



# Reactive-sputter-deposited $\beta$ -Ta<sub>2</sub>O<sub>5</sub> and TaON nanoceramic coatings on Ti-6Al-4V alloy against wear and corrosion damage



Jiang Xu <sup>a,\*</sup>, Wei Hu <sup>a</sup>, Zong-Han Xie <sup>b,d</sup>, Paul Munroe <sup>c</sup>

<sup>a</sup> Department of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing 210016, PR China

<sup>b</sup> School of Mechanical & Electrical Engineering, Wuhan Institute of Technology, 693 Xiongchu Avenue, Wuhan 430073, PR China

<sup>c</sup> School of Materials Science and Engineering, University of New South Wales, NSW 2052, Australia

<sup>d</sup> School of Mechanical Engineering, University of Adelaide, SA 5005, Australia

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## ABSTRACT

In this study, two different types of nanoceramic coatings; namely,  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> and TaON, were synthesized by double glow discharge plasma technique on Ti-6Al-4V alloy to improve its wear and corrosion resistance. The new coatings were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The two coatings were found to have a thickness of about ~25  $\mu$ m and exhibit similar microstructural characteristics, i.e., composed of equiaxed grains with an average grain size of ~15 nm. They are tightly adhered to the Ti-6Al-4V substrate. Nanoindentation was used to determine the hardness and elastic modulus of the two coatings and the adhesion strength between the coatings and substrate was also evaluated by scratch testing. Dry sliding wear tests were performed using a ball-on-disk type tribometer, in which the two coatings were slid against Si<sub>3</sub>N<sub>4</sub> ceramic balls under applied loads ranging from 2.3 N to 5.3 N at room temperature. Compared with the Ti-6Al-4V, the coated samples showed a decrease of two orders of magnitude in the specific wear rate, and the specific wear rates of the two coatings were also insensitive to the applied normal loads. The electrochemical behavior of the two coatings was characterized by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis in a naturally aerated 5 wt.% HCl solution. While both types of coatings were able to greatly improve the corrosion resistance of Ti-6Al-4V alloy, the TaON coating exhibit a higher corrosion resistance than the  $\beta$ -Ta<sub>2</sub>O<sub>5</sub>, due primarily to the TaON coating with a lower carrier density.

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## 1. Introduction

Over the past several decades, titanium alloys, especially Ti-6Al-4V, have become widely used in a range of structural applications including the aerospace, automotive, chemical, marine and biomedical industries because of their unique combination of high specific strength and excellent corrosion resistance. However, the widespread use of titanium alloys is hindered by their poor tribological properties, which are manifested by high friction coefficients and low abrasion resistance [1]. Such problems are believed to originate from their low surface hardness, low heat-transfer capability and susceptibility to oxidative wear [2–4]. The excellent corrosion resistance of titanium alloys in a variety of industrial environments arises from the existence of a protective oxide film that forms naturally upon exposure to air [5]. Unfortunately, the passive films formed on titanium alloys in acidic chloride solutions undergo transient microscopic breakdown, which occurs below the pitting potential [6].

Since both wear and corrosion behaviors of materials are controlled by the microstructure and the composition of near-surface regions, introducing a protective coating using various surface modification methods is considered to be an economic yet effective means to resist the surface degradation of titanium alloys caused by wear and corrosion during service [7,8]. Significant improvements on the tribological properties of titanium alloys have been reported through the application of various surface modification techniques [1,2], but these approaches have brought only limited benefits to the corrosion protection of these alloys, and in some cases it has resulted in deterioration in corrosion resistance [9–11]. For instance, Yilbas et al. [9] investigated the effects of both a plasma nitrided layer and a TiN coating on the corrosion resistance of Ti-6Al-4V held in a 0.1 N H<sub>2</sub>SO<sub>4</sub> + 0.05 M NaCl solution. They found that plasma nitriding reduced the overall corrosion performance of the coated alloys due to the implanted N<sup>+</sup> ions not being uniformly distributed in the surface region of the substrate. Moreover, the presence of defects in coatings, such as pinholes, pores and macro-droplets, may act as pathways for the penetration of corrosive species into the substrate [10,11], leading to galvanic corrosion between the coating and substrate.

