CHARACTERIZATION AND TRIBOLOGICAL TESTING OF A CARBON-BASED NANOLAYER PREPARED BY ION BEAM ASSISTED DEPOSITION

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Abstract

Carbon-based nanolayers have been attracting much attention due to their excellent low-friction properties, their high hardness and their good wear resistance. In this work we present the results of material research aimed at reducing the friction of the functional surfaces of titanium implants, and thus extending their lifetime to reoperation. Nitrogen ion beam assisted deposition of a carbon-based nanolayer was applied to modify the surface properties (i.e. sliding and wear) of Ti6Al4V biomedical titanium alloy. Ion bombardment caused structural changes, which led to an increase in surface hardness by a factor of 1.86 in comparison with a surface modified by a carbon nanolayer without nitrogen ion bombardment. An analysis of the chemical composition showed that the modified surface is composed of a carbon-based nanolayer, a mixed interface, and a nitrogen-enriched sublayer. Raman spectroscopy showed the DLC character of the carbon-based nanolayer with sp2 rich bonds. A TiN compound was detected by X-ray diffraction in the modified surface area. A very low friction coefficient below 0.1 was maintained for a normal load of 2N. The sliding behavior of the head (Ti6Al4V) and the shell (PEEK) tested on a joint wear simulator showed that surface modification of the head of the implant under optimized deposition conditions provides protection for the functional surfaces, leading to a reduction in wear and a substantial increase in lifetime.

Keywords: Nanolayer, friction, nanohardness

1. INTRODUCTION

This paper deals with characterizing and tribological testing of a carbon-based nanolayer on the Ti6Al4V alloy. This alloy is widely used in biomedical engineering (e.g. for joint replacements and for dental implants) because of its high tensile strength, its good biocompatibility and its low elastic modulus [1]. However, the surface properties (e.g. the tribological properties and the surface hardness) are not fully satisfactory for use in this field, and they need to be modified [2]. The risks of allergic reactions to titanium and its alloys, have come under discussion [3]. Carbon-based nanolayers have been attracting much attention due to their excellent low-friction properties, their high hardness and their good wear resistance. Many methods are used for depositing carbon-based layers [4, 5]. Ion bombardment during deposition modifies the structure and the properties of carbon-based nanostructures and affects their adhesion [6, 7]. It is known that the properties of carbon-based nanolayers depend on the type of bonding between the atoms and on the chemical composition, which is influenced by the deposition conditions [8]. In this work, we present improved tribological behaviour of the Ti6Al4V alloy modified by ion beam assisted deposition of a carbon-based nanolayer. The friction coefficient was measured using a pin-on-disc tribometer. The sliding behavior of the modified head (Ti6Al4V) against the shell (PEEK) was tested on a joint wear simulator. We also investigated the surface morphology by atomic force microscopy (AFM), hardness by naniondentation, C-C bonds by Raman spectroscopy, phase composition by X-ray diffraction (XRD), and the chemical composition by auger electron spectroscopy (AES).

2. EXPERIMENTAL PART

The substrates were made of Ti6Al4V titanium alloy in the form of a cylinder 20 mm in diameter and 8 mm in height. The roughness of polished samples was Ra = 0.02 µm. The substrates were ultrasonically cleaned in isopropyl alcohol before the deposition process. The deposition of carbon-based nanolayers proceeded by electron beam evaporation of a carbon target with simultaneous nitrogen ion bombardment (ion beam assisted deposition - IBAD). The thickness of the nanolayer was measured by a quartz thickness monitor located in the apparatus, and was approximately 20 nm (IBAD 20 nm modification) and 40 nm (IBAD 40 nm modification). The nanolayers were irradiated with nitrogen ions with energy of 90 keV and fluence of $1 \cdot 10^{17}$ cm^{-2} for structure modification. Both electron beam evaporation and nitrogen ion bombardment were carried out in the apparatus, which was presented schematically in our previous work [8].

The chemical composition was measured by means of auger electron spectroscopy (AES) in a PHI SAM 545 spectrometer. For excitation, an electron beam of 3 keV and 1 µA, with a diameter of 40 µm, was used. The samples were sputtered by two symmetrically inclined Ar ion beams of 1 keV. The sputtering rate was estimated to be about 2.0 nm/min on an Ni/Cr multilayer of known thickness. This estimated sputtering rate is valid for metals. For carbon, the sputtering rate is estimated to be 0.7 nm/min. A lower sputtering rate is also expected for other lighter elements.

