Wear and corrosion resistance of tantalum coating on titanium alloys for biomedical implant applications

Ay Ching Hee

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Wear and corrosion resistance of tantalum coating on titanium alloys for biomedical implant applications

Ay Ching Hee

This thesis is presented as part of the requirements for the conferral of the degree:

Doctor of Philosophy

The University of Wollongong
School of Mechanical, Materials, Mechatronic and Biomedical Engineering

December 2017
Declaration

I, Ay Ching Hee, declare that this thesis submitted in partial fulfilment of the requirements for the conferral of the degree Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Ay Ching Hee

Ay Ching Hee

Date: 11/12/2017
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Abstract

Titanium alloys are used extensively in orthopaedic implants because of their high strength to weight ratio, resistance to corrosion, and biocompatibility, but the poor wear resistance of Ti-based implants and the stress at the articulating surfaces release wear debris and metal ions. As the average life expectancy of the world population increases, the development of long lasting implants is essential. The aim of this thesis is to modify the surface of titanium alloys by depositing a highly adherent thin film using physical vapour deposition methods to enhance its wear and corrosion resistance in a biological environment.

The effect that a titanium buffer layer has on the structure of sputtered Ta films and coating-to-substrate adhesion was investigated. Since Ta films have a dual-phase structure with a body centred cubic (α-Ta) and tetragonal (β-Ta), the amount of alpha phase in the Ta film increased when titanium was introduced because the lattice match between α-Ta and α-Ti becomes closer. This titanium buffer layer also reduces the residual stress of the films by 25% compared to pure Ta film on a Ti6Al4V substrate, which also improve adhesion between the coating and substrate interface. Ta films also enhance the corrosion resistance of Ti6Al4V substrate by presenting a stable surface layer with negligible capacitive behaviour.

Ta films about 100 nm thick were deposited onto Ti6Al4V substrate using the filtered cathodic vacuum arc deposition system. The structure of this deposited film at zero substrate bias exhibits pure tetragonal phase (β-Ta), and a body-centred cubic structure (α-Ta) is formed as the substrate bias increased to −100 V. The film deposited at −100 V bias shows a significant improvement in cohesion compared to film deposited without substrate bias. Potentiodynamic polarisation and electrochemical impedance tests in a phosphate buffered saline solution revealed that Ta film at −100 V bias has good corrosion resistance and a low corrosion current density of 0.009 μA·cm⁻². The film has hydrophobic characteristics, low surface free energy, and an inert surface presenting a uniform oxide layer.
The effect that the level of nitrogen has on the microstructure and coating to substrate adhesion of the Ta and Ta-N thin films was demonstrated. Hexagonal Ta-N was observed with increasing N₂/Ar gas ratio and the Ta and Ta-N films enhanced the corrosion resistance of Ti6Al4V substrate, with the best protective characteristics achieved in Ta-N film deposited at a 0.25 N₂/Ar gas ratio, however, increasing the N₂/Ar gas ratio increased its susceptibility to pitting corrosion. The corrosion and coating to substrate adhesion of the Ta-N films decreased as the thickness of the film increased. This enhanced corrosion resistance was attributed to the formation of tantalum oxide and an oxynitride compound at the surface, as verified by X-ray photoelectron spectroscopy.

Tantalum coatings were deposited by filtered cathodic vacuum arc deposition to improve the wear and corrosion resistance of Ti13Nb13Zr alloy for load-bearing biomedical applications. The Ta coating has an amorphous structure which changes to a mixture of α and β phases as the substrate was heated to 300 °C during deposition. Tribo-corrosion tests were carried out using a ball-on-disk tribometer under a simulated biological fluid at 37 °C by sliding the uncoated and Ta coated surfaces with alumina balls as counterparts. The results showed that the Ta coatings had a significant reduction in the coefficient of friction. The wear rates of the Ta coated disk surfaces are slightly lower than the bare Ti13Nb13Zr alloy, whereas the wear rate of alumina balls was one order of magnitude higher when it slid against the Ta coated samples than against the bare Ti13Nb13Zr alloy. The wear debris generated by the Ta coated samples sliding against the alumina ball is smaller than of the debris generated by the sliding pair of uncoated surface and alumina ball counterpart. The wear characteristic of Ta coatings do not favour using such coating as implant materials because the coatings wear out after severe sliding and produced wear debris which may induce inflammatory reactions. In fact the Ta coatings had a strong capacitive response and provided corrosion protection to the Ti13Nb13Zr alloy.

