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Tribocorrosion response of PVD Mo-N coated Ti-6Al-4V

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INTRODUCTION

Driven by factors such as sedentary lifestyles and age-related degeneration, the increasing prevalence of musculoskeletal disorders has heightened the need for innovative orthopaedic solutions [1]. Biomedical alloys, meticulously designed to operate within the complex and demanding environments of the human body, have transformed medical technologies. Titanium alloy, Ti-6Al-4V is a widely used biomedical material, valued for its biocompatibility, high corrosion resistance, and high specific strength (strength to weight ratio) [2]. However, its poor tribocorrosion performance limits its use for bearing surfaces in human joint replacements [3], [4], [5]. This issue can be addressed by applying hard biocompatible coatings to the Ti-6Al-4V surfaces [6], [7], [8]. Of these, titanium nitride (TiN) and diamond-like-carbon (DLC) coated Ti-6Al-4V have previously been evaluated in-vivo. The latter has proven problematic due to premature blistering and coating loss, whilst the former is used only in very limited quantity. Of alternative coating materials (for application to Ti-6Al-4V) those based on Mo-N compounds appear promising [9].

Molybdenum, a key component of Mo-N coatings, plays a vital role in human biological processes, primarily existing as bioavailable molybdate anions [10]. These anions are essential for critical enzymatic functions [10]. In physiological solutions, molybdenum dissolves without significant concerns, with the human body maintaining homeostatic regulation at levels of 10 to 15 mg [11]. Recommended dietary intakes suggest an allowance of 45 to 50 µg molybdenum per day for adults [12], [13]. Mo-N has a closed-packed metallic structure in which nitrogen occupies the interstitial sites [14]. Its bonding is predominantly strong polar covalent bonding resulting in high bulk moduli and mechanical hardness [15], [16]. These attributes make Mo-N a potential candidate for the protection of biomedical implants, not only by reducing alloy degradation but also by offering a more predictable and controllable biodegradation profile [17], [18], [19]. Given that molybdenum is naturally regulated in the human body at trace levels, the concept of leveraging nitrogen to modulate its dissolution introduces a compelling approach for enhancing implant performance while ensuring the controlled release of degradation products.

This study characterised and investigated the corrosion and tribocorrosion behaviour of Mo-N coatings deposited on Ti-6Al-4V at two different nitrogen partial pressures. By subjecting the coated samples to conditions simulating physiological solutions, this work aimed to replicate in vivo conditions to better understand the performance of these coatings in terms of both tribocorrosion resistance and controlled degradation.

METHODOLOGY

Mill-annealed, extra-low interstitial grade 5 Ti-6Al-4V rods (Brindley Metals, UK) were cut into circular coupons using Struers Accutom-10 precision cutter (Struers Inc., Denmark). Samples were ground and polished to a mirror finish and ultrasonically cleaned. Mo-N coatings were deposited onto these samples via reactive close-field unbalanced magnetron sputtering using a custom-built PVD coating facility (Boride Services Ltd., UK). Two coating deposition runs, C1 and C2, at nitrogen partial pressures of 0.021 Pa and 0.043 Pa were carried out.

The coating thickness was measured using a Tecvac ball cratering calo tester (Tecvac Ltd., UK) and by a direct measurement of a polished cross-section taken perpendicularly using a Zeiss field emission scanning electron microscope (SEM) with a Gemini II Column (Carl Zeiss Microscopy GmbH, Germany). Semi-quantitative elemental analysis of the coating composition was achieved with an energy dispersive X-ray spectroscopy (EDS) detector (EDAX Ametek Inc., USA). NanoMap-500LS surface contact profilometer (AEP Technology Inc., USA) equipped with a stylus having a tip radius of 1 µm was used to measure the surface roughness. Zeiss Axioscope 5 light optical microscope (LOM) (Carl Zeiss Microscopy GmbH, Germany) facilitated topographic examination at different magnifications. Structural analysis was assessed via X-Ray diffraction (XRD) using a Rigaku Ultima IV diffractometer (Rikagu Corp., Japan). Mechanical properties were evaluated using a Micromaterials NanoTest 600 Nanotester (Micromaterials Ltd., UK) through nano-indentation (Berkovich indenter, 20 mN load) and nano-scratch testing (conical indenter, 450 mN max load).

Potentiodynamic corrosion testing was performed in Ringer's solution at 37 ± 1°C following ASTM G5-14 and ASTM G5-94 standards [20], [21]. Tribocorrosion behaviour was studied using a custom-built reciprocating sliding tribometer (University of Malta, Malta) connected to a three-electrode cell set up with a Gamry Reference 1000 potentiostat (Gamry Instruments Inc., USA). Tests involved reciprocating sliding under open circuit

potential (OCP) and anodic potential (AP) conditions of 100 mV vs. SCE, using a 12.7 mm alumina test sphere counterface with a 3 N load (688 MPa max Hertzian pressure) for a stroke length of ~6.4 mm at a frequency of 1 Hz, creating a bidirectional ball-on-disc movement. Tests were carried out at a temperature of $37 \pm 1^{\circ}$ C. The mechanistic approach proposed by Uhlig [22] was implemented under AP conditions to calculate total tribocorrosion volume loss, V, as the sum of mechanical wear, $V_{me}\boxtimes_{h}$, and wear due to chemical oxidation $V\boxtimes_{hm}$ [22]. $V\boxtimes_{hm}$ includes wear-accelerated and passive corrosion, determined using Faraday's second law. For these computations, the theoretical density of Mo-N was estimated using the NaCl prototype crystal model [23]. Valence states for Ti-6Al-4V and Mo-N were determined from oxidation reactions. As suggested in the Pourbaix diagram for molybdenum [10], at a pH of 7.4 and a potential of +100 mV vs. SCE, Mo-N oxidizes to molybdate anion (MoO₄⁻) and nitrogen gas (N₂). While this approach captures the main oxidation pathway, it is limited in the account for potential intermediate oxidation states or competing reactions, such as oxygen evolution.

