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Synthesis and biological characterization of zirconium oxynitride thin film growth by radio-frequency sputtering

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ABSTRACT

Thin films of zirconium oxynitride were grown on common glass, silicon substrates (100) and on stainless steel 316L using the reactive RF magnetron sputtering technique. The films were analyzed through structural, morphological, and biocompatibility studies. The structural analysis was carried out using X-ray diffraction (XRD), and the morphological analysis was carried out using scanning electron microscopy (SEM) and atomic force microscopy (AFM). These studies were done as a function of growth parameters, such as power applied to the target, substrate temperature, and flow ratios. The studies of biocompatibility were carried out on zirconium oxynitride films deposited on stainless steel 316L through proliferation and cellular adhesion. The XRD analysis showed that films deposited at 623 K, with a flow ratio $\Phi N_2/\Phi O_2$ of 1.25 and a total deposit time of 30 min grew preferentially oriented along the (111) plane of the zirconium oxynitride monoclinic phase. The SEM analyses showed that the films grew homogeneously, and the AFM studies indicated that the average rugosity of the film was 5.9 nm and the average particle size was 150 nm. Finally, through the analysis of the biocompatibility, we established that the films have a better surface than the substrate (stainless steel 316L) in terms of adhesion and proliferation of bone cells.

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1. Introduction

Biomaterials with orthopedic uses must have excellent physical–chemical properties that should allow the osseointegration of the biomedical devices and implants, but despite the good mechanical properties of biomaterials, the loosening of the implant as a result of poor osseointegration remains a frequent complication. To avoid this problem, and knowing that "the initial response of the living tissue to the biomaterial depends on the surface properties" [1], over the last few years surface modification techniques for biomaterials have been developed. "In this way, it is possible to make biomaterials with ideal surface attributes, such as topography and functionality, to enhance the osseointegration of the implant, for example, by altering the functionality through the deposition of a thin film, the physical–chemical properties of the surface of a biomaterial can be modified, in order to increase its bioactivity" [2].

For the foregoing reasons, thin films of metals such as Ti and alloys (Ti6Al4V and AISI 316L steel) have been used in biomedical applications [3–5]. For these biomedical applications, during recent decades Ti and its oxides have been the materials most widely used, because they have a high anticorrosive resistance within the aggressive body environment; however, nowadays research is being carried out that seeks to increase the lifespan of the prosthesis through processes of proliferation and adhesion of bone cells on thin films of, for example, niobium, zirconium, and tantalum and its oxides [5].

Taking advantage of the fact that the surface characteristics are relevant for the interaction between the implant and the living tissue [6,7], we proposed to make use of thin film technology to modify any base material with a biocompatible coating. The coating material would be ceramic, such as zirconium oxynitride (ZrO_xN_y), a material that can be easily and inexpensively produced through thin film deposition techniques.

The growth of oxynitride films is strongly influenced by the amount of oxygen molecules and nitrogen present in the deposition chamber. This influence has been studied by Martin et al. [8], who deposited TiN_xO_y using the pulsing gas technique and found that the chemical composition, structural evolution, and electrical response vary as a function of the values of x and y. The techniques mostly used to prepare oxynitride films are reactive RF/DC magnetron sputtering, and cathodic reactive arc evaporation [9].

The purpose of the present study was to evaluate the biocompatibility of zirconium oxynitride thin films deposited on stainless

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steel, using reactive RF magnetron sputtering, through the analysis of the proliferation and adhesion of bone cells.

2. Experimental techniques

2.1. Growth of the ZrN_xO_y films

The equipment used to grow the ZrN_xO_y films was an Alcatel HS 2000, described in previous papers [10]. The ZrN_xO_y films were obtained from a 4 in. × 1/4 in. Zr (99.9%) target (CERAC, Inc.). The parameter set used during the deposition process was: base pressure at 2.0×10^{-3} Pa, total working pressure at 7.4×10^{-1} Pa, deposition time of half hour, target–substrate distance at 5 cm, and argon (99.999%) flow at 20 sccm. We studied the influence of several deposition parameters, such as: power supplied to the target (from 200 W to 350 W), substrate temperature (which varied from 287 K to 623 K), and flow ratios of N_2 (99.99%) and O_2 (99.99%) (1.0, 1.25, and 1.50) inside the deposition chamber. The final working pressure was maintained using a valve controller for all the ratio flow values given above. The temperature of the substrate was measured with a thermocouple type K, and the argon, nitrogen and oxygen flows were controlled with mass flow controllers. The structural characterization of the films was performed through X-ray diffraction (XRD) with a Philips diffractometer operated at 30 kV and 20 mA, working in the Bragg–Brentano configuration and using Cu Kα radiation. The average crystalline size was calculated from $s = 0.9\,k/B\cos\theta$, where $B = B_m - B_i$, B_m being the broadening of the diffraction line measured full width at half maximum (FWHM), and B_i the instrument peak width [11]. Surface morphology was characterized by imaging the secondary electrons with a Quanta 2000 scanning electron microscope operating at 15 kV and 10 mA and with a non-contact atomic force microscopy (AFM) Autoprobe cp Park Scientific instrument with a tip radius of 10 nm, study area of 25 μm^2, and frequency of 10 Hz.

