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Ultrananocrystalline diamond integration with pyrolytic carbon components of mechanical heart valves

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ABSTRACT

In this report, an idea of integrating ultrananocrystalline diamond (UNCD) with pyrolytic carbon (PyC)-based mechanical heart valves, has been demonstrated. The report addresses the strategies to avoid graphitization and film delamination during the diamond coating. Raman and scratch tests showed that a UNCD film with high purity could adhere to the PyC substrate strongly. A thrombin generation study demonstrated an excellent biocompatibility of UNCD towards fresh human platelets. These results suggest that UNCD could be a good candidate of surface material for next generation heart valves and other implantable devices.

1. Introduction

Pyrolytic carbon (PyC) is the most widely used structural material for mechanical heart valves due to its biocompatibility, low cost and ease of manufacturing [1]. However, PyC components still fail and release carbon particles into blood due to scratches at valve hinge area, which may cause blood contamination [2–3]. At the same time, although PyC has better biocompatibility than many other materials currently employed for medical purposes, patients who receive mechanical heart valves still need to take anticoagulation drugs for the rest of their life [4]. As an alternative, tissue valves eliminate the usage of anticoagulants, but the lifespan of tissue valves is usually less than 15 years and the patients may need to go through multiple thoracic surgeries. Therefore, a better material may help to optimize the mechanical heart valve design and lead to the next generation of heart valves, with both longer lifetime and less anticoagulant dependence. UNCD has been reported to have exceptional chemical inertness, biocompatibility, especially mechanical durability and tribological properties due to its diamond nature and unmatched smoothness [5–6]. The idea of this report is to integrate a thin layer (a few microns) of UNCD onto PyC heart valves, to enhance the performances of the heart valves, while not sacrificing PyC's original advantages of low cost and ease of manufacturing.

Like graphite, PyC tends to absorb carbon species if it is loaded in a chemical vapor deposition (CVD) reactor for diamond deposition. As a result, the regular UNCD deposition process is seriously prone to produce graphite which affects the film purity and performance. At the same time, the generated graphite is porous, such that even if some diamond crystallites are eventually growing, they cannot anchor on a solid substrate. Therefore, the film's adhesion on PyC is usually poor. With the intrinsic stress, diamond film usually delaminates from the substrate during or soon after the deposition. Due to such a technical challenge, successful diamond coating on PyC, pyrolytic graphite or other graphite forms was rarely reported. In this work, we minimized the graphitization during the deposition and improved the diamond adhesion with a few methods including introducing an interlayer, stress matching and carbide bonding between the film and the PyC substrate.

2. Experimental procedures

The pyrolytic carbon coupons, leaflets and orifices of heart valves were used for the diamond deposition. Manufacturing of PyC has been well developed [7]. The PyC substrates were firstly coated with a thin, 20–100 nm tungsten layer via either sputtering or atomic layer deposition (ALD). ALD was preferred because of its extremely conformal coating on a complicated 3-D structure. A seeding process was thereafter conducted to have diamond seeds attached on the surface of the substrates as initial nucleation centers. The seeding was achieved by commonly-accepted processes, either with surface mechanical abrasion with diamond particles or with sonication in seeding slurries containing diamond nanoparticles [8]. A hot filament chemical vapor deposition (HFCVD) reactor was employed for the UNCD coating. The setup and gas chemistry of the UNCD deposition were reported previously [9]. In

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the present study, we employed a similar process to simulate PyC deposition at approximately 800 °C in a CH_4–H_2 environment within a HFCVD reactor, rather than within a plasma enhanced reactor with C_3H_6–N_2 or only CH_4 [10–11]. This process consumed part of the carbon radicals at the beginning of the deposition to form a solid, PyC-like substance to gradually continue the PyC substrate, while preventing PyC from producing porous graphite. After this transit step, the gas ratio was gradually adjusted to match regular UNCD growth conditions. The overall thickness of the UNCD film was 1–2 μm.

A high resolution SEM was used to characterize the UNCD grains and surface morphology. The accelerating voltage, aperture size and working distance of the SEM were 10 kV, 10 μm and 10 mm, respectively. Optical profilometry (Wyko NT1100) was used to measure the surface roughness of the samples before and after diamond deposition. Raman spectra were obtained using a spectrometer (Control Development 2DMPP) with an frequency-doubled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. The laser wavelength and power were 532 nm and 5 mW, respectively. The film stress was measured by a Flexus Stress Measure System (Tencor FLX-2320) on Si witness wafers coated in parallel with the PyC samples, with input of thicknesses of the diamond film and the parameters of the substrate. The film adhesion was characterized via a Nanovea Scratch Test station and a Rockwell Ball Indenter with a Thomson Precision Ball (ceramic, 1/16″), following ASTM C1624-05, i.e. “Standard Test Method for Adhesion Strength and Mechanical Failure Modes of Ceramic Coatings by Quantitative Single Point Scratch Testing”. To evaluate the biocompatibility of diamond coated components towards platelets, fresh human platelets were incubated with diamond samples for 1 h. Thrombin generation was measured using a modified prothrombinase assay [12]. Calcium Ionophore A23187 was used to induce maximum platelet activation and thrombin generation, as a positive control. Untreated platelets were used as the negative control. The arithmetic average from experiments ($n = 9$) was used as a measure of thrombin generation rate induced by different surfaces. Statistical analysis was conducted by ANOVA using Microsoft EXCEL, and significant difference was set as $P = 0.05$.