The phase composition was investigated by the X-ray diffraction method (XRD). Cobalt radiation with wavelength 0.1789 nm and geometry with the parallel beam with an incident angle of 0.5° was used. The Raman spectra were measured using a Renishaw RM 1000 Raman microscope with Ar laser excitation at 514.5 nm. Anatomic force microscopy (AFM) in tapping mode was used to characterize the surface topography.

The surface hardness was investigated by nanoindentation. The partial unload function was used for measurements of the depth profile of the surface hardness. The maximum indentation load was 5000 μN. 12 indents were performed in a 3×4 matrix. The coefficient of friction was investigated on a pin-on-disc tribometer with a 100Cr6 steel ball 6 mm in diameter. The normal load was 2 N, the radius of rotation was 4 mm, and the velocity was 6 $cm \cdot s^{-1}$. The sliding behavior of the modified head (Ti6Al4V) 10 mm in diameter and the shell (PEEK) was tested on a joint wear simulator (**Figure 1**).

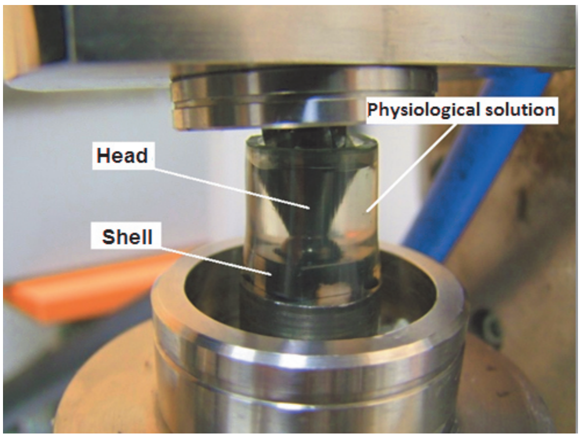

Figure 1 Joint wear simulator

3. RESULTS AND DISCUSSION

Figure 2 shows the typical concentration profiles of the elements in the modified area of the IBAD 20 sample. The thickness of the carbon-based nanolayer corresponds to the nominal deposited thickness of the carbon-based nanolayer (20 nm; 28 min of sputtering). Increased concentration of oxygen is observed at the interface between the carbon-based nanolayer and the Ti-6Al-4V substrate. This may be due to surface contamination by the atmosphere. The assistance of nitrogen ion bombardment causes nitrogen to penetrate into the carbon-based nanolayer and mainly into the Ti6Al4V substrate. The TiN phase was formed during ion bombardment in the modified surface region, where the nitrogen concentration is at its maximum.

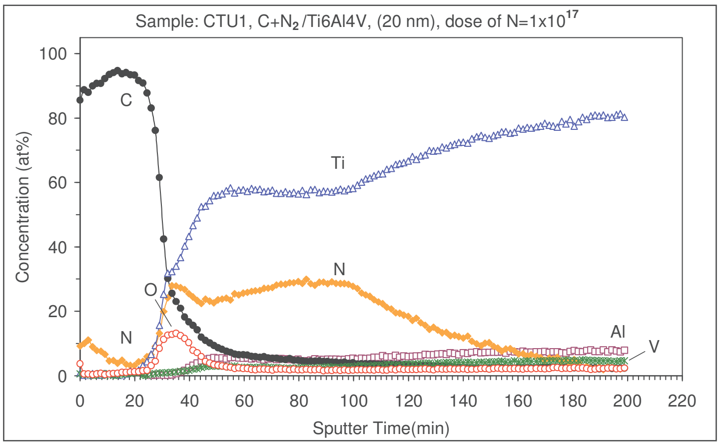

Figure 2 AES concentration profiles of elements in the modified Ti6Al4V alloy

The phase composition was investigated by means of X-ray diffraction (XRD). The alpha structural phase of the Ti6Al4V alloy was observed. No beta structural phase was identified in the diffraction spectrum. Non-stoichiometric TiN phase and graphite were observed in the surface area. Chemical composition analysis and phase analysis proved that a thin carbon-based nanolayer, a mixed interface and a nitrogen-enriched sublayer with a titanium nitride phase are formed in the modified surface area.

