
Vol. 517 No. 3
1 December 2008
ISSN 0040-6090
ELSEVIER
thin solid films
International Journal on the Science and Technology of Condensed Matter Films
Proceedings of the 35th International Conference on Metallurgical Coatings and Thin Films (ICMCTF)
San Diego, California, April 28–May 2, 2008
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Thin Solid Films 517 (2008) 1146–1150
www.elsevier.com/locate/tsf

Mechanical stability of the diamond-like carbon film on nitinol vascular stents under cyclic loading

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Available online 4 September 2008

Abstract

The mechanical stability of diamond-like carbon (DLC) films coated on nitinol vascular stents was investigated under cyclic loading condition by employing a stent crimping system. DLC films were coated on the vascular stent of a three dimensional structure by using a hybrid ion beam system with rotating jig. The cracking or delamination of the DLC coating occurred dominantly near the hinge connecting the V-shaped segments of the stent where the maximum strain was induced by a cyclic loading of contraction and extension. However the failures were significantly suppressed as the amorphous Si (a-Si) buffer layer thickness increased. Interfacial adhesion strength was estimated from the spalled crack size in the DLC coating for various values of the a-Si buffer layer thickness.

Keywords: Diamond-like carbon (DLC); Nitinol; Vascular stent; Cyclic loading

1. Introduction

A vascular stent is used to hold abnormally narrowed artery or vein in the body opened by its circumferential expansion to a large diameter, allowing blood to flow through it. However, a metallic stent may release its metallic elements which can cause allergic reaction or form thrombogenicity of blood in complicated and aggressive physiological environment [1]. Thus, the ideal stent requires not only mechanical properties of a sufficient radial strength and low recoil but also a good biocompatibility of the stent surface for preventing a thrombogenicity and a metallic ion release [1]. In order to improve both mechanical properties and biocompatibility, a metallic stent has been functionally coated by carbon [2], silicon carbide [3], titanium nitride [4], or tantalum [5]. Among these materials, diamond-like carbon (DLC) has emerged as a potential coating material due to its excellent mechanical and biological properties such as high hardness, high wear and corrosion resistance, chemical inertness, excellent smoothness and low thrombogenicity [6]. However, it must be noted that the vascular stent may locally undergo a large deformation of tension, compression, or rotation as the extension and contraction occurs during clinical operation. The large deformation could cause failures in the coating layer such as cracking or spallation [7,8], which results in a severe problem in the lifetime of the coated stent.

In the present study, we investigated the failure behavior of diamond-like carbon (DLC) film on self-expandable vascular stents under cyclic loading condition of contraction and extension by using a stent crimping system. The cohesive crack and spallation in the film were explored by employing a focused ion beam (FIB) system. Amorphous Si (a-Si) buffer layer was widely used as an interlayer for improving adhesion between a thin film and substrate [9–10]. We estimated the adhesion strength of the DLC coating on the stent for various values of the a-Si buffer layer thickness.

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doi:10.1016/j.tsf.2008.08.175

2. Experimental details

The self-expandable vascular stent (MeKo, Germany) was provided as the samples, manufactured by laser machining of superelastic nitinol tube (SE 508 tube, Nitinol Devices and Components Inc., USA). The vascular nitinol stents of diameter 6 mm and length 18 mm consists of V-shaped segments attached to each other at three sites as shown in Fig. 1(a). Prior to DLC coating, the uncoated nitinol stents were cleaned with methyl alcohol in an ultrasonic bath, followed by blow-drying with nitrogen gas.

The hybrid ion beam system has been used for the surface pretreatment and the DLC coating. Fig. 1(b) shows the schematic of the deposition system, which combined a linear ion gun with a magnetron sputter gun. The substrate holder was rotated at a speed of 3.33 rpm for uniform pretreatment and coating on the entire surface of the stent. Base pressure in the chamber was less than 5×10^{-3} Pa and a radio frequency (RF) bias voltage was applied to the substrate holder.

