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Tribocorrosion response in biological environments of multilayer TaN films deposited by HPPMS

Lucia Mendizabal [a,*], Ainara Lopez [b], Raquel Bayón [b], Pilar Herrero-Fernandez [c], Javier Barriga [a], Javier J. Gonzalez [d]

[a] Department of Surface Physics and Technology, IK4-TEKNIKER, Iñaki Goenaga 5, 20600 Eibar, Spain
[b] Department of Tribology, IK4-TEKNIKER, Iñaki Goenaga 5, 20600 Eibar, Spain
[c] Instituto de Ciencia de Materiales, CSIC, S. Ángela de la Cruz 3, 280046 Cantoblanco, Madrid, Spain
[d] Department of Materials Science, ETSIB University of Basque Country, Alameda de Urquijo s/n, 48013 Bilbao, Spain

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ABSTRACT

Biomedical implant failure arises mainly from the degradation caused by tribological processes occurring in the corrosive environment the human body represents, known as tribocorrosion. The material loss and metal ion release resulting from tribocorrosion processes compromise the biocompatibility of metallic implants. The deposition of protective coatings on metallic substrates is a promising solution to overcome this problem. Pure titanium (Ti-cp) is widely used as an implant material due to its excellent corrosion resistance and high biocompatibility. However, its mechanical properties must be improved in order to ensure a longer durability. For this purpose, TaN monolayer and multilayer coatings were deposited on medical grade Ti-cp to enhance its tribocorrosion performance in simulated body fluids. TaN coatings were deposited by recently developed High Power Pulsed Magnetron Sputtering (HPPMS) technique. HPPMS enables the deposition of extremely dense coatings with superior properties compared to the ones grown by conventional sputtering. Columnar-free TaN monolayer and multilayer films were developed exhibiting corrosion resistances in the MΩ range, one order of magnitude higher than for Ti-cp. Friction coefficient of Ti-cp was reduced from 0.58 to 0.25 while wear rate was considerably decreased. The determined material loss after tribocorrosion tests for Ti-cp was 0.4 mm^3. It was reduced up to 1.55×10^{-3} mm^3 by the application of best-performing TaN multilayer film.

1. Introduction

Changes in life expectancy as well as in life style of the population particularly in the industrial nations lead to significantly increasing demands for total joint arthroplasty, a trend which is likely to continue for the next decades [1–3]. Hip and knee joints are the two most common replacements nowadays and they exhibit an excellent success rate of about 95%. However, they can assure a lifetime service of around 10–15 years but not longer, and the actual society is demanding long-term durability artificial joints since the implants are now expected to serve for a much longer period of time without failure or revision surgery. The main drawbacks to ensure a longer lifetime for the implants include both the biocompatibility decrease due to the release of metal ions into the body [4,5] and the material loss caused by tribocorrosion mechanism which involves the synergistic effect of wear and corrosion processes simultaneously [6,7].

Generally, the most common materials used in orthopedic implants are metals. Currently, the most representative metallic biomaterials are stainless steels, cobalt (Co)–chromium (Cr) alloys, and titanium (Ti) and its alloys. Among these metallic biomaterials, Ti-based alloys exhibit the highest biocompatibility, corrosion resistance, and specific strength (ratio of the tensile strength to density) [8]. However, Ti and its alloys exhibit poor wear resistance and high coefficients of friction. Poor abrasive wear resistance results in the formation of wear debris at the implant area, inducing metal ion release, inflammation and pain. Significant improvements can be obtained by the application of protective hard coatings (e.g. some transition metal nitrides) characterized by high hardness and toughness, low elasticity modulus, and enhanced wear and corrosion resistance in body fluids along with good biocompatibility [9].

This paper presents an investigation about the corrosion-wear behavior of different tantalum nitride (TaN) coatings deposited by High Power Pulsed Magnetron Sputtering (HPPMS) technique intended to be used as protective films for orthopedic implant applications. TaN is a transition metal nitride characterized by high hardness and wear resistance [10]. Besides this, tantalum is one of the most chemically inert and biocompatible material, showing an outstanding corrosion performance in many corrosive environments, even comparable to that of noble metals [11].

* Corresponding author.
E-mail address: lucia.mendizabal@tekniker.es (L. Mendizabal).

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HPPMS is an ionized physical vapor deposition (i-PVD) technology developed in the 90s in order to overcome the main drawback of dc-magnetron sputtering, i.e. the low ionization degree of sputtered atoms (<5%). During HPPMS discharge, the power is applied to the cathode in very short pulses of low duty cycle and frequency which prevents target overheating while increasing peak power density values up to several kW cm^{-2} (2 orders of magnitude higher than during dcMS discharge) [12,13]. Such high peak power density values lead to the generation of ultra-dense plasmas, characterized by high ionization degree of sputtered particles. Consequently, thin film growth can be assisted by energetic ion flux bombardment from sputtered material, allowing the modification and densification of film microstructure and development of coatings characterized by excellent adhesion and flat surface. The possibility to control the direction of the ions by substrate bias promotes the deposition of uniform coatings in complex-shape substrates [14–16].

