



## Wear and corrosion properties of *in-situ* grown zirconium nitride layers for implant applications



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### ARTICLE INFO

**Keywords:**  
Zirconium  
Nitriding  
ZrN  
*In vitro*  
Wear  
Corrosion

### ABSTRACT

Zirconium (Zr) and its alloys are considered as promising materials for implant applications due to their excellent biocompatibility. However, the poor tribological properties of Zr are limiting its widespread applications. Therefore, in this investigation thermal nitriding of laser processed Zr was carried out with an aim to improve its wear and corrosion properties for potential wear resistant implant applications. The influences of nitriding temperature and time on the nitride layer thickness, phase constituents, wear and corrosion properties of nitrided Zr layer were studied. The Zr samples were nitrided at 600 °C and 800 °C for 2 and 6 h in flowing nitrogen. The results demonstrated that the nitriding temperature had relatively stronger influence on the nitride layer thickness, wettability, hardness and wear resistance than nitriding time. In general, the nitride layers found to contain ZrN and ZrO<sub>2</sub> as major phases and Zr<sub>2</sub>N and Zr<sub>7</sub>O<sub>8</sub>N<sub>4</sub> as minor phases. The nitride layer thickness increased from 5 ± 0.7 μm to 26 ± 5 μm with increase in the nitriding temperature and time. Nitriding also enhanced the wettability and passivity of Zr. The samples nitrided at 600 °C for 2 h resulted in noblest E<sub>corr</sub> of -130 mV vs SCE with I<sub>corr</sub> of 0.001 μA/cm<sup>2</sup> in Hank's balanced salt solution. Lowest *in vitro* wear rate of 4.4 × 10<sup>-7</sup> mm<sup>3</sup>/N·m was recorded, against Al<sub>2</sub>O<sub>3</sub>, when the samples were nitrided at 800 °C for 6 h, which is 93% lower than that of pure Zr. These results demonstrate that thermal nitriding of Zr can be used to increase the corrosion and wear resistance of Zr in physiological environment.

### 1. Introduction

Total Joint Replacement (TJR) is currently a well-established surgical technique for the patients suffering from severe joint pain and in India around one million people receive TJR every year [1]. It has been predicted that by 2030 around 80 million people, below 40 years of age, require hip implants worldwide [2]. In general, the average service life of a typical hip implant varies between 10 and 15 years. Currently materials such as 316L stainless steel, cobalt chromium alloy, Al<sub>2</sub>O<sub>3</sub> and zirconia-toughened alumina are commonly used as femoral component of total hip replacement (THR) prosthesis, articulating against ultra high molecular weight polyethylene (UHMWPE). It is known that the wear of UHMWPE is a major concern of THR that leads to osteolysis, implant loosening and failure of the implants. Ries et al. [3] attempted to reduce the wear rate of UHMWPE via design modifications. However, the counter surface properties such as coefficient of friction and resistance to roughening found to have strong influence in reducing the wear of UHMWPE [4,5] compared to the proposed design modifications. In addition, the ions released from metallic articulating materials

such as CoCrMo alloy, found to be toxic leading to swelling and implant loosening [6,7]. As a result, ceramic-on-ceramic configurations have been proposed to reduce the wear rate of UHMWPE and eliminate ion release, which demonstrated extremely low wear rates [8]. The superior tribological performance of ceramics than metals, against UHMWPE, has been attributed to their ability to chemisorb lubricating compounds from the physiological media as result of their high surface energy and wettability providing low friction surface [9–11].

Since bulk ceramics are inherently brittle, ceramic coated metal surfaces have gained significant importance, in the recent past, due to their high wear resistance, wettability and low coefficient of friction which can potentially reduce the wear of UHMWPE [12] and also act as barriers to ion leaching from the metals beneath. Several hard coatings such as titanium nitride (TiN), titanium niobium nitride (TiNbN), diamond-like carbon, zirconium oxide and TiB-TiN metal matrix composite coatings have been developed to address the wear induced osteolysis in THR [12–16]. These ceramic coatings found to exhibit good *in vitro* wear resistance and biocompatibility [13–17].