The Raman spectra in **Figure 3** show one main peak located at ~1500 cm^{-1}, with a shoulder at a lower frequency. The shoulder becomes visible in the spectra of the carbon-based nanolayer deposited with ion assistance. Ion bombardment during the deposition process increased the intensity of the low-frequency peak. The Raman spectra in **Figure 3** have a DLC (diamond-like carbon) character; i.e. they are composed of a D peak (disordered graphitic carbon - at ~1350 cm^{-1}) and a G peak (graphitic carbon - at ~1550 cm^{-1}) [8]. The spectra show that the carbon-based nanolayer has a DLC character with sp^2 rich bonds. The correlation with the hardness results shows that the surface hardness increases due to structural changes induced by ion bombardment.

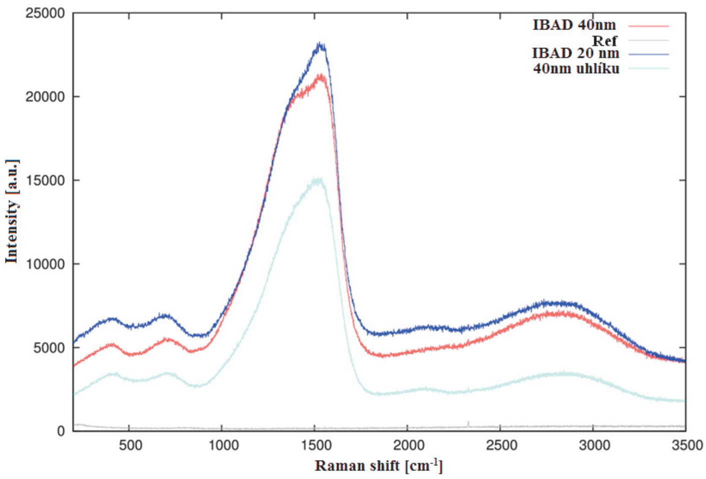

Figure 3 Raman spectra of amorphous carbon nanolayer bombardment with nitrogen ions (a-C:N) and without ion bombardment (a-C)

The depth profiles of the indentation hardness are presented in **Figure 4**. The minimum indentation depth at which we are able to obtain the mechanical properties are limited by the sharpness of the tip and by the roughness of the sample surface. The indentation hardness values *(H_{IT})* are calibrated from a contact depth of h_c ~ 8 nm. The maximum indentation hardness values H_{IT} ~ 13 GPa were measured on the IBAD 40 nm sample at contact depths of h_c ~ 13 nm. The sample coated with carbon nanolayer (40 nm) without ion assistance (*C 40 nm* sample) had maximum indentation hardness values of H_{IT} ~ 7 GPa at a contact depth of h_c ~ 8 nm. The two measured surface modifications (IBAD 40 nm and IBAD 20 nm) exhibit comparable hardness. The depth profile of the indentation hardness on the IBAD 20 nm sample indicates deeper hardening due to a thinner carbon-based nanolayer and a greater range of N ions. The maximum indentation hardness of the reference sample is H_{IT} ~ 5.5 GPa. The H_{IT} of the modified samples has a sharply decreasing trend with increasing h_c, whereas the depth profile of the H_{IT} of the reference sample has a constant trend.

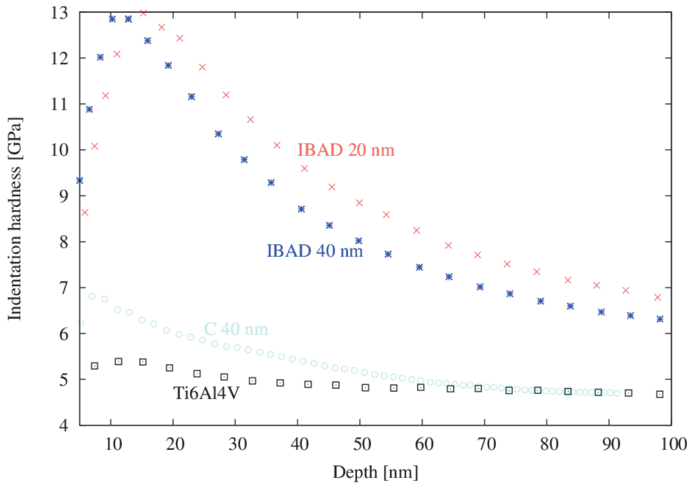

Figure 4 Depth profiles of the indentation hardness

The surface topography of the samples was characterized by atomic force microscopy. The surface topography of the modified samples and of the unmodified substrate was almost the same. The root mean square (RMS) roughness of all modified samples ranges between 2.56 nm and 8.07 nm.

