Vacuum 86 (2012) 675–680

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Relationships between the fretting wear behavior and mechanical properties of thin carbon films

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Keywords:
Fretting wear
Nanohardness
Orthopedic implants
Carbon films

ABSTRACT

Mechanical load can drastically affect the properties of orthopedic implant materials. Damage of these materials usually occurs in contact surfaces, caused by abrasion, adhesion, fretting, delamination, pitting and fatigue depending on friction, lubrication, contact area, surface finish and level of loads (stresses).

Carbon-based films are biocompatible with good bearing capacity, wear resistance, corrosion resistance and have a low coefficient of friction. However, great intrinsic stress prevents their wider application, mainly as implant coatings. To reduce this undesirable effect special deposition procedures are under development and/or the films are doped with suitable elements. It must be emphasized that DLC is not a material but a group of materials with a variety of properties. The relationships between the fretting wear behavior and mechanical properties of films based on carbon deposited by DC using the pulsed arc discharge PVD nitrogen doped (a-C) and the filtered pulsed arc discharge deposition system (ta-C) were tested.

The composition of carbon films (sp^3, sp^2) was determined by Raman spectroscopy. Mechanical properties of elastic modulus and hardness were determined by a NanoTest apparatus with diamond Berkovich tip using the Oliver-Pharr procedure and adhesion was measured by nanoscratch tests. Tribological behavior was analyzed by fretting tests with a corundum ball under dry sliding lubricated conditions.

The good performance of the hard carbon coatings is often discussed. Results from this study of fretting and the associated lubrication (bovine serum) show that ta-C coatings, despite their high hardness, have very low friction coefficients and low volume losses.

1. Introduction

Materials scientists have investigated metals, ceramics, polymers and composites as biomaterials. Mechanical load can drastically affect properties of orthopedic implant materials. The high wear resistance of diamond makes it a candidate for biotribological applications as thin coatings [1]. Diamond-like carbon (DLC) films could be widely used in biomedical applications because of their biocompatibility, chemical inertness, low friction coefficient, high hardness and wear and corrosion resistance.

DLC films, which present a metastable form of carbon in an amorphous structure with a mixture of sp^2 and sp^3 C–C bonds, have a wide range of potential applications [2]. Numerous types of DLC films can be deposited using a variety of plasma deposition techniques [3–5]. The sp^3/sp^2 ratio of DLC films depends on the deposition conditions and techniques, hydrogen concentration and the presence of other elements in the film. Typical DLC films are amorphous carbon (a-C) films with lower sp^3 content and tetrahedral carbon films (ta-C) with a higher sp^3 (up to 85%) content. The mechanical properties of DLC films are directly related to the fraction of sp^3 C–C bonds.

In recent years, the wear mechanism of thin diamond films has been investigated [6]. Additionally, DLC is an excellent base coating to be alloyed with different other elements. The amorphous nature

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doi:10.1016/j.vacuum.2011.07.011

of DLC opens the possibility to introduce certain amounts of additional elements, such as Si, F, N, O, W, V, Co, Mo, Ti and their combinations, into the film and still maintain the amorphous phase of the coating [7,8]. Understanding the wear mechanism of diamond coatings in friction process is of great technological and scientific interest. Also characterization of their tribological properties is required. In this context, it is reasonable to investigate the performance of diamond coatings under fretting friction conditions [9,10].

Fretting is a wear phenomenon occurring when two contacting solids are subjected to a relative oscillatory tangential motion of small displacement amplitude. Even displacement amplitudes in the sub-micron range can result in wear damage. Fretting becomes an important aspect to designers when the functionality of a component deteriorates or its lifetime is reduced by the induced material damage. In severe cases, the material damage initiates or promotes other failure mechanisms, such as fretting fatigue, fretting corrosion, or stress-corrosion cracking.

Most important are the contact conditions (displacement stroke, vibration frequency, contact pressure), the environmental conditions (temperature, relative humidity, lubricants), and the material properties (hardness, yield strength, fracture toughness, chemical inertness). A real vibrating contact is often characterized by an extremely complex interaction of these variables making fretting a true system property.

Fretting wear combines most of the existing wear mechanisms, such as abrasive, adhesive, oxidative and fatigue [11]. Moreover, fretting wear can be easily produced on hard surfaces with minimal energy input into the friction surfaces, since wear is concentrated in a small contact area between the two contacting solid surfaces. In addition, fretting conditions are dynamic and simulate the behavior of many mechanical systems.

In this study, the relationships between the fretting wear behavior and mechanical properties of carbon-based films deposited using the pulsed arc discharge PVD nitrogen doped (a-C) and filtered pulsed arc deposition (ta-C) were tested.