It is well known that the long-term stability of hard ceramic

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coatings, on metals, depend on the coating-substrate interfacial characteristics such as sharp interface, bond strength and inter diffusion of the coating and the substrate materials. Therefore, the coatings which are *in-situ* grown can provide superior interfacial characteristics than externally deposited coatings, thus ensuring long-term stability of these wear resistant coatings [12]. Commercially available material known as OXINIUM™ (oxidized zirconium-2.5% niobium alloy) with 5 µm thick monoclinic ZrO<sub>2</sub> layer, grown *in-situ* using thermal treatment, is one such example. Wear testing of oxidized Zr-Nb alloy, under *in vitro* conditions, revealed low coefficient of friction against UHMWPE and thus decreased its wear by five times [18]. The joint simulator testing on these oxidized Zr implants also showed significantly lower friction and wear of UHMWPE inserts compared to that of CoCrMo alloy implants [19,20]. Tribological studies using hip joint simulators demonstrated that the wear of highly cross-linked UHMWPE against oxidized Zr is 15 times less and the wear debris generation was also four times less compared to standard CoCrMo alloy implant [21]. It is also known that the roughness of articulating implants changes during service, due to pitting and third body wear, which can influence the long-term stability and wear performance of these materials. However, DesJardins et al. [22], demonstrated that intentionally roughened oxidized Zr-Nb alloy generate significantly less wear debris (16.6 ± 7.6 mg/million cycles) compared to CoCrMo alloy (92.0 ± 24.4 mg/million cycles). Recently, a two-step oxidation of Zr-Nb alloy has been proposed to increase the critical load required to break the top ceramic layer [23]. In this process, initially the alloy is thermally oxidized in air to thicken the hardened layer (below the top ceramic layer) by diffusion of oxygen from the top ceramic layer followed by a vacuum heat treatment. Similarly, Balla et al. [16] formed fully dense and strongly adherent 7.0 ± 2.5 µm thick *in-situ* grown ZrO<sub>2</sub> layer on zirconium (Zr) using laser assisted oxidation. This non-toxic oxide layer exhibited low coefficient of friction and wear rate due to its high surface energy and wettability. Such *in-situ* grown oxide or nitride layers would become potential articulating surfaces with excellent wear and corrosion resistance properties in hostile environments such as found in human body. Moreover, these *in-situ* grown layers are strongly adherent to the substrate and therefore not susceptible to delamination or catastrophic fracture. Therefore, in this study we have attempted to grow *in-situ* nitride layer on Zr using conventional thermal treatment. The hard nitride layer is expected to provide good wear, scratch and corrosion resistance to underneath Zr substrate. The influence of heat treatment temperature and time on the layer thickness, wettability, hardness, *in vitro* wear and corrosion resistance was evaluated. Within our knowledge there is no reported work on the formation of *in-situ* nitride layer on Zr using conventional heat treatment. If successful the proposed thermal nitriding can be extended to Zr alloys currently in use for THR.

## 2. Materials and methods

### 2.1. Preparation of Zr and *in-situ* grown ZrN layers

Zirconium (Zr) metal powder (TLS Technik GmbH & Co., Germany) with 99.9% purity and 50 to 120 µm size was used as precursor material to fabricate cylindrical samples (Ø 10 mm and 60 mm long) using laser engineered net shaping (LENS™) (LENS MR7, Optomec Inc. Albuquerque, NM, USA). The LENS™ system is equipped with 500 W continuous-wave Ytterbium doped fiber laser. Based on our preliminary experiments, 300 W laser power, 15 mm/s scan speed and 3 g/min powder feed rate was used to achieve fully dense Zr cylinders. The fabricated cylindrical samples of Zr were sliced into 2 to 2.5 mm thick discs and the surfaces of the discs were polished following standard metallographic sample preparation steps. All samples were ultrasonically cleaned in acetone before thermal treatment. To grow thick nitride layer the polished Zr disks were heat treated in a standard tubular furnace, under flowing 99.98% pure N<sub>2</sub> gas (3 ltr/min at 1.5 bar), at 600 and 800 °C for 2 and 6 h. The furnace was evacuated

(~5 × 10<sup>-3</sup> Torr) for 30 min before releasing the N<sub>2</sub> gas followed by heating (4 °C/min) to required nitriding temperature. After soaking for predetermined time at desired nitriding temperature, the samples were cooled to room temperature at a rate of 4 °C/min under flowing N<sub>2</sub> gas. The nitrided samples were referred as ‘temperature-time’ i.e., samples nitrided at 600 °C for 2 h were named as 600-2.