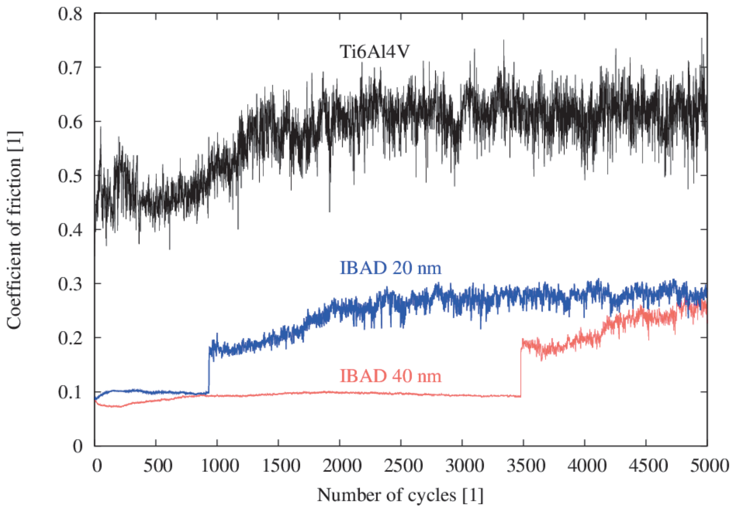

Figure 5 Coefficient of friction versus the number of cycles for modified samples and for the Ti6Al4V reference sample

Figure 5 shows the evolution of the coefficient of friction for the modified samples and for the substrate as a function of the number of cycles. The coefficient of friction of the modified samples decreased to approximately 0.1. The two surface modifications (IBAD 40 nm and IBAD 20 nm) have comparable coefficient of friction values. A thicker nanolayer increased the duration of the lubrication effect. Carbon-based nanolayers show a much lower coefficient of friction than for the uncoated Ti6Al4V alloy (about 0.6 - see **Figure 5**).

The proposed IBAD 40 nm surface modification was tested on a model of a finger joint replacement (the head - surface modified Ti6Al4V, and the shell - PEEK) on a joint wear simulator (**Figure 1**) with normal loads of 100 N. The course of the contact pressure between the head and the shell was simulated by FEM analysis in the Abaqus program. The load corresponds to the normal load at tribological test with a coefficient of friction of 0.1. The maximum contact pressure was 4 MPa at the deepest point (see **Figure 6**). Because of the complex convex-shaped head of the joint and the concave shape of the shell, the sliding tests were only qualitatively evaluated. The unmodified Ti6Al4V head showed drastic wear both of the head and of the shell after 10,000 cycles (**Figure 7**) in comparison with the modified head. The first local wear fault of the IBAD 40 nm modification was observed after 240,000 cycles (**Figure 8**). A global wear fault occurred after 510,000 cycles.

