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Tribo-mechanical and electrochemical properties of plasma nitriding titanium

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ABSTRACT

Titanium nitrides have good tribo-mechanical and biomedical properties. They are employed to harden and protect cutting and sliding surfaces for industrial purpose and as a non-toxic outer-surface for bio-medical applications. In this study, pure titanium was nitrided using RF plasma technique. The microstructural, mechanical, tribological, electrochemical and biomedical properties of nitrided titanium were investigated. The X-ray diffraction demonstrates the formation of ε-Ti_2N and the cubic δ-TiN phases after plasma nitriding. The microhardness of the nitride samples increases as the plasma-processing power increases up to 1300 $HV_{0.1}$. That represents approximately 7-fold increment in the microhardness in comparison with the untreated titanium. High nitriding rate of 0.17 $\mu m^2/s$ was recorded for the sample that was treated at 650 W. The wear and corrosion resistance are improved after plasma nitriding. Moreover, the friction coefficient is reduced from nearly 0.75 for the untreated titanium to 0.25 for the nitride one. An enhancement in the biocompatibility of the nitrided titanium has been achieved. The number of grown mesenchymal stem cells was higher for nitrided substrates compared to that of the untreated titanium. The improved tribo-mechanical and electrochemical performance of the nitrided titanium can be attributed to the formation of super-hard titanium nitrided phases.

1. Introduction

Titanium and titanium alloys have excellent properties including lightweight, high strength-to-weight ratio and outstanding corrosion performance [1–3]. Further, they are suitable to work under high stress conditions and indicated no toxicity effects with biological environments [4]. For these attractive properties, titanium and its alloys are widely used for aerospace, chemicals and petrochemicals, automotive, orthopedic implants, dental and endodontic instruments and other industrial and biological applications. However, they are still suffering from tribological drawbacks; mainly the low wear resistance and high friction coefficient that limit some of their practical applications [5]. Different surface treatment techniques have been successfully developed to overcome these drawbacks and to provide these surfaces with more desired properties and functionalities for exceptional applications. In this regard, plasma-based nitriding and ion nitriding are well-known technologies used for many years among various plasma surface engineering techniques. Plasma nitriding [6–9], plasma carburizing [10] and plasma carbonitriding [11] are typical methods used for surface treatment purposes. The significant advantages of plasma nitriding over conventional nitriding methods include a reduce in operating coast (gas and energy consumption), and a complete elimination of environmental pollution. Further, controlling the treatment temperature during the process leads to control the formation of nitrided layer with a specific phase composition and less shape distortion with free porous zone [12,13]. As reported in a previous literature, the surface treatment of titanium is better to be performed at low temperature range, up to ~950 °C in order to reduce the fatigue strength of the treated titanium [14]. Plasma nitriding of titanium based on thermal diffusion mechanism produces a compound layer formed from δ-TiN on top and ε-Ti_2N beneath; giving a hardness of about 1500–3000 HV [15]. A diffusion layer of solid solution phase α-Ti(N) can create underneath as a consequence of incorporation of nitrogen into titanium matrix which results in hardening of dislocation-pinning effects [16]. It has been found that, the nitrided titanium surfaces lead to significant changes in surface topography beside the physiochemical features and tribo-mechanical properties [14,17,18]. A reduction in the wear rate to a value of 4.8×10^{-7} mm^3/Nm has been reported for nitrided titanium [19,20]. From another side, such nitrided layers have interesting features in biomedical applications especially towards cell adhesion, proliferation, and differentiation and ultimately the interfacial tissue formation [21–25].

The current study focuses on improving the tribo-mechanical properties of commercial titanium by RF plasma nitriding. Further, it was extended to study the surface energy characterization and corrosion behavior of the nitrided layers as a function of plasma processing power. Furthermore, cell adhesion and cell spreading were correlated

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to the physiochemical and surface topography features in order to preliminary evaluate the biocompatibility performance.

2. Experimental

2.1. Sample treatment

Titanium with purity of 99.96% was cut into small coupons with dimensions of 10 mm × 10 mm × 1 mm. The samples were ground and polished mirror like, washed in ethanol for 15 min using an ultrasonic cleaner and then installed in the RF plasma system. Detailed information about the RF nitriding process can be found elsewhere [26,27]. Fig. 1 displays a schematic of the nitriding system. This system comprises a quartz tube (reactor) with 500 mm in length and 41.5 mm in diameter evacuated by a two stage rotary pump to a base pressure of 1.0×10^{-2} mbar. The titanium samples were centered in the RF coil on a supported titanium bar of 2.9 cm length and 1 cm diameter which is fixed on a water cooled copper sample holder. Nitrogen (N_2) gas was fed into the reactor tube to establish a working gas pressure of 7.5×10^{-2} mbar; measured by means of a capacitance manometer. The induction copper coil was energized by a 13.65 MHz RF power generator (model HFS 2500 D) via a tunable matching network. The samples were nitrided at a varied plasma-processing power from 400 up to 650 W and for a processing time of 15 min. It is important to state that this treatment process was performed without using any external source of heating. The sample temperature was measured by means of a Chromel–Alumel thermocouple just placed close to the surface of the sample. At the end of the nitriding process, the samples were allowed to cool down to room temperature in the evacuated reactor tube. The processing temperature of the treated substrates increases rapidly to steady state temperature within the first 2 min of plasma processing with an average heating rate of approximately 8 °C/s. A fast temperature stabilization and good plasma stability has been reported previously in plasma surface treatment using inductively-coupled RF power source [28]. Fig. 2 displays a linear trend of increasing the treatment temperature with increasing plasma-processing power. As one can observe from this figure, the treatment temperature increased from 850 °C at a plasma-processing power of 400 W to reach a maximum value of 1050 °C at a plasma power of 650 W. The treatment temperature plays a significant role in affecting the structure, nitriding rate and the tribo-mechanical properties of titanium.