3. Results and discussion

By adding tungsten interlayer before UNCD deposition and a transit step at beginning of UNCD deposition as described above, we were able to integrate UNCD with PyC components. Fig. 1a shows that when we used conventional deposition process, the diamond film catastrophically delaminated, while when we added these adhesion promoting steps (W interlayer and gradual PyC-to-UNCD transitioning), the UNCD film adhesion on the PyC substrates was significantly enhanced (Fig. 1b). Fig. 1c and d demonstrates that the UNCD-coated PyC components were assembled into a mechanical heart valve. Film measurements indicated that the UNCD thickness was between 1.5–2 μm. The optical profilometry measurement showed that before and after UNCD coating, the surface roughness maintained almost the same, between 50 and 80 nm (root mean square roughness) in a 237 μm × 178 μm field of view. UNCD is well known for being the smoothest as-deposit surface in the diamond family, with a typical roughness of 5–8 nm (root mean square) [9]. Fig. 4d and e depicts that the grains and grain clusters of UNCD are much smaller than the feature size of the PyC microstructure, therefore coating UNCD does not essentially add any more roughness to the substrate.

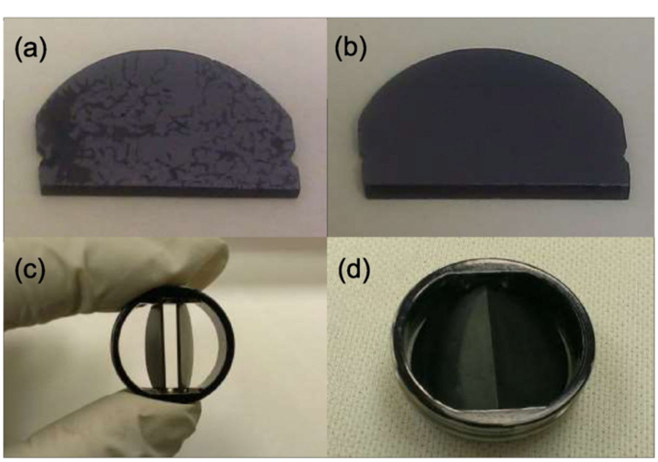

Fig. 1. Leaflets that a) covered by delaminated diamond film coated with conventional technique and b) covered by solidly integrated diamond film with developed integration technique, c) are assembled into a mechanical heart valve with open status and d) with close status.

Film stress is another factor that directly affects film adhesion and shape distortion of the coated samples. It is well known that diamond film stress decreases as the deposition temperature increases. For a deposition temperature increasing from 600 °C to 850 °C, the film stress can drop from −600 MPa (− represents compressive) to ±100 MPa (+ represents tensile), i.e. nearly stress free. Straight forward methods to raise temperature of the substrate include increasing the power of the reactor, or elevating the substrates closer to the filament. However, these methods are not practical for mass production, as raising power would interfere with the carburization balance of the filaments, which could cause tungsten filament breakage or releases tungsten carbide dust that contaminates the deposited film. Elevating the substrate closer to the filament would not only risk uneven surface heating especially for 3-D geometries, but also cause significant non-uniformity of the deposition rate across the substrate surface. More importantly, these methods would change the diamond deposition chemistry from UNCD to MCD (microcrystalline diamond). MCD is significantly rougher than UNCD and is not a favorable option to improve the antithrombogenicity of the resultant surfaces [16]. Here we developed a technique to minimize the residual film stress. Briefly, the coated samples were exposed to hot hydrogen right after the diamond deposition steps, which caused the sample surface temperature to be approximately 50 °C higher than the deposition temperature. This was a relatively short (5–35 min compared to hours for the main deposition steps) process, as more H atoms decarburized the filament and quickly raises the temperature of the substrate, similar to the anneal process for other coating techniques, but not in inert gases. In addition, in such a short time without involving carbon-related gases, the film thickness and grain size did not change. Fig. 2 demonstrates that 25 min of such treatment can achieve a stress close to 0 MPa, and can avoid the drawbacks caused by the aforementioned methods. When the stress is under 200 MPa, the curvature change of a leaflet is not measurable. Because of very small thickness and low stress introduced, the leaflets and orifices could be easily assembled without impacting the geometry of the valves.

A more thorough test on the adhesion of UNCD on PyC was conducted through a scratch test. Before adding the tungsten interlayer and the

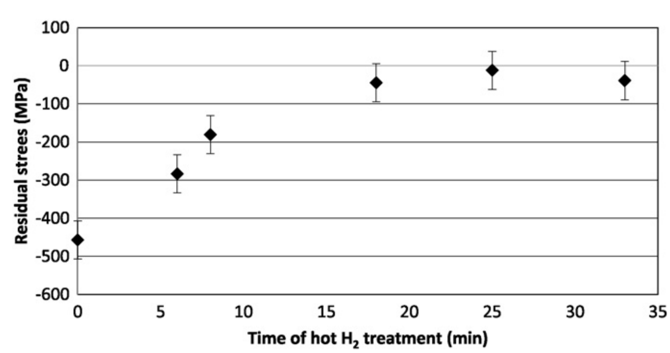

Fig. 2. Residual stress vs. time of hot H_2 treatment. The film thickness is 1 μm on average. The stress was measured by a Tencor Flexus on 4″ Si witness wafers with 525 μm thickness.