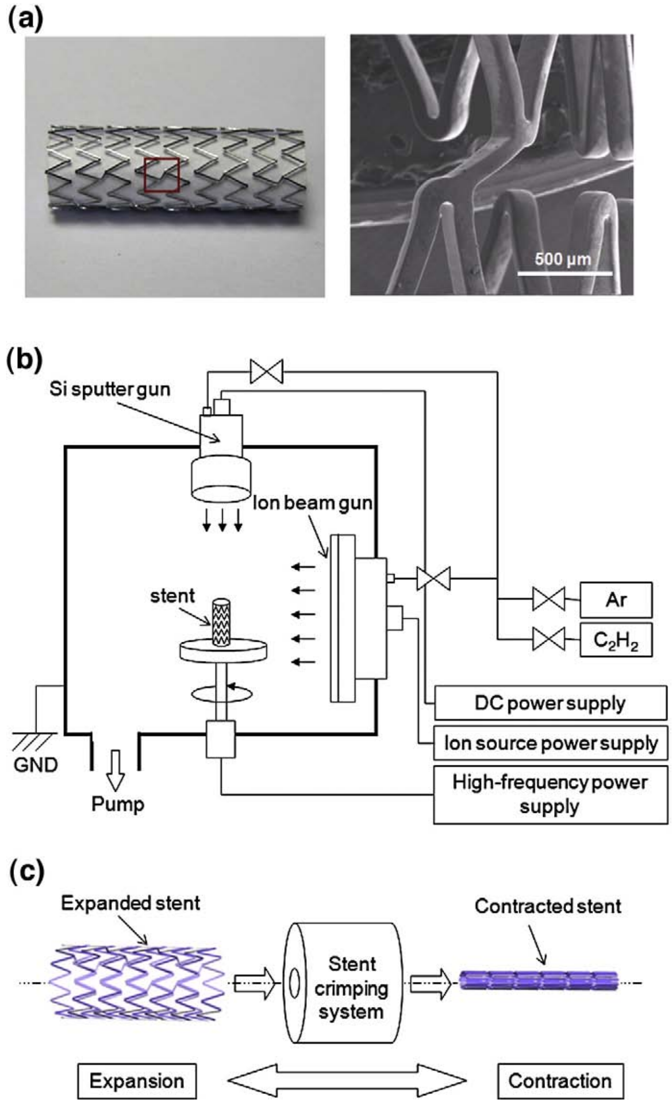

Fig. 1. (a) An optical image of a nitinol vascular stent (Length: 18 mm, Diameter: 6 mm) (left) and a magnified SEM image of a square box (right). Hybrid ion beam deposition system equipped with a magnetron sputter gun and a rotation stage. (c) A schematic diagram of a stent crimping system for applying a cyclic loading of contraction and expansion.

The Ar pre-cleaning and the deposition of a-Si buffer layer were performed for the improvement of interfacial adhesion strength between the stent and DLC film. The bare nitinol stents were cleaned for 30 min using Ar ion gun at the anode voltage 1.5 kV, the pressure of 0.06 Pa and the substrate bias voltage of −300 V. Sputtering of a silicon target (99.99% pure) was used for a-Si buffer layer deposition. Si was sputtered by Ar at the pressure of 0.26 Pa and the target bias voltage of −590 V. The a-Si layer thickness was controlled by varying the sputtering time from 0 (no a-Si buffer layer), 15, 30, 60, to 300 s. The a-Si deposition rate was estimated to be about 6 Å/min as measured by both an atomic force microscope (Autoprobe CP research system, Thermo Microscope Inc, USA) and transmission electron microscope (TEM) cross section microstructure. Finally, DLC film was coated on the stent by an ion beam deposition method using acetylene (C_2H_2) as the precursor gas. The ion gun was operated at the anode voltage of 1.5kV and the gas pressure 0.08 Pa. During deposition, bias voltage of −200 V was applied on the substrate. The thickness of DLC film was 120±5 nm as measured by a surface profilometer (alpha-step 200, TENCOR Instruments).

For producing a similar strain hysteresis in the DLC coated stent inserted in the body conduit, a cyclic of contraction and extension of the maximum strain 100% was applied to the stent using a stent crimping system shown in Fig. 1(c). The surface of the DLC coated stent was then investigated under FIB/SEM system (Nova 200, FEI Company) to observe the distribution of cohesive cracking and interface delamination of the DLC coating and their cross section microstructure. Sample for TEM microstructure was prepared using the stent after the cyclic loading, where a-Si buffer layer was deposited for 5 min followed by the DLC coating for 90 min. The composition and structure of the interlayer was analyzed in the cross section image using a TEM equipped with energy dispersive X-ray spectroscopy (JEOL, JEM-3000F).

