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Enhancement of adhesive strength of DLC film prepared by PBIID on Co–Cr alloy for biomaterial

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Abstract

Diamond-like carbon (DLC) film was prepared on Co–Cr alloy used for femoral head material of total hip arthroplasty by a hybrid process of plasma-based ion implantation and deposition using hydrocarbon gas. The tension test showed that the adhesive strength of DLC film was increased from 0.4 MPa without ion implantation to 2.8 MPa with carbon ion implantation. Furthermore, implantation of mixed carbon and silicon ions to the substrate led to considerable enhancement of adhesion strength up to 39 MPa that was comparable strength with the epoxy resin glue. DLC coating on Co–Cr alloy reduced the wear loss of ultra high molecular weight polyethylene (UHMWPE) used for a counterpart material in artificial joints.

Keywords: Plasma-based ion implantation (PBII); Deposition; Diamond-like carbon (DLC); Total hip arthroplasty; Adhesion strength; Wear resistance

1. Introduction

In recent popular total hip arthroplasty, ultra high molecular weight polyethylene (UHMWPE) has been commonly used as material of acetabular cup because of its superior properties such as ductility and impact load damping [1]. Polyethylene wear debris, however, have been recognized as a long-term cause of loosing and failure of artificial hip joints due to osteolysis [2,3]. Gamma ray irradiation has been successfully used to improve the wear resistance of UHMWPE [4]. Preparation of diamond-like carbon (DLC) film coating on the metal femoral head is a promising method to reduce wear debris of UHMWPE cup, because DLC has excellent properties such as low friction coefficient, strong wear resistance, and good corrosion resistance. Many studies on mechanical properties of DLC films on the Co–Cr alloys for orthopaedic applications have been reported [5–10]. However, enhancement in adhesion of DLC films has not sufficiently studied yet. It is now known that DLC can be produced by a wide range of methods [11,12] such as vacuum arc deposition, ion beam deposition, plasma CVD, sputtering, and laser plasma deposition. The use of a hybrid process of plasma-based ion implantation and deposition (PBIID) [13] enabled us to realize uniform coating of thick DLC films with the thickness of more than 5 μm on three-dimensional substrates [14]. From the AES measurement of carbon depth profile, it was found that the amount of carbon ion implantation and deposition was dependent on a kind of hydrocarbon gases [15]. Carbon ions from methane (CH_4)

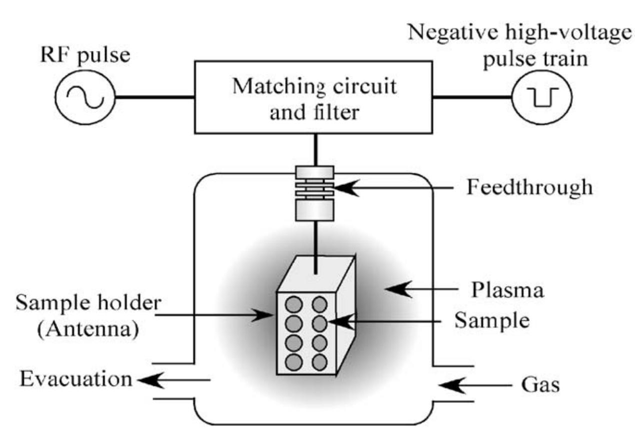

Fig. 1. A schematic diagram of the hybrid process of plasma-based ion implantation and deposition.

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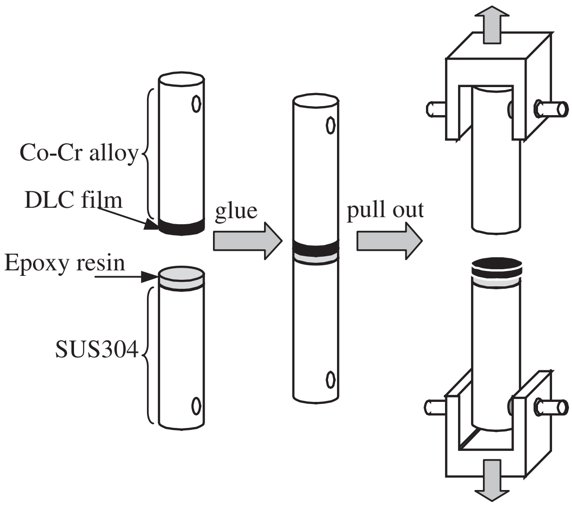

Fig. 2. The procedure of tension test for measurement of adhesion strength.

plasma are implanted into the substrate, but little deposition. The use of acetylene (C_2H_2) plasma resulted in implantation as well as deposition of carbon. When using the toluene ($C_6H_5CH_3$) plasma, the deposition rate of carbons was increased approximately 10 times than using the C_2H_2 plasma, but little implantation, realizing the high-speed deposition. The use of the $C_6H_5CH_3$ plasma and ion implantation by −5 kV pulse during deposition reduced the residual stress in film to several MPa [16]. These results suggested a processing recipe for thick DLC film with enhanced adhesion [14–16].