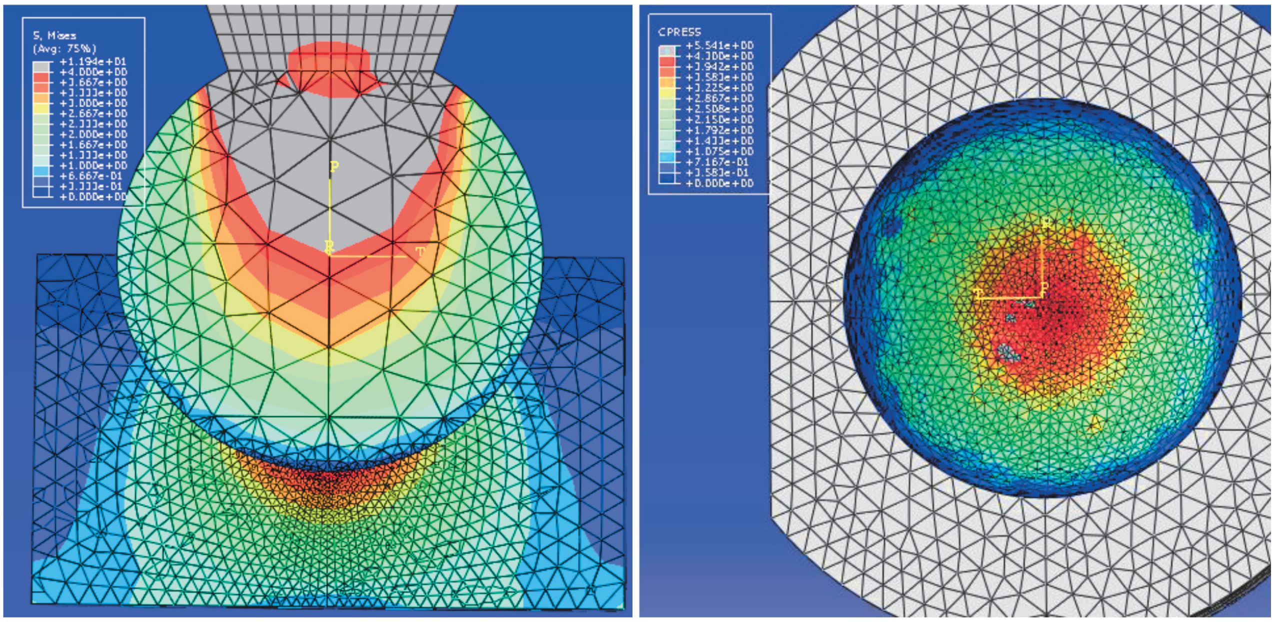

Figure 6 Contact pressure distribution simulated by FEM analysis in the Abaqus program

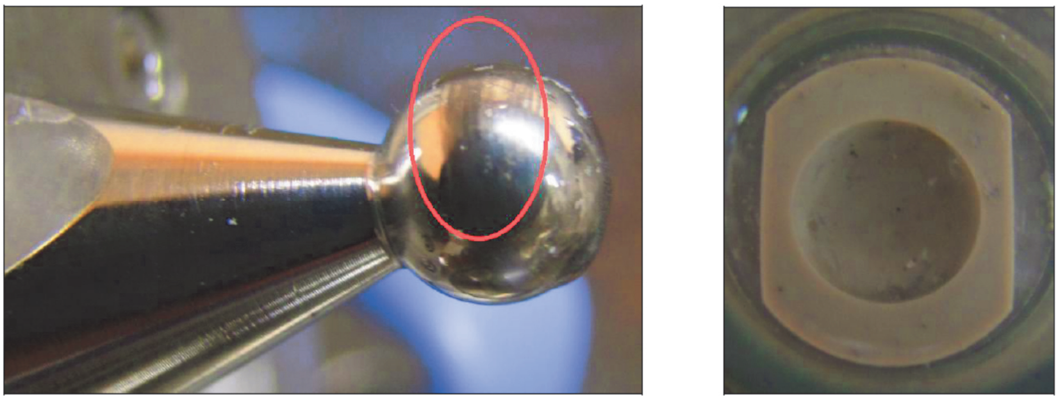

Figure 7 Unmodified Ti6Al4V head and the shell after 10 000 cycles

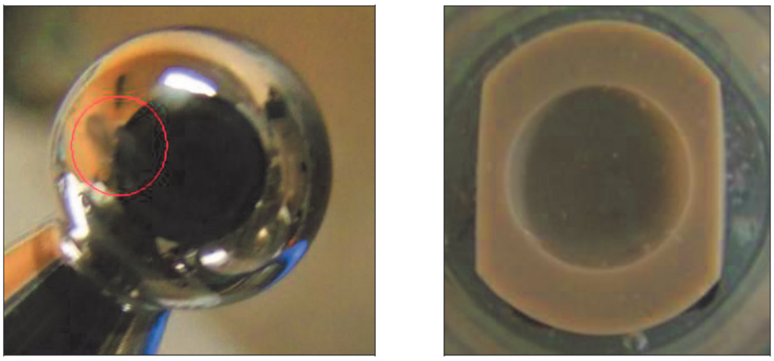

Figure 8 First local wear fault of the BAD 40 nm modification

4. CONCLUSION

Nitrogen ion beam assisted deposition of a carbon-based nanolayer was applied to modify the surface properties of the Ti6Al4V biomedical titanium alloy. The modified surface consisted of a carbon-based nanolayer, a mixed interface, and a nitrogen-enriched sublayer. Ion bombardment caused structural changes, which led to an increase in surface hardness and a decrease in the friction coefficient. The proposed surface modification of the Ti6Al4V joint head under optimized conditions provides protection for functional surfaces, with a resulting reduction in wear and a significant increase in lifetime.

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