3. Results and discussion

When the stent is strained along in-plane direction, the metallic stent transfer force to the DLC film by the well-known shear lag mechanism [11,12]. The stress in the film increases with straining the stent and reaches the critical fracture strength of the film resulting in the film cracking or spallation. With one cycle of contraction and expansion in the stent, DLC coating without a-Si buffer layer was delaminated and spalled in most of the surface area on the stent as shown in Fig. 2. It was reported that the buckling delamination has a characteristic width with respect to the thickness, stress and elastic modulus of thin film and its interfacial adhesion strength [13,14]. The cross section of the delaminated region revealed that DLC film was delaminated at the interface between DLC film and nitinol stent substrate (see Fig. 2(c)): For protecting the delaminated region from the ion beam damage during focused ion beam milling, Pt layer was deposited prior to cross sectioning the

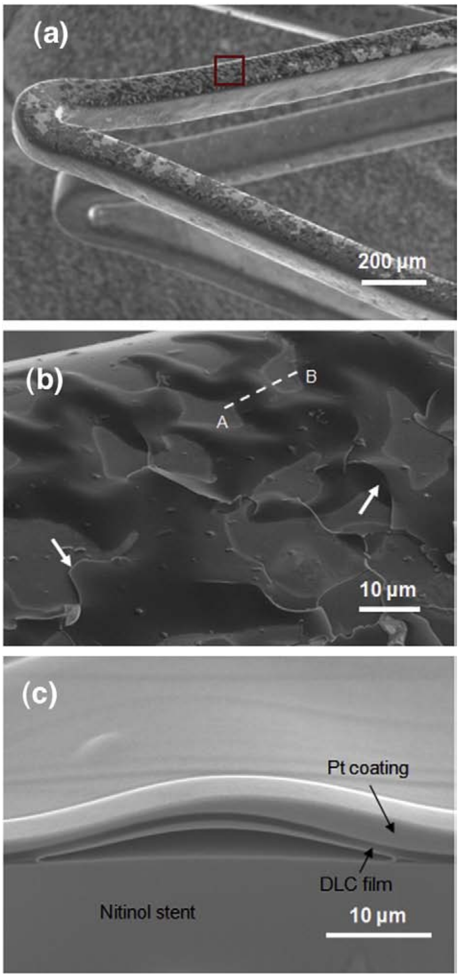

Fig. 2. (a) SEM image for cracking and delamination in DLC film without a-Si buffer layer after a cyclic loading. (b) A magnified SEM image of a square box in (a): crack extension at the top (white-arrowed) or perimeter of buckle delamination. (c) Cross sectional SEM image of the buckle delamination taken by FIB/SEM system (A–B dotted line in (b)).

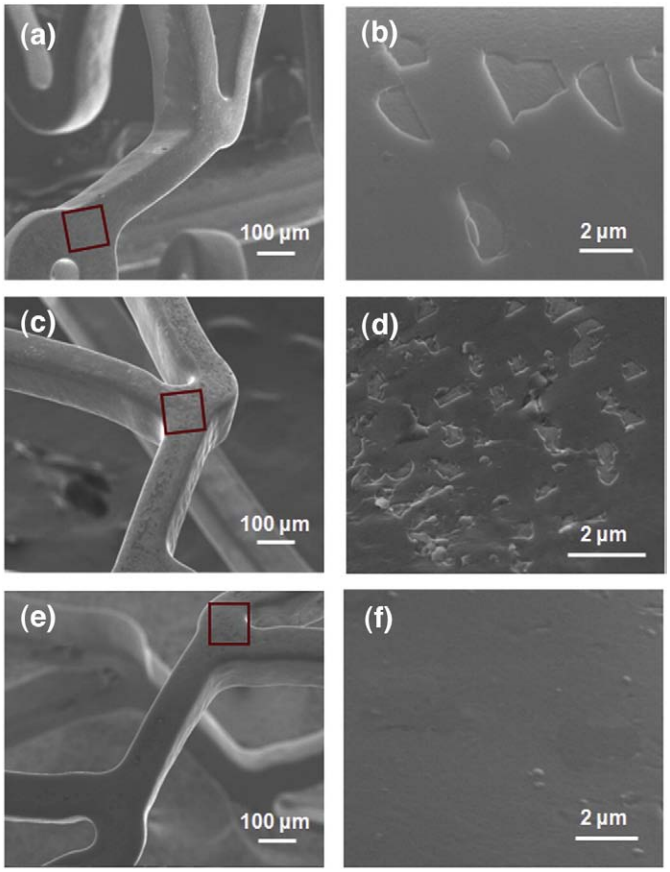

Fig. 3. SEM images showing failure behavior as a function of a-Si buffer layer: (a) Si buffer layer for 15 s, (b) the magnified image of square box in (a), (c) a-Si buffer layer for 30 s, (d) the magnified image of square box in (c), (e) a-Si buffer layer for 1 min, (f) the magnified image of square box in (e).

delaminated region. Fig. 2(b) shows that DLC film was cracked at the perimeter or top of the buckling delamination (indicated by arrows). The through-thickness cracking can cause complete spallation as reported in the previous works [15–17].

