Effect of Plastic Strain of Diamond-like Carbon Coated Stainless Steel on the Corrosion Behavior in Simulated Body Fluid Environment

Heon Woong Choi[1,2, a], Kwang-Ryeol Lee[1,b], Se Jun Park[1,c], Rizhi Wang[3,d], Jung-Gu Kim[4,e] and Kyu Hwan Oh[2,f]

[1]Future Technology Research Division, Korea Institute of Science and Technology, Seoul, 130-650, KOREA

[2]School of Materials Science and Engineering, Seoul National University, Seoul, 151-744, KOREA

[3]Department of Metals and Materials Engineering, University of British Columbia, Vancouver, BC, V6T 1Z4, CANADA

[4]Department of Advanced Material Engineering, Sungkyunkwan University, 300 Chunchun-Dong, Jangan-Gu, Suwon 446-746, KOREA

[a]joiner03@snu.ac.kr, [b]krlee@kist.re.kr, [c]tolive4@kist.re.kr, [d]rzwang@interchang.ubc.ca, [e]kimjg@yurim.skku.ac.kr, [f]kyuhwan@snu.ac.kr

Keywords: Diamond-like Carbon Film, Stability, Tensile Test, Potentiodynamic Polarization Test

Abstract. We investigated the effect of plastic deformation of diamond-like carbon (DLC) coated stainless steel on the corrosion resistance in the simulated body fluid environment. We deposited the DLC film on 304 stainless steel specimens by radio frequency plasma assisted chemical vapor deposition(R.F.-PACVD) method, followed by a tensile test to apply plastic stain on the coated specimen. Corrosion behavior in the simulated body fluid environment was studied by a potentiodynamic polarization test. As the tensile deformation progressed, the cracks of the film were observed in the perpendicular direction to the tensile axis. Further deformation increase both of the cracks and the spallations. Estimated porosity and corrosion current density increased and thus the protective efficiency decreased at the strain of 2 %. In spite of the degradation, the anti-corrosion properties were significantly improved comparing to the uncoated stainless steel. However, significant increase in porosity and corrosion current density was observed at the strain of 4 %.

Introduction

DLC coating has been considered as a strong candidate for various biomaterials due to its excellent mechanical properties and biocompatibility. Various DLC coated implants such as hip replacement, knee joint and cardiovascular stent are intensely investigated. Especially, the importance of stent has grown rapidly because it can prevent a sudden death caused by myocardial infarction. In general, diameter of the stent enlarged by at least twice after expanding in the vain. Furthermore, the stent should endure the environmental pressure in the range of 10-20 atm in human body that induces stenocardia. Thus, as a medical device, the stent should have sufficient structural strength in addition to the biocompatibility [1]. Typically, two kinds of materials are used for stent: nitinol and stainless steel. In both cases, it is also desirable to coat the stent surface by anticorrosion layer to prevent release of potentially harmful metal ions [2].

The DLC film have been considered as a protective layer for the medical implant materials [3] that can meet the requirements of suppressing the harmful ion releasing, wear debris formation, and undesirable biological reactions with the surrounding tissue. However, DLC film has a disadvantage of their poor adhesion on metal substrate due to stability of the carbon-carbon bonds that reduce chemical affinity to different material or due to compressive residual stress up to 10 GPa which can induce a delamination of film [4]. In order to enhance their practical application for medical devices, the stability of DLC coating should investigate under the deformation of substrate. In the present work, we deposited the DLC film on 304 stainless steel of tensile specimen and then imposed tensile strain. Anticorrosion behaviors of the specimen were evaluated in the simulated body fluid.

Experiment

We synthesized the DLC film by R.F.-PACVD method on 304 stainless steel substrate using benzene as the precursor gas. The stainless steel substrates were electrochemically polished to obtain smooth surface. In order to focus on the interfacial characteristics between the substrate and the film, we deposited the film which has the same thickness and the same properties. Before the film deposition, the substrate was sputter cleaned by Ar plasma at the bias voltage -600Vb for 60min. Thin Si buffer layer of thickness ranging from 19 to 84 nm was then deposited to improve the adhesion of the DLC layer. In this experiment, typical deposition parameters are found in reference [5]. We performed the tensile test using micro-tensile tester with 0.2 mm/min strain rate. Potentiondynamic polarization test was carried out in a 0.89 wt. % NaCl solution of pH 7.4 at 37° that was thoroughly deaerated by high purity nitrogen gas for 1h. Prior to the beginning of the potentiodynamic polarization test, the samples were kept in the solution for 6h in order to set up the open circuit potential. Scanning electron microscopy (SEM) was also used to investigate the corroded surfaces morphology of tested samples.