\* Corresponding author.

E-mail address: [xujiang73@nuaa.edu.cn](mailto:xujiang73@nuaa.edu.cn) (J. Xu).

In our previous work [12], a double glow discharge plasma technique has been employed to fabricate a series of hard coatings on titanium alloy substrates, and the resultant coatings, which exhibit a dense structure, provide efficient protection to the underlying substrate from corrosion attack. Transition metal nitrides and oxides have been used for several decades as hard, attractive wear- and corrosion-resistant candidate coatings due to their inherent high hardness, chemical stabilities and strong covalent bonds. Among them, tantalum oxide and nitrides have received much attention with a wide-range of technological applications, e.g. as a precise and stable thin-film resistor used in silicon-based integrated circuits [13], an excellent diffusion barrier, and as bioactive coatings [14]. Nonetheless, although they have various unique chemical and physical properties, up to now, little effort has been devoted to investigate their corrosion and wear behaviors.

In the present study, the potential application of tantalum oxide and oxynitride as surface protection coatings was explored, motivated by their high hardness and good chemical stability. To do so, first,  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> and TaON coatings were fabricated onto Ti-6Al-4V substrates using reactive sputter deposition enabled by double glow discharge plasma technique. Then, dry sliding wear tests and electrochemical measurements were performed to evaluate the wear and corrosion resistance of the two coating at room temperature. The results obtained show a clear dependence of the surface degradation resistance on distinct ceramic types in the coatings and a strong correlation with the nanostructure characteristics achieved by unique processing routines.

## 2. Experimental details

### 2.1. Coating specimen preparation

Specimens ( $\varnothing 40 \times 3$  mm) used as substrates were machined from a medical grade Ti-6Al-4V alloy rod. The chemical composition of the substrate in wt.% was: Al, 6.42; V, 4.19; Fe, 0.198; O, 0.101; C, 0.011; N, 0.006 and Ti, the balance. Prior to sputter deposition, the Ti-6Al-4V substrates were ground by different grades of silicon carbide papers and mechanically polished with diamond paste to obtain a mirror-like appearance. The polished substrates were then rinsed with ethanol followed by acetone using ultrasonic cleaner, and dried in warm air. The  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> and TaON coatings were deposited onto the polished Ti-6Al-4V substrates using a double cathode glow discharge apparatus. In the process of double cathode glow discharge, one cathode serves as the target fabricated from the desired sputtering materials, and the other cathode as the substrate material, as described elsewhere [12]. When two different voltages are applied to the two cathodes, glow discharge occurs. In this work, a 99.99% pure Ta disk with dimensions  $\varnothing 100 \times 5$  mm was used as the sputtering target. Prior to the deposition, the surfaces of the samples were further cleaned by Ar ion bombardment at  $-650$  V for 10 min to remove residual surface contamination. The base pressure in the chamber was  $5 \times 10^{-4}$  Pa and the working pressure was 35 Pa during depositions. Synthesis of the  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> coating was conducted in a flowing Ar + O<sub>2</sub> gas mixture, with an Ar:O<sub>2</sub> flux ratio of 10:1, while the TaON coating was grown with a flux Ar:O<sub>2</sub>:N<sub>2</sub> ratio of 100:10:1. The flow rates of these three gases were monitored by mass flow controllers. The detailed deposition parameters were as follows: target electrode bias voltage with direct current,  $-750$  V; substrate bias voltage with impulse current,  $-275$  V; substrate temperature,  $800$  °C; target/substrate distance, 10 mm; and treatment time, 1.5 h.