Fig. 3 shows the cracking and delamination behavior of a DLC film for three different thicknesses of a-Si buffer layer. DLC film was delaminated and spalled at almost entire region of the stent without a-Si buffer layer as shown in Fig. 2. However, the film cracking and spallation was significantly suppressed in DLC coated stent by depositing the a-Si buffer layer. Fig. 3(a) to (d) show that the cracking and spallation of the coating is observed dominantly at the hinge regions connecting the V-shaped segments of the stent. Deformation due to contraction and expansion of the stent is highly localized at the vicinity of the hinge regions with high stretching strain, which is in good agreement with a previous work calculated using a finite element simulation [18]. This result suggests that the strain distribution in the DLC film were localized on the specific region of the hinges indicated in square boxes in Fig. 3.

As discussed in the previous report [15], the film would first form cohesive cracks along the perpendicular direction to the loading due to tensile strain, while buckle at interface due to Poisson's compression, resulting in a half-circular shaped spallation. As can be shown in Fig. 3(a)–(d), similar failure behavior was observed on the nitinol stent: the local stain on the specific region caused a film cracking and remained semi-

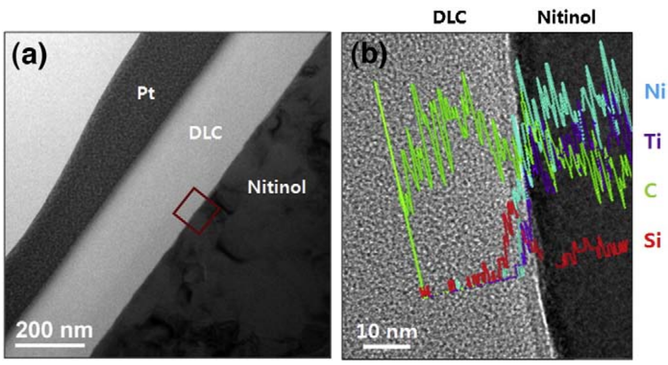

Fig. 4. (a) TEM cross sectional image of DLC coating when a-Si buffer layer was deposited for 5 min with DLC coating for 90 min. (b) TEM-EDS data at interface between DLC film and Nitinol stent (red, green, blue, and violet note Silicon, Carbon, Nickel, and Titanium, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

circular shaped spallations with similar size at the same deposition process. It was found that the spalled area width significantly decreased as a-Si buffer layer thickness increases. When a-Si buffer layer was deposited for 1 min, no cracking and spallation was observed in DLC coating as shown in Fig. 3(e) and (f). DLC coating becomes stable when the a-Si layer was deposited for 1 min (approximate thickness 6 Å). TEM cross section in Fig. 4(a) revealed that DLC film was uniformly coated on the stent. The a-Si buffer layer at the interface between DLC film and nitinol stent was also identified by the line scan of TEM-EDS in Fig. 4(b). EDS analysis shows that the thickness of the a-Si buffer layer is about 4 nm for 5 min deposition, of which growth rate is similar to that measured by AFM (about 6 Å/min). It must be further noted that intermixing occurs between DLC and a-Si layer, significantly improving the interfacial strength.

Fig. 5 shows the spalled area width normalized by the thickness of DLC film varying with the thickness of a-Si buffer layer. The width of half-circular shaped spallation was adopted to estimate the critical adhesion strength at the interface between the DLC film and the nitinol stent as in the previous work [15]. Here, we observed no cracking when the a-Si buffer layer was deposited for more than 5 min. The condition for film cracking and spallation was generally found in DLC coated metallic substrate under external loading [15]. As increased the external loading (σ) or thickness of films (h_f), the strain energy per unit area (G_o) of the DLC films competes with the interfacial adhesion strength (Γ_c) ($G_0 \geq \Gamma_c$), resulting in an instability of the system. The strain energy per unit area is expressed as follows