The cytocompatibility of the Ta films deposited at different substrate biases was examined using rat bone marrow stem cells. The Ta films deposited with substrate bias of −100 V and −200 V show a mixture of predominantly β phase and minority of α phase. The Ta/−100 V film shows adhesive failure at the Ti/Ta interface and a
cohesive fracture is observed in Ta/−200 V film. The Ta/−100 V showed a significant improvement in corrosion resistance, which is attributed to the stable oxide layer. The *in-vitro* cytocompatibility test shows that Ta films have no adverse effects on mammalian cell adhesion and spreading proliferation.
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**Introduction**

Titanium (Ti) alloys are widely used as biomaterials particularly in cardiovascular, dental, and orthopaedic applications, due to their lower elastic modulus, enhanced biocompatibility, and better corrosion resistance than cobalt-based alloys and conventional stainless steels [1–3]. Nevertheless, the high wear rate and high friction coefficient associated with these alloys limits their lifespan as suitable implant materials. Humans suffer from premature joint degeneration due to increased joint loading, and the increasing demand for hip and knee replacement for younger patients and the increasing life expectancy of the older population, means that long-lasting implantable medical devices have become necessary. Revision arthroplasty surgery to replace diseased joints may cause extra damage and increase medical expenses, which is why a lot of research has been carried out to improve the performance of titanium-based implant devices.

The overall objective of this thesis is to improve the biocompatibility, wear and corrosion resistance of Ti alloys. Tantalum (Ta) has a good potential for biomedical coating due to its bio-inertness, good mechanical strength, and excellent corrosion resistance [4]. The formation of a bone-like apatite layer onto Ta metal in simulated biological fluid increases its bone-bonding ability [5], but the utilisation of Ta implants in orthopaedics and dentistry has been restricted because they are very hard and difficult to machine, and Ta metal is very expensive. This means that applying a layer of Ta film as surface coating on Ti alloys substrates may provide a desirable combination of corrosion and wear resistance.

The specific aims of this study are as follows: 1) Improve the mechanical strength of titanium implants by depositing tantalum film on Ti alloy substrates. 2) Optimise the physical vapour deposition parameters to achieve a dense, uniform, and adherent coating. 3) Improve the wear resistance of titanium-based alloys. 4) Enhance the corrosion resistance of the implant surface used in a human body. 5) Verify that the surface of the coating is non-toxic and free from allergenic effects.
A brief overview of the chapters is as follows:

Chapter 1 is a literature review of the development of metallic implants, physical vapour deposition methods, including the effect that the deposition parameters have on properties of tantalum films and characteristics of tantalum and titanium alloys for biomedical applications.

Chapter 2 introduces the overall experimental details, including substrate preparation, film synthesis, and mechanical and corrosion characterisation methods.

Chapter 3 presents the effect a titanium buffer layer has on the structure, and the mechanical and electrochemical properties of tantalum coatings prepared by magnetron sputtering. The corrosion performance of the tantalum coatings and bare Ti6Al4V substrate in a phosphate buffered saline solution using different scan rates on the potentiodynamic polarisation curve were compared. The mechanical bonding between the tantalum coatings and the Ti6Al4V substrates with and without the titanium buffer layer was investigated using indentation testing.

Chapter 4 demonstrates the corrosion performance and microstructure of tantalum films on Ti6Al4V substrate deposited by filtered cathodic vacuum arc deposition. The wettability and electrochemical measurements are used to study the chemical stability of the tantalum films.

Chapter 5 is a comparative study of Ta and Ta-N films prepared by filtered cathodic vacuum arc deposition at different nitrogen to argon gas ratios. The effect of coating thickness on the coating-substrate adhesion and corrosion performance of the deposited films is analysed.

Chapter 6 investigates the tribo-corrosive performance of tantalum coatings on Ti13Nb13Zr alloy substrate prepared using filtered cathodic vacuum arc deposition. The morphology and size of the wear particles generated provide a better understanding of how to use tantalum films as surface coatings on implant materials.
Chapter 7 examines the cytocompatibility of tantalum films on Ti6Al4V substrate. The relationship between defects in the film deposited at different substrate biases and corrosion performance are characterised. The results of cell adhesion and proliferation of the tantalum films are analysed.