Results and discussion

Fig.1 shows the fracture behaviors of DLC film by increasing the strain. Fig. 1(a) clearly shows no crack formation at 2 % strain [5]. However, as increasing of strain from 4% to 8 %, the crack formation and spallations of film were simultaneously produced. It is also noticed that spallations of the film occurred with the crack propagation, although the number density of the spallations is very low. Further increasing the strain to 6 % and 8 % increased both the crack density and the number of the spallated area as shown in Fig. 1(c) and (d), respectively. The spallations area in the slip band was compared to characterize the adhesion of the DLC film between the samples.

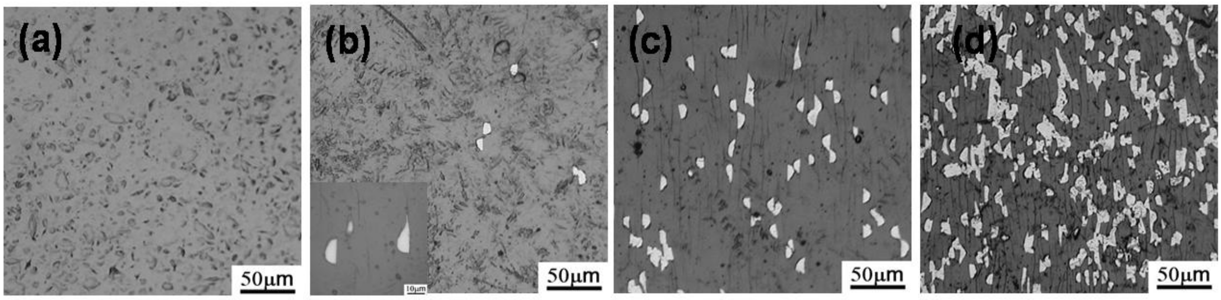
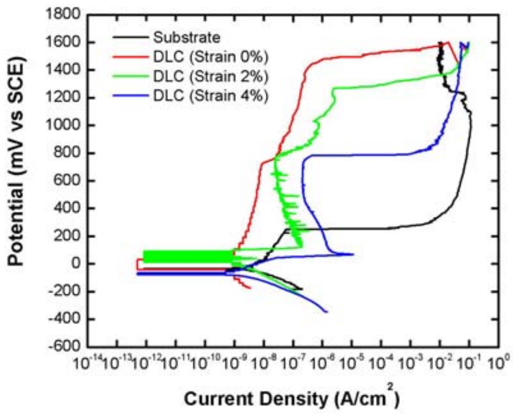


Fig.1 SEM microstructure of the sample surface after imposing tensile strain of (a) 2%, (b) 4%, (c) 6% and (d) 8%

With the aim of study the protection abilities and stabilities on localized corrosion of coating, potentiodynamic polarization measurements were carried out in the simulated body fluid condition with enhanced adhesion by controlling of Si buffer layer thickness and its curves for DLC films are shown in Fig. 2 and electrochemical parameters are summarized in table1.



Strain (Coated DLC)	Ecorr (mV)	icorr (nA/㎠)	βa (V/decade)	βc (v/decade)	Rp ($\times 10^3 \Omega$㎠)	Protective efficiency(%)	Porosity
Bare substrate	-33.9	6.557	0.2981	0.0693	3726.2217	-	-
0%	-32.55	0.312	0.2284	0.1425	122441.5576	95.25	0.0301
2%	-29.86	1.126	0.4851	0.1137	35566.7122	82.83	0.1015
4%	-69.32	4.720	0.1000	0.1041	4698.2691	28.02	0.6033

Fig. 2 Potentiodynamic polarization curves in deaerated 0.89% NaCl solution at 37˚C pH=7.4)