2.2. Sample characterization

Different characterization techniques have been used in order to study and correlate the properties of the untreated and treated samples.

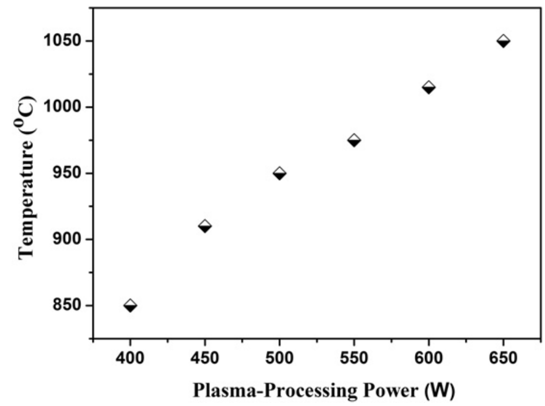

Fig. 2. Sample temperature as a function of RF plasma-processing power.

X-ray diffraction (XRD) using Philips-PW1710 diffractometer with Co K_α radiation of $\lambda = 1.78896$ Å was used to characterize the crystallographic configuration of the samples. The XRD scan was run between 35° and 95°, with step interval of 0.02° and scan rate of 2°/min. The treated samples were exposed to the standard metallo-graphic procedure including sectioning, mounting, grinding, polishing and etching. The etching process was performed using 100 ml H_2O + 50 ml ethanol + 2 g ammonium hydrogen fluoride for time of few seconds to and up to 1 min. The surface and cross-section morphologies of the treated samples were investigated using Olympus BX51 optical microscope. Vickers microhardness measurements of the untreated and nitrided titanium were carried out using a Leitz Durimet microhardness tester with a contact load of 100 gf. The microhardness measurements were performed according to ASTM E384-11 standard test method at temperature of 25 °C ± 3 °C [29]. The microhardness tester has been accredited according to ISO/IEC 17025:2005 requirements. The wear and friction coefficient measurements were conducted using a ball-on-disk tribometer at a mean sliding speed of 2 mm/s with a normal load of 1 N. A 6 mm diameter Al_2O_3 ball was used as a counterpart against the untreated and treated Ti without lubrication. The environmental conditions were T = 25 ± 3 °C and 35% relative humidity. The wear measurements were performed according to ASTM G 133-10 standard test method (linearly reciprocating ball-on flat sliding wear). The oscillating ball-on-disk type tribometer is accredited according to ISO/IEC 17025:2005 requirements. The surface roughness of the investigated samples was performed using a Form Talysurf 50, which has been accredited according to ISO/IEC 17025:2005 requirements. The water contact angle measurement, at room temperature, was performed using Phoenix 300 (Contact Angle Analyzer manufactured by S.E.O. Co.

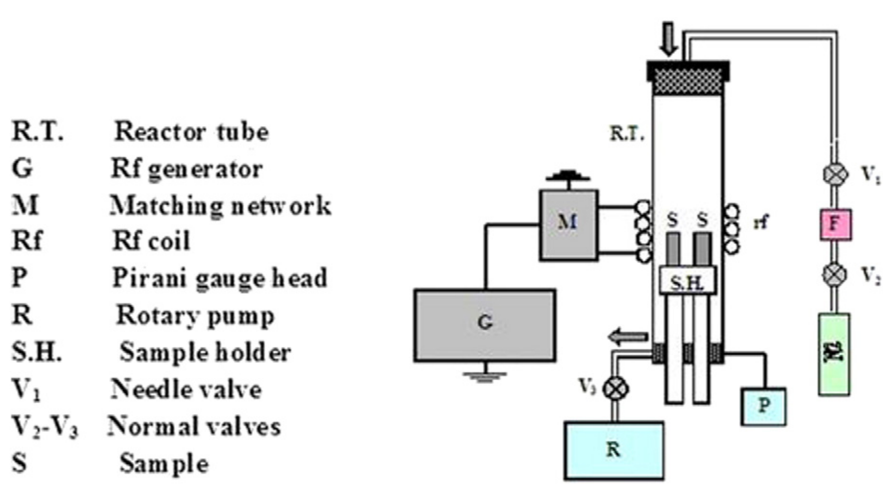

Fig. 1. A schematic of the nitriding system.