The deposition technique employed during this investigation is a variation of traditional HPPMS, the so-called modulated pulsed power magnetron sputtering (MPPMS) [17,18]. The waveforms of the target voltage, current and power in one MPPMS pulse can be arbitrarily modulated to different steps and durations, which provide more flexible deposition process control than traditional HPPMS [19]. The MPPMS generator offers the possibility to develop structurally laminated multilayer films by alternately switching between different pulse shapes in the same target within one overall process. This mode of operation has been defined by J. Lin and co-workers as multipulse MPPMS technique [20]. Each pulse is applied to the target for a certain duration (t) which mainly determines the thickness of each nanolayer and the bilayer period of the multilayer film. The application of different pulse shapes leads to the development of different plasma discharge characteristics defined by distinct peak power (P_p), peak current (I_p) and peak voltage (V_p) values. It is well-known that plasma features strongly influence the properties of the growing films. Hence, the application of different pulse shapes along the deposition process creates alternate TaN nanolayers featured by different microstructures and properties leading to structurally laminated TaN multilayer films. Multilayer films commonly exhibit better wear and corrosion resistance than monolayer ones. The presence of a higher number of interfaces preventing the movement of dislocations and the propagation of micro-cracks increases wear resistance [21]. The re-nucleation process present in multilayer structures reduces the amount of pores, thereby resulting in better corrosion resistance compared to monolayer films [22].

In the current study, three different TaN systems have been analyzed. Two different multilayer TaN films, characterized by different bilayer periods deposited by multipulse MPPMS using two pulse shapes with different pulse repeat durations and a monolayer TaN film deposited by a single MPPMS pulse on pure titanium (Ti-cp) substrates. The microstructure and mechanical properties of these films were correlated with the corrosion and tribocorrosion response of these coatings and compared with the uncoated Ti-cp.

2. Experimental details

The coating processes were performed in a closed field unbalanced magnetron sputtering semi-industrial system designed at IK4-TEKNIKER and equipped with three rectangular evaporators (500 × 133 mm). A metal Ta target (99.9% purity) was reactively sputtered in Ar + N_2 atmosphere using a MPP power supply (SOLO/AXIS-180™ Pulsed DC Plasma Generator, Zpulser LLC.).

The TaN films were deposited on pure titanium (grade 2) disks of 24 mm in diameter and silicon wafers. Prior to deposition, the substrates were subjected to 10 min of Ar plasma etching to remove surface contaminants and enhance the adhesion between the substrate and the coatings. The selected process parameters were previously optimized for the deposition of columnar-free and most corrosion-resistant TaN monolayer film. The working pressure was 0.6 Pa with a constant argon-to-nitrogen ratio of 0.25. For all coatings, a thin Ta interlayer of 100 nm was applied for enhancing the adhesion. The average power was set to 4 kW during all TaN deposition processes. Two fold substrate rotation and 350 °C substrate temperature were used during depositions, while a bias potential of −50 V was applied on the substrate. The deposition time was established at 125 min.

The voltage–current characteristics of the two pulse shapes (pulses 1 and 2) employed for TaN multilayer depositions are shown in Fig. 1. Pulse 1 was also utilized for the deposition of TaN monolayer film. The pulse length, frequency, pulsing parameters and deposition rate for each pulse shape are summarized in Table 1. Two pulses with high variation on peak current density were selected to obtained nanolayers with different hardness, density and wear resistance. The industrial deposition chamber configuration does not allow the measurement of the ion flux at the substrate. The time during which a given pulse shape was applied, i.e. pulse repeat duration (t), was 5 and 2 min for TaN multilayer_1 and TaN multilayer_2, respectively, which lead to different bilayer periods for each coating as shown in Table 2.

The natural physiological environment contains not only inorganic species but also organic molecules such as serum proteins [23]. Thus, a Phosphate Buffered Solution (0.14 M NaCl, 1 mM KH_2PO_4, 3 mM KCl, 10 mM Na_2HPO_4) plus 1 g of albumin was chosen as experimental electrolyte for this study in order to accurately reproduce the human body fluid environment [24,25].

The thickness and coating composition was analyzed by glow discharge optical emission spectroscopy (GD-OES) using a GD-PROFILER 2 manufactured by Horiba Jobin Yvon. GD-OES is a qualitative method. Quantified profiles can be obtained after calibration. Calibration procedure is based on the comparison between measured intensities of the unknown sample with those measured using a standard material of known composition. An adequate calibration would need different elemental composition TaN reference sample measurements to compare with the unknown sample. In this study, just Ta reference samples of known composition were used to establish a relationship between emission intensities and elemental composition of TaN_x coatings. Hence, the given elemental composition values of TaN_x are relative. Microstructure and wear tracks after tribocorrosion tests were studied using the High Resolution FE-SEM Ultra plus Zeiss equipment, a scanning electron microscope with field emission gun. Cross-sectional samples deposited onto Si substrates were prepared for transmission electron microscopy (TEM), by dimple-grinding with a Gatan 656 dimpler and Ar ion-milling with a Fischione 1010 model until an electron transparent area was obtained at the center of the sample. The procedure is fully described in reference [26]. Transmission electron microscopy studies were done using a JEOL 3010F microscope with a field-emission gun, 300 kV acceleration voltage and 0.17 nm of structural resolution. Image processing of the high-resolution images was carried out using Gatan Digital Micrograph and Image J software packages. For hardness measurements, a Fischerscope H100VP was employed with Vickers indentation equipment, and the value was calculated from the application of Oliver and Pharr method [27].

Before the corrosion and tribocorrosion tests, the samples were cleaned with isopropyl alcohol and then 1 cm^2 and 2.54 cm^2 areas were delimited with the help of a Slotowax sealant for corrosion and tribocorrosion tests, respectively. The corrosion and tribocorrosion performance was analyzed by using a potentiostat PGSTAT 30 N Autolab-Metrhom connected to a three-electrode electrochemical cell. The reference electrode was an Ag/AgCl (KCl 3 M) with a potential of 0.207 V versus standard hydrogen electrode; a platinum wire was the counter electrode and the surfaces evaluated were the working electrodes. Tests were carried out at room temperature and under aerated conditions.

The corrosion performance was studied by using electrochemical impedance spectroscopy (EIS) technique. Electrochemical Impedance Spectroscopy (EIS) measurements were registered at open circuit

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