$$G_0 = \left[\frac{(1-v_f)h_f}{E_f}\right]\sigma^2, \qquad (1)$$

where E_f and v_f are the elastic modulus and Poisson's ratio of the DLC film, respectively. In order to prevent a film from delaminating or spalling over the substrate, the strain energy should be reduced, which can be achieved by decreasing film thickness (h_f) or increasing the interfacial adhesion strength (Γ_c). In this work, the thickness of DLC film was deposited to about 120 nm thick. The strain energy (G_0) was evaluated using Eq. (1), using the pre-determined values of the film thickness, residual stress, elastic modulus, and Poisson's ratio of 120 nm, 0.9 GPa, 110 GPa, and 0.33, respectively. The critical strain energy of the DLC film on the nitinol stent could be estimated by considering the dimension of spalled area widths in DLC film with 30 s deposition of Si buffer layer. The critical strain required for calculating the strain energy was deduced by interpolation of the previous data [15] because the critical interfacial strain of the DLC film cannot be obtained due to complex strain distribution in the stents during a cycle of contraction and expansion. The strain energy for DLC film with 30 s deposition of a-Si buffer layer was expressed as the critical toughness. The interfacial adhesion strength was about 19.67 J/m^2, above which no delamination was observed. The estimated values of the interface adhesion energy in this work were larger than those for DLC film with the condition of spontaneous buckling delamination (4–6 J/m^2) [14]. On the other hand, this value is lower than that required for the suppressing the failure of DLC film on the stent surface. The proper thickness of a-Si buffer layer for no film cracking and spallation was obtained over 1 min deposition (over 6 Å thick), indicating that a-Si layer could be uniformly deposited on the entire surface of the nitinol vascular stent. On the other hand, it should be cautious that the thick a-Si layer can induce the fracture inside of the buffer layer because of the brittle property of a-Si, which will be studied in further work.

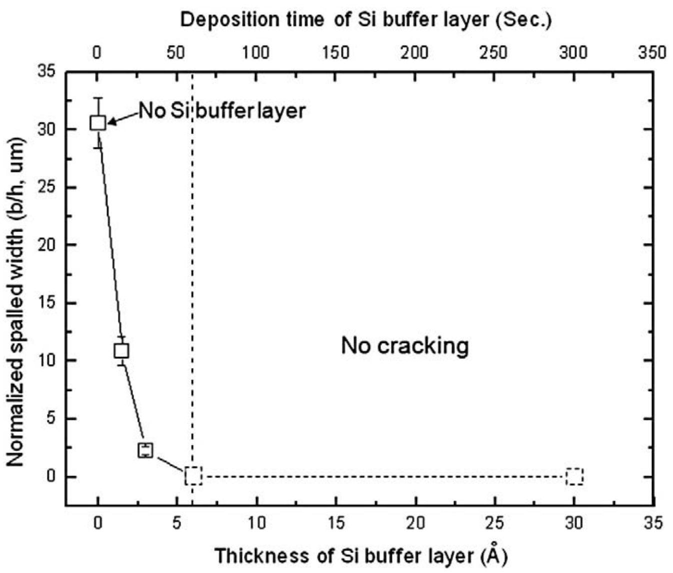

Fig. 5. Spalled area width of the DLC films as a function of the a-Si buffer layer thickness: 'b' and 'h' indicate the half width of spalled region and thickness of DLC film, respectively.

4. Summary

The self-expandable vascular stent was coated with uniform DLC film using a hybrid ion beam system equipped with a rotation jig for uniform pretreatment and deposition. Failure behavior of DLC film on metallic vascular stent was investigated under the cyclic loading of contraction and expansion using a stent crimping system. Upon contracting and expanding the DLC coated stent, a major strain for the failure was locally induced at the hinge region connecting V-shaped segments of the stent, and the delamination or spallation of the DLC coating extensively occurs. It was found that the delamination occurs at interface between film and stent substrate using FIB sectioning analysis. The interfacial strength was estimated by measurement of the spallation width, strongly depending on the thickness of a-Si buffer layer. With higher thickness in the a-Si buffer layer, delamination of the DLC films was significantly suppressed.

Acknowledgement

This research was supported in part by a grant (code number: 06K1501-01610) from the 'Center for Nanostructured Materials Technology' under the '21st Century Frontier R&D Programs' of MEST of Korea and in part by a grant of 2E20580 from KIST.

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