2.2. Biological tests

Bone lineage cells from nursing mice were suspended in a 1:1 solution of DMEM (Dulbecco's Modified Eagle's Medium) supplemented with 10% fetal bovine serum, 100 U/mL penicillin, 100 mg/mL streptomycin, 0.25 mg/mL amphotericin B, 10 mM betaglicerofosfato, 100 uM L-ascorbic acid-2-phosphate, and 10 nM dexamethasone. This was centrifuged at 1200 rpm for 10 min, and the precipitate was suspended in 1 mL of the medium described. The solution was transferred to a well of 35 mm^2 with an additional 1 mL of the medium and transferred to an incubator at 310 K with an atmosphere of 5% CO_2 in order to allow cell adhesion. At 48 h, there was 100% confluence, and the first cell passage was made. Stainless steel samples with and without coatings were sterilized by autoclaving for 30 min at 423 K and placed in boxes of six wells. Then, they were added with 10,000 cells, which were obtained from the first passage, and suspended in the medium described. These samples were incubated at 310 K with an atmosphere of 5% CO_2.

When cell confluence was obtained, the samples were extracted from the culture medium and washed three times with PBS (Phosphate Buffer Solution) at 310 K. The PBS solution was discarded, and the samples were immersed in 2 mL of 2.6-diamidino-2-phenylindole (DAPI) (SIGMA D9542) at a concentration of 1 mg/mL at 277 K. After 12 h, the samples were removed and washed three times with PBS at 277 K in order to be deposited on glass slides.

DAPI-stained cells on coated and uncoated stainless steels were observed using fluorescence confocal microscopy (NIKON C1-Plus) and were captured in photographs. For image analysis, a series of algorithms was used, which were merged into the program Matlab (image toolbox) in order to convert the original color images to grayscale and apply algorithms and image processing (segmentation, threshold and filtering) to reduce the noise.

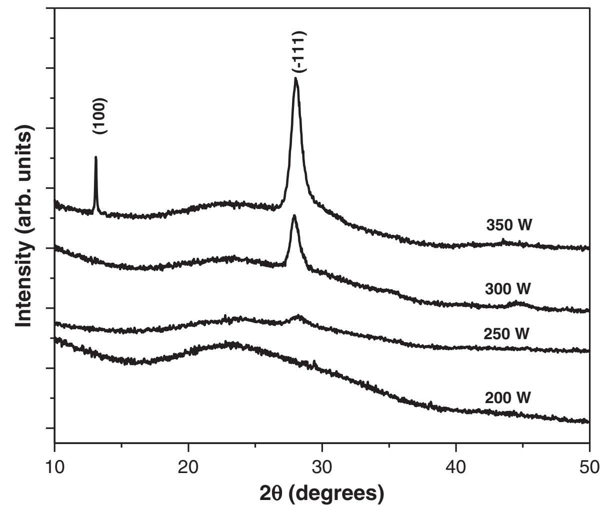

Fig. 1. XRD patterns recorded from ZrN_xO_y films deposited on common glass substrate at 623 K, 2.0 sccm of oxygen and 2.5 sccm of nitrogen flows at different powers.

To do the cell counting, conventional border detection was performed, and the regions with the cells to be studied were identified, considering the edges and the fixed threshold. Two masks were applied, binary gradient and expansion gradient, obtaining binary images, segmented and linearized with threshold contrast to label the cells in order to determine their distribution and number.

3. Results and discussion

3.1. Structural and morphological analyses of ZrN_xO_y thin films

X-ray analysis was carried out to determine the evolution of the structure of the ZrN_xO_y films as a function of the different parameters of growth. Fig. 1 shows the XRD pattern of the ZrN_xO_y thin films grown at 623 K with various degrees of power supplied to the target and keeping the ratio between N_2 and O_2 at 1.25″ constant. The XRD study established that the films evolved from an amorphous phase (200 W) on monoclinic polycrystalline film (350 W), which has two planes, the first located at 12.96° and the other at 27.94°. The first plane has been reported by Mazzoni et al. [12] as the (101) plane of the β′ phase of the $Zr_7O_{11}N_2$ (PDF 48–1637), and the second as the

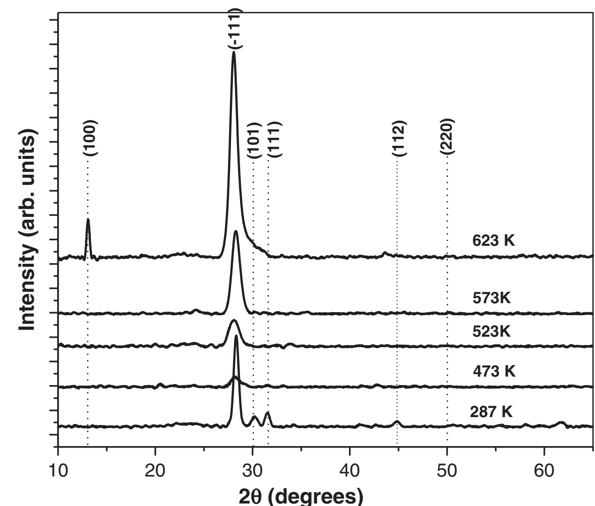

Fig. 2. XRD patterns recorded from ZrN_xO_y films deposited on common glass substrate at 350 W, 2.0 sccm of oxygen and 2.5 sccm of nitrogen flows at different substrate temperatures.

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