Materials Science and Engineering C 34 (2014) 22–28

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Influence of albumin on the tribological behavior of Ag–Ti (C, N) thin films for orthopedic implants

C.F. Almeida Alves [a,*], F. Oliveira [a], I. Carvalho [a], A.P. Piedade [b], S. Carvalho [a,b]

[a] Universidade do Minho, Departamento de Física, Campus de Azurém, 4800-058 Guimarães, Portugal
[b] CEMUC, Departamento de Engenharia Mecânica, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, 3030-788 Coimbra, Portugal

ARTICLE INFO

Article history:
Received 29 April 2013
Received in revised form 28 August 2013
Accepted 22 September 2013
Available online 5 October 2013

Keywords:
Nanostructured coatings
XPS
Hydrophobic surface
Lubrication limit
Critical wetting tension

ABSTRACT

With the increase of elderly population and the health problems arising nowadays, such as cancer, knee and hip joint prostheses are widely used worldwide. It is estimated that 20% of hip replacement surgeries simply fail after 5 years, due to wear loosening, instability and infection. In this paper it is reported the study of advanced materials with the ability to overcome some of these drawbacks. The development of ceramic coatings, based on carbonitrides of transition metals, such as TiCN, doped with silver, Ag, may represent an effective solution. Thin films of Ag–TiCN were produced by dc reactive magnetron sputtering with silver contents ranging from 4 to 8 at.%. The physical, chemical, structural, morphological/topographical, mechanical and tribological properties were evaluated. The tribological tests were performed in a unidirectional wear simulator, pin on disk, being the antagonists of a ceramic Al_2O_3 ball, and using simulate body fluids as lubricant. Hank's Balanced Salt Solution (HBSS) and bovine serum albumin (BSA) in HBSS were chosen, in order to evaluate the lubrication ability of the solution containing the protein, albumin.

The results revealed that the coatings with Ag content ranging from 4 to 8 at.%, were the most promising, as the tribological properties were superior to the results reported by other authors, which also developed Ag–TiCN coatings containing similar Ag contents and using similar test conditions. The presence of albumin leads to a lower wear in all the test conditions, and this enhancement was higher in the hydrophobic surfaces.

1. Introduction

The number of hip arthroplasties has been growing in recent years as a result of increased life expectancy of the world population. The development of materials with the ability to reduce the number of revision arthroplasties is an emerging field, thus contributing to reduce the costs associated with these surgical procedures and above of all to improve of patient's life quality. Considering the aggressive environmental conditions to which they are subjected to, these materials must meet several requirements, namely: biocompatibility, wear and corrosion resistance and resistance to microbial colonization [1]. The development of ceramic coatings, such as DLC [2], transition metal (e.g. Ti, Zr) carbides [3,4], nitrides [5,6] and carbonitrides [7], has been perceived as one of the solutions able to increase the lifetime of orthopedic prosthesis. TiCN coatings are able to comprise low wear rates, low friction coefficients [8] and good corrosion resistance [9], which makes them good candidates for orthopedic implant applications. Despite the major developments in biomaterials field, microbial colonization of the implant surface and consequent infection remains an unsolved problem. In order to overcome this limitation great efforts have been dedicated to the development of biodevices with antibacterial surfaces, being most of them based on the incorporation of Ag nanoparticles [10,11]. Moreover, it is reported that the incorporation of small amounts Ag in TiN [12], CrN [13], ZrN [14], DLC [15] and TaN [16] matrixes is able to reduce the friction coefficient and improve the wear resistance of the base coating, due to the lubricant properties of this metal. Sánchez-López [10] claimed that the incorporation of Ag up to 6 at.% promoted an increase in the TiCN wear resistance. However, for higher Ag contents an opposite trend was reported. Similar results were also found for Ag–TiN, Ag–CrN and Ag–ZrN coating [13]. Furthermore, the addition of high contents of Ag may induce cytotoxicity in the host tissue and consequent rejection of the biomaterial [17]. Also, the incorporation of higher Ag contents promotes the increase in Ag cluster size, thus reducing the surface area and consequently their antimicrobial effect [9]. In this sense, the amount of Ag incorporated in the coatings must be tailored in order to obtain good tribological properties, good corrosion resistance, biocompatibility and antibacterial properties. According to previous studies [9,10] the best compromise for Ag–TiCN coatings was obtained for Ag contents up 6 at.%.