Chapter 8 concludes the major findings of this thesis and makes suggestions for future work. The references are compiled at the end of each chapter.
References


Chapter 1. Literature Review

1.1 Background

1.1.1 Development of Metallic Implants

Degenerating joints and inflammatory joint disease are inevitable for older people because of the loss of minerals in bone tissue, the lack of exercise that causes cartilage to shrink, and decreasing joint mobility [1]. With the increase in longevity and life expectancy of the world’s population over the years, the demand for surgical procedures involving the implantation of prostheses is growing rapidly and therefore the need to improve biomaterials for orthopaedic and dental implants is rather urgent. The three main types of biocompatible metals used for orthopaedic implants, cardiovascular appliances, and dental implants are stainless steels, cobalt-chromium alloys, and titanium and its alloys. Stainless steels were the most viable implant material in the early days of arthroplasty surgery because of its availability and ease of processing; with 316 L stainless steel being used as fracture plates, screws, and hip nails [2]. An experiment was carried out on tibial fractures by inserting an intramedullary rod made of low modulus \(\beta\)-type Ti-29Nb-13Ta-4.6Zr (TNTZ), \((\alpha+\beta)\)-type Ti-6Al-4V alloy, and stainless steel 316 L into the intramedullary canal. A large amount of fracture callus formed with stainless steel 316 L, but not quite as much and at a slower rate when TNTZ and Ti6Al4V alloys were used [3]. Cobalt-chromium based alloys have greater wear resistance than stainless steel and titanium alloys, so they can be used for a prosthesis femoral head. Wrought Co-Cr based alloys contain a large amount of Ni, which imposes the risk of an allergic reaction [4], while the release of Cr from Co-Cr based alloys can lead to oxidative stress in DNA, apoptosis (programmed cell death), and changes in gene expression [5]. Table 1.1 is a comparison of the advantages and disadvantages of metallic implants [6].
Table 1.1 Overview of metals used for implantable medical devices [6].

<table>
<thead>
<tr>
<th>Metallic implants</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L stainless steel</td>
<td>• High ductility</td>
<td>• Fatigue strength lower than of other implant alloys</td>
</tr>
<tr>
<td></td>
<td>• Good machinability</td>
<td>• High elastic modulus</td>
</tr>
<tr>
<td></td>
<td>• High wear resistance</td>
<td>• Inferior corrosion resistance and biocompatibility compared to other implant alloys</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Relatively high metal ion release and adverse host response</td>
</tr>
<tr>
<td>Cobalt-chromium based alloys</td>
<td>• High static and fatigue strength</td>
<td>• High elastic modulus</td>
</tr>
<tr>
<td></td>
<td>• High wear resistance</td>
<td>• Less corrosion resistant and biocompatible than Ti alloys</td>
</tr>
<tr>
<td></td>
<td>• High corrosion resistance and good biocompatibility</td>
<td>• Adverse host response to released metal ions (Ni, Cr)</td>
</tr>
<tr>
<td>Commercially pure titanium</td>
<td>• Excellent corrosion resistance</td>
<td>• Static and fatigue strength too low to be used in load-bearing implants</td>
</tr>
<tr>
<td></td>
<td>• High biocompatibility, direct bone apposition</td>
<td>• Poor wear resistance</td>
</tr>
<tr>
<td></td>
<td>• Relatively low elastic modulus</td>
<td></td>
</tr>
<tr>
<td>Ti6Al4V alloy</td>
<td>• Excellent corrosion resistance</td>
<td>• Poor wear resistance</td>
</tr>
<tr>
<td></td>
<td>• High biocompatibility, direct bone apposition</td>
<td>• The release of Al and V ions may cause health problems</td>
</tr>
<tr>
<td></td>
<td>• High static and fatigue strength</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Relatively low elastic modulus</td>
<td></td>
</tr>
<tr>
<td>NiTi (Nitinol)</td>
<td>• Shape memory and super-elastic effects.</td>
<td>• Adverse host response to released Ni ions.</td>
</tr>
<tr>
<td></td>
<td>• Low stiffness.</td>
<td>• Poor wear resistance</td>
</tr>
<tr>
<td></td>
<td>• Good corrosion resistance and biocompatibility</td>
<td>• Complex fabrication process.</td>
</tr>
</tbody>
</table>