Table 1. Results of potentiodynamic polarization test

The corrosion density of 6.55 nA/cm^2 for uncoated sample, 0.31 nA/cm^2 for 0% strained sample, 1.12 nA/cm^2 for 2% strained sample and 4.72 nA/cm^2 for 4% strained sample, were observed. It was seen that the passive region was produced on the all the DLC films. The protective efficiency of strained DLC film decreased from 95 % to 28 % with increasing the strain from 0 % to 4%. However, the coated samples showed the improved protective efficiency even after the plastic strain up to 2 %. This protective efficiency is related with crack formation, spallations of film and porosity in DLC film. The lower measured protective efficiency, the higher crack formation, spallations of film and porosity as shown in Fig.3 and Table1 which shows the surface morphologies of the specimens after potentiodynamic polarization test. This is closely consistent with the corrosion protective ability and durability of coatings under conditions of applications. In addition, by controlling the Si buffer layer thickness we obtained the adhesion enhanced film. Fig.2 (b) and Fig.

3(b) showed the surface morphology of the same 2 % strained specimen. When increased the Si buffer layer thickness from 19 to 98nm, we observed the absence of crack formation and spallations as shown in Fig. 1(b) to Fig. 3(b).

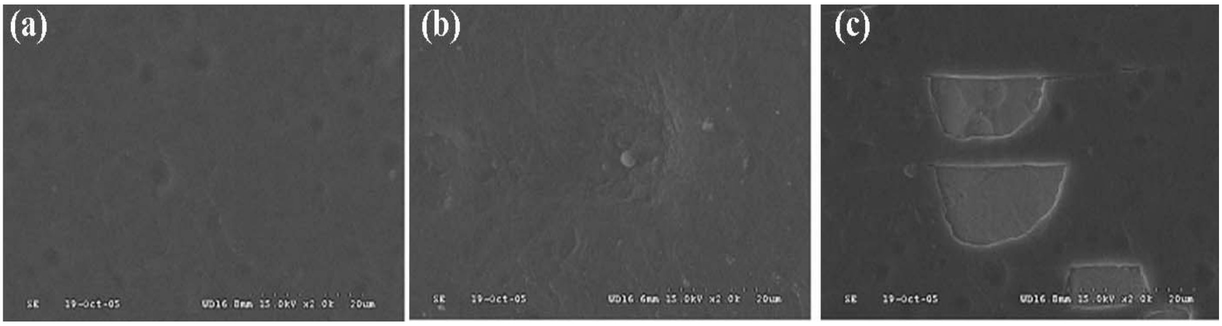


Fig. 3. The surface morphologies of the specimen after potentiodynamic polarization test at (a) 0 % (b) 2% and (c) 4% which all controlled Si buffer layer thickness to 98nm to enhance the adhesion

Summary

We studied the corrosion resistance of diamond-like carbon film by tensile and potentiodynamic polarization test in the simulated body conditions. We observed that the adhesion of DLC film was enhanced by increasing the thickness of Si buffer layer. When 2 % of strain added to the sample, we didn’t observed the crack however, there was 13% decreasing of protective efficiency due to increasing of porosity in the film. And 4% of strain applied to the sample, both the crack and spallations were developed and there was a significant reduction of protective efficiency. Nevertheless, the coated samples show the better protective efficiency than the uncoated sample. Therefore the DLC film shows the possibility of application as a coating of stent for protecting harmful ion releasing.

Acknowledgement

This research was supported by a grant (code number: 06K1501-01600) from ‘Center for Nonostructured Materials Technology’ under’21^{st} Century Frontier R&D Programs’ of the Ministry of Science and Technology, Korea

Reference

[1] P.D. Maguire, J.A. McLaughlin, T.I.T. Okpalugo, P. Lemoine, P. Papakonstantinou, E.T. McAdams, M. Needham, A.A. Ogwu, M. Ball, G.A.Abbas, Diam. Rel. Mater. 14, 1277 (2005)

[2] H. Hara, M. Nakamura, J. C. Palmaz, R. S. Schwarts, Advan. Drug Delivery, In press (2006)

[3] R. Hauert, Diam. Rel. Mater. 12, 583 (2003)

[4] G. Taeger, Mat. –wiss. U. Werkstofftech. 34, 1094 (2003)

[5] H. W. Choi, K. –R. Lee, R. Wang. K. H. Oh, Diam. Rel. Mater. 15, 38 (2006)