### 2.2. Structural and morphological characterization

The surface morphologies of the specimens before and after coating deposition were analyzed by an atomic force microscope (AFM, VeecoNanoscope V) equipped with NanoScope imaging software (Digital Instruments, Inc.). An area of  $1 \mu\text{m} \times 1 \mu\text{m}$  was scanned under contact mode with a NSC36 tip and scan rate 1.0 Hz for each measurement.

Topographic images were collected at five different positions to evaluate surface roughness and the average value was reported.

The crystal structures of the as-deposited coatings were characterized by a D8ADVANCE X-ray diffraction (XRD) instrument with Cu K $\alpha$  irradiation ( $\lambda = 0.15406$  nm), operated at 35 kV and 40 mA. X-ray data were collected over a  $2\theta$  range from  $20^\circ$  to  $80^\circ$  using a  $0.05^\circ$  step scan with a count time of 1 s. The cross-sections of the as-deposited coatings were etched using Kroll's reagent (10 ml HNO<sub>3</sub>, 4 ml HF and 86 ml distilled water) for 15–20 s to obtain a clear visibility of the coating/substrate interfaces. A field emission scanning electron microscopy (FE-SEM, SHitachi, S-4800, Japan) equipped with an energy-dispersive X-ray (EDS) analyzer (EDX-4; Philips) was used to observe the cross-sectional morphology and chemical composition of the coatings. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010 microscope operated with an accelerating voltage of 200 kV. Plan-view TEM samples were cut from the outermost part of the coatings and prepared using single-jet electrochemical polishing technique starting from the untreated side of the substrates. All X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS Ultra ESCA System containing an Al K $\alpha$  X-ray source with an energy of 1486.71 eV. The accelerating voltage and emission current of the X-ray source were kept at 12 kV and 12 mA, respectively. The base pressure of the sample analysis chamber was maintained at  $\sim 10^{-10}$  Torr. The pass energy was selected at 80 eV, for survey scans, and 10 eV, for feature scans, to ensure both high resolution and good sensitivity. After subtracting the background signal, the spectra were fitted using both Gaussian and mixed Gaussian/Lorentzian functions. Peak positions were then calibrated with respect to the C1s peak at 284.8 eV from hydrocarbon contamination. Peak identification was performed by reference to the NIST XPS database (V4.0).

### 2.3. Nanoindentation and scratching tests

Nanoindentation tests were conducted on the as-deposited coatings using a nanoindentation tester (NHT) equipped with a Berkovich diamond tip. This system comprises two main components: a measuring head for performing indentation and an optical microscope for selecting indentation sites. The system has load and displacement resolutions of 10  $\mu\text{N}$  and 1 nm, respectively. Fused silica was used as a standard material for the tip calibration. The indentation was performed by driving the indenter at a constant loading rate of 40 mN/min into the material surface with the maximum applied load of 20 mN. The standard analysis procedure proposed by Oliver and Pharr was used to determine the hardness of the specimens from the unloading curve. For each sample, nanoindentation was conducted for five indentations to ensure the repeatability of the experimental data.

A commercial scratch tester (WS-97) with a Rockwell-shaped diamond indenter of 200  $\mu\text{m}$  radius was used to evaluate the adhesion strength between the as-deposited coatings and the Ti-6Al-4V substrate. The test was carried out by continuous loading with a normal force from 0 to 100 N and the load was increased using a constant loading rate of 20 N/min at a scratch speed was 1 mm/min. During scratching, an acoustic emissions (AE) sensor was attached near the diamond indenter to detect the acoustic signals emitted when the coatings cracked. The minimum load at which the coating fracture occurred was as also called the critical load ( $L_c$ ) that represents the coating adhesion strength. Such a load was determined by a sudden increase in the intensity of acoustic emission, which was further confirmed by scanning electron microscope (SEM) examination. Five experiments were carried out for each coating/substrate system.

### 2.4. Friction and wear tests

The friction and wear tests were conducted on a CFT-I reciprocating motion ball-on-disk tribometer under dry conditions at room temperature in air with a relative humidity of 40–45%. In the present work, the

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