Titanium and its alloys have been commercially available as surgical implant materials since the 1960s [7,8]. Titanium has a hexagonal closed packed structure (α-phase) which undergoes an allotropic transformation to a body-centred cubic structure (β-phase) at 882
°C [9]. As a result of this transformation, titanium alloys exist in three structural forms, namely α alloy, α+β alloy, and β alloy. Pure titanium has a high melting temperature of 1668 °C and reacts with oxygen and impurities at elevated temperatures [9,10]. Pure titanium with α-phase has excellent corrosion resistance but have limited low temperature strength. Titanium alloys such as Ti6Al4V, Ti6Al7Nb, and Ti13Nb13Zr have been developed to improve the strength of pure titanium. Ti6Al4V is still the most common titanium alloy used for biomedical applications, has excellent cold formability and good corrosion resistance [11]. Ti alloys have shown better corrosion resistance than other surgical metals such as stainless steel and cobalt-chromium based alloys, due to the formation of TiO2 on their surface [12–14], but they do have a low load-carrying capacity, low surface hardness, and poor wear resistance for load bearing applications [15,16]. Moreover, the elements V and Al can be released into cell tissue by the dissolution of passive film and wear, which could pose the risk of long term health problems such as neurological disorders, senile dementia, and allergic reactions [17–19]. Aluminium is claimed to be a neurotoxin that inhibits the growth of bone and poses the risk of Alzheimer’s disease [20], while studies have shown that vanadium shows cell toxicity that results in cardiac or renal dysfunction [21]. Ti alloys with a combination of biochemical compatibility and low elastic modulus have been developed to avoid stress shielding after implantation [22]. For example, Ti13Nb13Zr alloy has a lower elastic modulus of 79–84 GPa than Ti6Al4V alloy (110 GPa), which can reduce the stress shielding caused by the difference in mechanical properties between an implant and the surrounding bone [23]. The Ti13Nb13Zr alloy possesses strong β-stabilising properties which give a strength/modulus of elasticity ratio almost twice that of the stainless steel used in the orthodontic field, whereas niobium increases cell activity and zirconium forms stable oxides that promote cell viability [24].

1.1.2 Requirements for Biomedical Implants

Implants can be broadly categorised into three groups, as shown in Figure 1.1 [1,25]. The implant materials must be compatible with the human body because a foreign substance can induce tissue reaction and an allergic reaction in the body. The modified layer with enhanced mechanical, physical, and chemical properties of the implant material should not cause any deleterious biological response or harmful systematic effects. A combination of
toughness, elasticity, hardness and ductility are the main contributing factors needed to meet the criteria of a specific implant part, and the device should be easy to manufacture and conform to all requirements specified for clinical applications. The cost of production is another concern with implant fabrication.

1.1.3 Surface Coatings for Biomedical Implants

Surface modifications such as anodisation, passivation, glow-discharge nitrogen implantation, plasma deposition, plasma spraying, and plasma sputtering and etching are used to enhance the surface properties and biocompatibility of titanium-based alloys for medical devices [2,14,26,27]. The surface coating acts like a barrier to minimise the release of ions attributing to tribocorrosion [28,29]. One basic requirement of a surface coating is that it should not hamper the integration of tissue so the coating needs to enhance osseointegration [30].

Titanium nitride (TiN) is a ceramic coating that can be synthesized by nitrogen ion implantation, physical vapour deposition, and plasma ion nitriding. TiN has encouraging
blood tolerability properties [31,32], which makes it suitable for blood contacting applications such as heart valves, ventricular assist devices, and heart pumps [33,34]. The surface properties and cyto-toxicity of three titanium nitride coatings, namely, TiN, TiNbN (titanium niobium nitride), and TiCN (titanium carbon-nitride) were investigated by Serro et al. [35]; these coatings were shown to be non-cytotoxic. The protein layer adsorbed better on the TiNbN coating, which is the main contributing factor for its better wear performance than TiN and TiCN [35].