Synovial joints are protected from external agents by articular capsules, containing synovial membrane and synovial fluid, whose role is to maintain the balance between secretion and adsorption of the fluid [18]. This fluid has an extreme complex chemical composition, being mainly composed of an electrolytic solution rich in proteins (mainly albumin), polysaccharides (hyaluronic acid) and water-solved compounds.

* Corresponding author. Tel.: +351 253 510 470.
E-mail address: alves.cristiana89@gmail.com (C.F.A. Alves).

0928-4931/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2013.09.031

Hyaluronic acid is claimed to guarantee a high degree of viscosity, which enables a hydrodynamic lubrication, while albumin is able to increase the lubrication when adsorbed on the surface of joint material. Some studies [19] performed in vitro studies which evaluated the effect of few synovial fluid components, with a special focus on: bovine serum albumin (BSA); hyaluronic acid (HA) and phospholipid suspensions. Each of these components is usually included in a solution with an ionic composition that is similar to the one found in biological fluids, such as Hank's Balanced Salt Solution (HBSS).

In the present study the wear behavior of Ag–TiCN coatings was evaluated for different Ag contents ranging from 0 to 8 at.%. In order to simulate the conditions present in the synovial joints, the tribological tests were performed in a pin-on-disk tribometer for the following conditions: i) without lubrication, ii) using Hank's Balanced Salt Solution (HBSS) as lubrication medium, and iii) using HBSS solution and bovine serum albumin (BSA) as lubrication medium. The objective of this work was to study the effect of albumin in tribological behavior.

2. Experimental details

Ag–TiCN coatings were deposited by reactive dc magnetron sputtering from a high-purity Ti target (200×100 mm^2) and a composed Ag–Ti target onto polished and ultrasonically cleaned 316L stainless steel (20×20 mm^2) and single crystalline silicon (100) (1×1 mm^2). In order to produce Ag–TiCN coatings, 8 Ag nuggets were incorporated on the Ti target, resulting in this composed Ag–Ti target in a relative Ag/Ti erosion area of 22%. To further vary the Ag content in the films the current density applied to each target was varied as indicated in Table 1. The substrates were previously sputter-etched for 20 min in an Ar atmosphere at constant current density of 10 mA/cm^2 and Ar flow of 60 sccm. The depositions were carried out in $Ar + C_2H_2 + N_2$ atmosphere, with the substrates rotating at 70 mm over the target at constant speed of 8 rpm. The base pressure in the deposition chamber was 1.4×10^{-3} Pa, the films were grown at a constant temperature (373 K) and with an applied bias voltage of -50 V. Argon flow was kept constant at 60 sccm while the reactive gas fluxes, C_2H_2 and N_2, were adjusted (in a range of 5.5–7 sccm) as can be depicted in Table 1.

The chemical composition of all surfaces was assessed by electron probe microanalysis (EPMA) using a Cameca, Camebax SX 50 equipment, operating at 10 kV and 40 nA. Ball crater tests were used to measure the film thickness. The structure and phase distribution of the films were determined by X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). XRD analysis of the coatings deposited on Si, was performed using a Philips X'Pert, at 40 kV and 35 mA, with Co radiation ($\lambda k_{\alpha 1} = 0.178896$ nm and $\lambda k_{\alpha 2} = 0.179285$ nm), equipped with collimator and Bragg–Brentano geometry. All the tests were performed with a step size of 0.025° and a time per step of 0.5 s, in 20–120° range. Raman spectra were acquired in a Renishaw 2000 apparatus, operating with an Ar laser (514.5 nm) and the spectra were acquired in a range of 150–2000 cm^{-1}. The XPS analyses were performed in a VG-ESCLAB 250iXL spectrometer. The pressure in the analysis chamber was kept below 5×10^{-8} Pa and the analysis was performed using monochromatic radiation Al-Kα ($h\nu = 1486.92$ eV). The photoelectrons were collected with an angle of 90° with respect to the surface of samples. The energy step was of 20 eV for the survey spectra and of 0.05 eV for the high-resolution spectra. The C1s line at 285.0 eV (hydrocarbon peak) was used to calibrate the binding energies. The XPS was also used for the in-depth analysis of the thin films by sputtering the surface with 3 keV Ar + beam. The chemical compositions were obtained using the sensitivity factor of the Scofield library.

