20 kilo-voltage negative pulse were applied on titanium samples. Which lead to form gradient transition in the upper surface layer between film and matrix and the strongly binging of the film to the transitional layer can be achieved at the atomic level. The process may also modulate the change of thermal expansion coefficient from DLC film to matrix gradually. This is a important advantage of DLC synthesis process of PIII comparing with other technology.

Although some works have been done to investigate blood compatibility of DLC films, but very few of them has deal with the mechanism of the behavior of DLC film interaction with blood. We suggest that the semiconductive nature of DLC film may be a factor contribute to its blood compatibility. It has been proved that at the preliminary step of blood coagulation some proteins such as fibrinogen adsorbed on materials and transfer its charges into material will lead to denaturation of the proteins and causeed further cascade reaction of blood coagulation [6]. Fibrinogen possess a semiconductive nature with a band gap of 1.8 eV [7], it has been reported that the band gap of DLC ranges from about 0.38 eV to 2.7 eV and the band gap will increase with sp3 bond content [2]. In our case the higher sp3 content and also a larger band gap of the DLC film than that of fibrinogen can be estimated because the energy applied on material was -100 V after first 10 minute implantation and deposition. When DLC film was contacted with fibrinogen, the valence band and conduction band of fibrinogen are located in the band gap of DLC, and the charge transfer process from fibrinogen to the materials can be inhibited. The further research will be performed to prove this hypothesis.

Conclusion

DLC film with higher adhesion strength on titanium was obtained by means of plasma immersion ion implantation and deposition process. Higher pulsed voltage applied on samples is responsible for improving the adhesion strength. The DLC film possess a much better interaction behavior to platelet comparing with TiNi alloy, and is as good as LTI carbon.

Acknowledgment

This work was supported by NSFC 39870199, G 19990964706 and 102-12-09-01

Reference

1 I Dion C. Baqney JR.Monties Int. J. Organs 1993 16 9 623

2 Hsiao-chu Tsai D.B. Bogy J. Vac. Sci. Technol., 1987,A5(6):3287

3.R.Lossy, D.L. Pappas, R.A. Roy, J.P.Doyle, J. J. Cuomo, J. Appl. Phys., 1995,77(9):4751

4. N. Huang, P.Yang, R. Guenzel, P.K. Chu, T. F. Xi, Processing and fabrication of advanced materials VIII, world Scientific Publishing, 1999, pp207

5. D. S. Knight and W. B. White, J. Mater. Res., 1989 **4**: 385

6. F. Gutmann and H. Keyzer, in *Modern Bioelectrochemistry*, New York: Plenum Press,1986.

7. P. Baurschmidt and M. Schaldach,. J. Bioengineering, **1(11)**, 261 (1977).