2. Experimental setup

The a-C films, deposited by pulsed arc discharge PVD vacuum equipment UVNIPA-1-001 [12], and ta-C coatings, prepared using the filtered pulsed carbon plasma technique [8], were used in this investigation. Deposition parameters are shown in Table 1. Samples were rotated in order to obtain uniform thickness. Film thickness was evaluated by calotest (CSM Instruments) with ball diameter 25 mm. Thickness of ta-C film was determined 0.70 μm and for a-C film was 1.25 μm.

The hardness H, elastic modulus E_{eff} and other mechanical characteristics were determined from depth sensing indentations (NanoTest NT600, Micro Materials, Wrexham, UK) apparatus at different maximum loads ranging from 5 to 50 mN with diamond Berkovich tip, using the analysis developed by Oliver and Pharr [13]. The indentation cycle was repeated five times in slightly different places for each maximum load. Hardness was evaluated according to basic principles shown in Table 2.

Table 2
The basic formulas for evaluation of hardness.

Parameter	Equation	Remark
Unloaded curve fitted by power low	$P = \alpha\,(h - h_f)^{\mathrm{m}}$	α, m … fitting parameters
Unloading stiffness	$S = [\mathrm{dP/dh}]_{h\,=\,h\mathrm{max}}$	
Contact depth	$h_{\mathrm{c}} = h_{\max} - \varepsilon(P_{\max}/S)$	for Berkovich indenter $\varepsilon \sim 0.75$
Indentation hardness	$H_{\mathrm{IT}} = P_{\max}/A_{(\mathrm{hc})}$	$A(h_{\mathrm{c}})$ projected contact area of the indenter in $\mathrm{N/mm^2}$
Effective elastic modulus	$E_{\mathrm{eff}} = [S\ \mathrm{SQRT}(\pi/A)]/(2\beta)$	for Berkovich indenter $\beta \sim 1.034$
Deformation of indenter is assumed	$1/E_{\mathrm{eff}} = [(1-\nu^2)/\mathrm{E}] + [(1-\nu_i^2)/E_i]$	(for diamond $\nu_i = 0.07$ and $E_{\mathrm{i}} = 1141$ GPa) index i means material of the indenter

The substrate material for all the coated samples was conventional CoCrMo (ISO 5832-4) for bio-implants, with hardness of 350–460 HV.

The adhesion of the coatings was investigated with a scratch tester (Revetest, CSM Instruments, Neuchatel, Switzerland). Scratch experiments were performed with a diamond Rockwell sphere-conical tip $r = 25$ μm; the length of the scratch was 1 mm; the load varied from 1 to 150 mN; the scan speed was 0.75 mN/s.

PVD coated CoCrMo substrates were used for the fretting tests. The samples were rubbed against a corundum ball (α-Al_2O_3) $d = 10$ mm (Ceratec, Geldermalsen, the Netherlands).

The coated sample discs ($d = 24$ mm) used for testing were combinations of CoCrMo/a-C and CoCrMo/ta-C [12]. Fretting wear experiments were conducted in humid air (RHE45%, $T = 21$ °C) at constant oscillating frequency of 10 Hz, with $F = 5$ N, number of cycles = 10,000, total sliding distance = 100 μm. For ta-C samples both unlubricated and lubricated contact sliding against corundum ball (α-Al_2O_3) were investigated. Bovine serum diluted to 25% with deionized water, with penicillin, streptomycin and sodium azide added, was used for lubrication.

The frictional force was digitally recorded throughout the test with a load transducer. Before the test the samples were ultrasonically cleaned in high-purity benzene and ethanol. A small amount of oil was spread on the surface of the flat specimen prior to each experiment. The wear volume was determined by Veeco Instruments profiler, which measures surface wear with high precision by using an optical system.

After the analyses, selected sample discs and corundum balls were examined using a scanning electron microscope (SEM) (JSM-T330A, Jeol Ltd., Peabody, MA).

The structure of the thin films was characterized by Raman spectroscopy (Dilor-Jobin Yvon-Spex, Longjumeau, France). The excitation source was a He–Ne laser with 632.8 nm wavelength operated at 15 mW. The spectrometer was calibrated to the 520.7 cm^{-1} band of single crystalline Si and 1332 cm^{-1} band of natural diamond. A scanning electron microscope LEO 1550 (Zeiss, Oberkochen, Germany) operating in the secondary electron mode was used to study the microtopography of DLC layers.

Table 1
Deposition parameter of DLC films.

Type of films	Ar_2 [cm^3/min]	N_2 [cm^3/min]	Arc voltage [V]	Pulse rate [Hz]	Pulse duration [microsec]	Deposition distance [cm]	Deposition time [min]	Deposition technique
a-C	70	60	400	3	300–500	20	30	pulsed arc discharge
ta-C[a]			500	10	100	10	30	FPAD

Deposition atmosphere: Vacuum, 10e^{-6} mbar/100 μPa.

[a] RCL-parameters:$R = 0.1$ Ohm, $C = 34.8$ μF and $L = 12$ muH.