The morphology/topography of the coatings, was evaluated by atomic force microscopy (AFM) using a NanoScopeIII a model from Digital Instruments operating in tapping mode. AFM images were taken over scanning areas of 10×10 μm^2. The wettability characteristics of the surfaces were assessed by measuring the static contact angle with 10 μl of distilled and deionized water, glycerol and formamide in a DataPhysics QCA-20 apparatus. For each sample, a minimum of seven measurements was taken, after allowing the system (air/water/surface) to reach equilibrium, and the average value was calculated.

The hardness and the Young modulus were measured by nanoindentation test (Micro Materials Nano Test) using a Berkovich indenter. The normal stylus load was 10 mN and the results are the average of 15 independent indentations.

The tribological properties of Ag–TiCN coatings were studied using a pin-on-disk tribometer. All the tribological measurements were performed at identical conditions: 10,615 laps at 1 Hz, total distance of 500 m, normal load 2 N, linear speed 50 mm/s, counterpart Al_2O_3 ball with a diameter of 10 mm, room temperature and relative air humidity of 35%. All coatings underwent testing at three different conditions: dry sliding in humid air, lubricated sliding in HBSS solution and lubricated sliding in a HBSS + BSA solution, which is the most common lubricant used to reproduce synovial liquids. The concentration of BSA used in all tribological tests was 10 g/l, in agreement with literature [20]. The tribological performance was examined with respect to the wear rates of the coating. The coating wear rate was evaluated on the basis of profile measurements on the wear track. The wear rates were determined according to ASTM G 99-04 (2004) Standard Test Method for Wear Testing with Pin-on-Disk Apparatus. In order to evaluate the dominant wear mechanism, the wear tracks were studied using 3D profilometry (Mahr RM600-S).

3. Results and discussion

3.1. Physical and chemical characterization

The deposition parameters, the chemical composition, the thickness and some mechanical properties of the coatings are summarized in Table 1. The deposition rate ranged from 1.1 to 1.6 μm increasing with the current density applied to both targets ($J_{Ti+Ag} + J_{Ti}$). Although a decrease on the density applied to the Ti target and an increase on the density on the TiAg target are observed, the sum of current densities applied to both targets is increasing. To justify the increased deposition rate one should take into account the increase on the sum of current density applied to both targets, which corresponds to an increase in ion bombardment and proportionally the amount of ejected atoms. The elemental chemical composition shows that by increasing the J_{TiAg}/J_{Ti} current density ratio, the Ti content in the coatings decreases from 37 to 21 at.% along with an increase in the Ag content from 0 to 8 at.%. The N content decreases slightly from 31 to 24 at.% and the C content increases from 28 to 42 at.%. In fact, the Gibbs free energy for the formation of TiN phases is -290 kJ/mol and for TiC is -180 kJ/mol. Therefore with decreasing Ti content an increase on the carbon content is observed since there is a clear trend to the formation of thermodynamically more stable carbon

Table 1
Chemical composition, deposition parameters, thickness, hardness and Young's modulus of the deposited samples.

Sample	Chemical composition (at.%)					$Ø_{C_2H_2}$ (sccm)	$Ø_{N_2}$ (sccm)	J_{Ti} (mA/cm^2)	J_{TiAg} (mA/cm^2)	J_{TiAg}/J_{Ti} (mA/cm^2)	Deposition rate (μm/h)	Thickness (μm)	Hardness (GPa)	Young's modulus (GPa)
	C	N	O	Ti	Ag									
TiCN	28	31	4	37	0	6	6	10	0	0	1.3 ± 0.06	2.1 ± 0.06	15 ± 1.1	232 ± 28
Ag4TICN	33	30	3	30	4	7	7	10	2.5	0.25	1.6 ± 0.04	2.0 ± 0.04	16 ± 1.5	214 ± 33
Ag8TiCN	42	24	5	21	8	5.5	5.5	5	3.75	0.75	1.1 ± 0.05	1.8 ± 0.05	14 ± 1.5	154 ± 14