### 2.2. Thickness, phase constituents and wettability of ZrN layers

The nitride layer thickness was measured using cross-sectional images recorded using scanning electron microscope (SEM, Phenom ProX, Netherlands). An average of 25 measurements at different locations along the layer length was reported. The composition of the nitrided layers was analyzed using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, Physical Electronics Inc., MN, USA) with Al-Kα source. After surface scan, for a quantitative analysis, narrow spectra were obtained for O<sub>1s</sub>, N<sub>1s</sub>, Zr<sub>3d</sub>. The atomic concentration of the species in the nitrided layers was determined using standard background subtraction and other signal intensity corrections. SEM was also used to examine the surface of nitrided samples before and after tribological and corrosion testing to evaluate the wear and corrosion damage, respectively. X-ray diffraction (XRD) analysis was carried out using D500 Kristalloflex diffractometer (Siemens) to evaluate the phases present in the nitride layers.

Surface roughness of the samples was measured using non-contact surface profilometer covering an area of 9.47 mm<sup>2</sup> and an average of 5 measurements was reported. In order to evaluate the wettability contact angle measurements were performed on Zr samples before and after nitriding. Before contact angle measurement, the samples were ultrasonically cleaned in the alcohol bath. For each sample and liquid (water) combination, an average of 5 measurements was reported. Vickers microhardness measurements (W4303, ESEWAY, UK) were performed on bare Zr and nitride surfaces at 50 g load.

### 2.3. *In vitro* tribological and electrochemical testing

Rotating ball-on-disk type wear testing machine (NANOVEA Microphotonics Inc., CA, USA) was used to perform *in vitro* wear tests in freshly prepared simulated body fluid (SBF) at 37 ± 1 °C. The test samples (n = 3) were rotated at a speed of 1800 mm/min against a stationary Al<sub>2</sub>O<sub>3</sub> ball of Ø 3 mm (NANOVEA Microphotonics Inc., CA, USA) for a sliding distance of 500 m. We have used Al<sub>2</sub>O<sub>3</sub> ball with hardness of ~1500 HV as a counter body to eliminate the effect of counter body wear on the wear properties of nitrided Zr. Our preliminary experiments using Al<sub>2</sub>O<sub>3</sub> on these nitrided samples confirmed the absence of any wear and damage on Al<sub>2</sub>O<sub>3</sub> counter body. The normal load used in the present work was 5 N resulting in initial contact stress of 1392 MPa and 2245 MPa on pure Zr and ZrN layers, respectively, with elastic modulus of 91 GPa for pure Zr, 300 GPa for ZrN [24] and 314 GPa for Al<sub>2</sub>O<sub>3</sub>. These contact stresses are ~10 times higher than the loads experienced by a 28 mm hip with a 50 µm radial clearance during level walking. Therefore, the present wear tests represent severe service conditions. After wear testing the wear track depth and width were measured using non-contact surface profilometer. The average wear rate (mm<sup>3</sup>/N·m) of the sample was calculated using measured wear track depth and width.

Electrochemical tests were performed in Hank's balanced salt solution (HBSS) using multichannel potentiostat/galvanostat (SP300, Bio-Logic SAS, France). A three electrode cell with saturated calomel electrode (SCE) as a reference electrode, platinum mesh as a counter electrode and the Zr disc, with and without nitride layer, as working electrode was used. All samples were ultrasonically cleaned in acetone for 10 min before corrosion testing. Prior to polarization study, the samples were allowed to stabilize in HBSS for 1 h to obtain a stable open circuit potential (OCP). The corrosion tests were performed between -0.25 V to +1.6 V vs OCP at a scanning rate of 10 mV/min. The

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