To confirm the effect of carbon ion implantation to the substrate on film adhesion, in this work, we present the preparation of the DLC film on Co–Cr alloy for biomaterial by the PBII&D process using hydrocarbon gas such as CH_4, C_2H_2, $C_6H_5CH_3$, and organic metal compound including silicon $[(CH_3)_3Si]_2O$. Effect of ion implantation on the adhesive strength of DLC film is experimentally studied by tension test. The wear loss of UHMWPE pin by pin-on-disk method is also presented.

2. Experimental

A schematic diagram of the hybrid process of PBIID is shown in Fig. 1. A cross-section of vacuum chamber was the horseshoe shape of 420 mm × 420 mm and its height was 420 mm. A square-pole sample holder (dimensions of each face: 60 mm in width and 170 mm in height) was set in the center of chamber using a single electrical feed-through. In this system, the RF pulse for plasma generation was supplied to the sample holder together with a negative high-voltage pulse for ion implantation through the feed-through using a joint matching circuit for both pulses. As the sample holder itself was used as an RF antenna, the uniform plasma was generated around the sample holder and the largest plasma density appeared near the substrate [13]. The RF pulse with the power of 300 W, the pulse duration of 50 μs, the frequency of 13.56 MHz, and the repetition rate of 1 kHz was used for plasma generation. The negative high-voltage pulse train with the voltage of −5 to −20 kV, the duration of 5 μs, and the same repetition rate as the RF pulse was applied to the substrate at the time of 50 μs later after each RF pulse. The afterglow plasma continued to exist during the RF off-time at the present experimental conditions, although the plasma density decreased in time.

The adhesive strength of DLC film prepared on Co–Cr alloy was measured by the tension test that procedure was shown in Fig. 2. The DLC film was prepared on a cross section of Co–Cr alloy cylindrical rod (12 mm in diameter and 60 mm in length). After a DLC-coated Co–Cr alloy rod was bonded with an uncoated SUS304 rod using epoxy resin glue, they were pulled out till the film or the resin were broken. The adhesive strength was determined with the cross section of rod and the tensile load at the breaking point. The DLC film was prepared with three kind of coating processes as shown in Table 1. Three processes were as follows: (a) DLC film deposited on non-implanted Co–Cr alloy, (b) DLC film deposited on C ion implanted Co–Cr alloy, and (c) DLC film deposited on C and Si ion implanted Co–Cr alloy. The gas pressure was maintained at $p = 0.5$ Pa during all processes in Table 1. The cylindrical rod was inserted in the hole of sample holder and set so that the head of cylindrical rod was the same height as the sample holder surface. The Co–Cr plate (20 mm in a diameter and 2 mm in thickness) for wear test was set on the surface of sample holder using adhesion tape. The sample surface, whose average roughness (R_a) is 0.1 μm or less, was polished to mirror finish prior to DLC coating.

Table 1
The procedure of DLC film preparation

	Stage	Sputter cleaning	Ion implantation				Deposition
(a) DLC film deposited on non-implanted Co–Cr alloy	Gas	Ar					$C_6H_5CH_3$
	Pulse voltage (kV)	−10					−5
	Process time (min)	30					120
(b) DLC film deposited on C ion implanted Co–Cr alloy	Gas	Ar	CH_4		C_2H_2		$C_6H_5CH_3$
	Pulse voltage (kV)	−10	−20		−20		−5
	Process time (min)	30	30		30		120
(c) DLC film deposited on C and Si ion implanted Co–Cr alloy	Gas	Ar	CH_4	CH_4+Si	C_2H_2+Si	C_2H_2	$C_6H_5CH_3$
	Pulse voltage (kV)	−10	−20	−5	−5	−20	−5
	Process time (min)	30	25	5	5	25	120