RESULTS AND CONCLUSIONS

Reactive magnetron sputter deposition was used to apply two coatings, C1 and C2, at two different nitrogen partial pressures, 0.021 Pa and 0.043 Pa, respectively. C1 exhibited intensity peaks corresponding to Im-3m (229) Mo and Fm-3m (225) MoN whilst the diffraction pattern of C2 matched reflections for Fm-3m (225) MoN phase. Both coatings had a thickness of ~4 μ m. The R_a values of C1 and C2 were 25.8 ± 2.1 nm and 17.9 ± 3.5 nm, respectively, compared to 5.9 ± 2.1 nm for the untreated Ti-6Al-4V. The SEM surface topography of the as-deposited coatings exhibited a fine topography, characterised by uniformly distributed dome-tipped asperities indicative of consistent nodular PVD growth [24]. SEM images of fractured C1 and C2 cross-sections displayed a dense columnar fibrous structure, with no apparent voids synonymous with a Zone T structure, according to Thornton's structural zone model [25], [26], [27].

The nano-indentation hardness values for C1 and C2 were 36.2 ± 2.0 GPa and 38.2 ± 1.8 GPa respectively, both much harder compared to 5.8 ± 0.1 GPa for the Ti-6Al-4V substrate. Molybdenum has an electronegativity of 2.16 and nitrogen has an electronegativity of 3.04, leading to predominantly strong polar covalent bonding, which results in such high hardness [15], [16]. During nano-scratch tests the untreated Ti-6Al-4V underwent gross plastic deformation and ploughing of the material which build up in front of the indenter. In contrast, C1 and C2 were resilient to plastic flow, with no signs of delamination or surface plastic deformation. Excellent adhesion between the coating-substrate interface is attested.

The total surface material losses due to tribocorrosion, produced when sliding against an Al₂O₃ test sphere under elastic contact conditions, under both OCP and AP conditions are significantly higher for the untreated Ti-6Al-4V substrate compared to the coated samples. Under OCP conditions, the untreated Ti-6Al-4V resulted in a TVL of 108.88 × 10⁻¹² m³, whereas C1 and C2 exhibited substantially lower values of 0.15 × 10⁻¹² m³ and 0.76 × 10⁻¹² m³, respectively. Similarly, under AP conditions, the TVL for the untreated Ti-6Al-4V was 143.37 × 10⁻¹² m³, while both C1 and C2 had a much lower TVL of 1.82 × 10⁻¹² m³ and 1.50 × 10⁻¹² m³, respectively. The average coefficient of friction, under OCP was ~0.33, 0.28 and 0.15 for the uncoated, C1, C2 and uncoated Ti-6Al-4V respectively, whilst under dynamic positive AP it was ~0.31 for the uncoated test-piece and ~0.35 for both coated materials. Under the latter conditions the dynamic corrosion current recorded was below 30µA for the coated material loss was often more than one order of magnitude less for the coated titanium alloy compared to the uncoated titanium. There was microscopy evidence of surface scratching produced via micro abrasion of coatings whilst many of the uncoated surfaces showed cyclic damage due to the removal and

repassivation of the TiO_2 passive layer as well as mechanical wear by superficial plastic deformation of the surface asperities, abrasive wear, and adhesive transfer. Chetcuti [28] reported the tribocorrosion behaviour of untreated CrN/S (where CrN is the outer layer and S-

phase is the inner layer) tribopairs on wrought CoCrMo. In her work, Chetcuti computed the TVL, following reciprocating sliding at 1 Hz with an applied normal load of 3 N in Ringer's solution, under both OCP and AP conditions. All parameters and equipment used in her work are identical to this study and hence comparable [28]. Under OCP, CrN/S lost a TVL of 0.44×10^{-12} m³, whereas under AP, CrN/S lost a TVL of 0.41×10^{-12} m³. Under OCP conditions, CrN/S proves to offer better tribocorrosion performance than C2. However, C1 shows better resistance to tribocorrosion wear than CrN/S as the TVL of CrN/S is ~3 times greater than the TVL of C1. Under AP conditions, CrN/S offers better wear resistance than both coatings, with less than ~0.25 the TVL for the same duration of sliding, under the same parameters. Under OCP measured TVL of the C1 and C2 thin films are comparable with those of CrN/S, suggesting that Mo-N coatings are also resistant against Type I corrosion wear showing promising results for tribological applications [24], [29], [30], [31]. Under AP, Mo-N experienced more material losses, which however are less detrimental than CrN. C1, with a lower nitrogen content, showed increased dissolution compared to C2, which has more molybdenum, indicating nitrogen can modulate dissolution. This holds promise for biomedical applications as it suggests minimal release of foreign Mo debris into the biological environment, enhancing biocompatibility and minimising the risk of adverse tissue reactions [32]. With controlled degradation, the coatings are likely to maintain their integrity and performance over time, ensuring the longevity and functionality of biomedical alloy implants [32], [33]. In conclusion, Mo-N coatings deserve further investigation under more advanced in-vitro tribocorrosion conditions and should be directly compared with CrN coated Ti-6Al-4V.

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