The demand for diamond-like carbon (DLC) coatings in the biomedical industry has increased due to their biocompatibility, chemical inertness, low coefficient of friction, and high wear resistance [36–38]. A DLC coating has better biocompatibility than TiN and TiC (titanium carbide) coatings in terms of protein adsorption, platelet adhesion, and activation [39], but the high internal stress of DLC coatings (0.5–7 GPa) confines their practical applications as the film would bulge and peel off from the substrate once a certain stress level is exceeded [40].

Calcium phosphates (CaP) have crystallographic features that are similar to the natural apatite present in bone, which makes it a good candidate for bone generation [41,42]. Calcium phosphate coatings are applied onto titanium implants by methods of fabrication reported in detail by Narayanan et al. [43]. There are several CaP phases, namely, hydroxyapatite (HA), dicalcium phosphate dehydrate (DCPD), tricalcium phosphate (TCP). The HA coating has attracted the attention of many researchers because it has the most stable form among the CaP phases, however, the poor mechanical strength of an HA coating has restricted its use to low load applications. Plasma sprayed HA coatings have been developed on metallic joint prostheses, but the apatite/titanium interface can be fractured under a low load due to the low joint strength and brittleness of the coating [26]. A multi-layered coating consisting of an underlying layer of titanium, an alternating layer, and a top layer of HA had good adhesive strength and high resistance to simulated body fluid attack [44].

Tantalum (Ta) has good bone–bonding ability, high fracture toughness, and high workability [45], so it has been utilised for endovascular stent grafting and it is a good substitute for 316L stainless steel and Nitinol in biomedical applications due to its radio-
opacity and excellent corrosion resistance [46]. When the surface of Ta metal is covered with a very high biocompatible dielectric layer of tantalum pentoxide (Ta$_2$O$_5$) it was utilised in the Bion™ implantable stimulator as a capacitor electrode [47]. The adhesion, growth, and differentiation of human osteoblasts on Ta metal are comparable to tissue culture plastic and some common metal-alloy implants such as titanium alloys and cobalt-chromium alloys [48]. A protective oxygen diffused Ta coating which increased the hardness of titanium substrates is suggested for load-bearing orthopaedic implants [49]. Tantalum oxide films were fabricated onto titanium substrates using polymer-assisted deposition, after which the films showed an improvement in their resistance to corrosion and proliferation of osteoblasts [50]. Similarly, thin films of ceramic tantalum oxide deposited by magnetron sputtering enhanced the corrosion and wear resistance of Ti6Al4V substrate [51,52]. Tantalum nitrides (TaN) synthesized by reactive magnetron sputtering had better blood compatibility than TiN, pure Ta, and low-temperature isotropic pyrolytic carbon, which suggests that TaN is a promising candidate for artificial heart valves [53].

### 1.2 Physical Vapour Deposition (PVD)

Physical vapour deposition (PVD) is a process that occurs in a vacuum chamber at a pressure below $10^{-1}$ mbar, where metal is vaporised and condensed to form a thin film on a substrate [54]. The most common PVD processes are evaporation, sputtering, electron beam, pulsed laser, and cathodic arc. Thin films have been applied onto semi-conductor devices, coated cutting tools for metalworking, and biomedical devices.

#### 1.2.1 Magnetron Sputtering

In the sputtering process, positively charged ions (argon) generated in the plasma bombard negatively charged electrodes (target) in low pressure gas environments releasing ions from the target. These ions then enter the vapour phase and condense on a substrate as a thin film of material. Sputtering utilises magnetic fields to enhance and confine the plasma close to the surface of the sputter target [55]. Sputtered atoms ejected from the target possess an energy distribution of 5–100 eV [56].

Some of the drawbacks of sputtering include low deposition rates, and a high thermal load to the substrate which influences the properties of the film. The challenge of depositing
film on a nanostripe surface is another disadvantage of the sputtering process. Because of the characteristics of sputtering and diffuse transport, their deposition onto a full shadow seems impossible because it is difficult to control the direction of the impinging atoms and this causes contamination problems. Moreover, a multilayer coating is difficult to achieve using magnetron sputtering which is why high power impulse magnetron sputtering (HIPIMS) is gaining interest due to its ability to obtain extremely dense plasma with a high ionization ratio, and high ion current densities. The advantage of HIPIMS technology includes thin film deposition on substrates with complex shapes, and dense coatings with extremely good adhesion between the coating and substrate interface [57,58].

### 1.2.2 Filtered Cathodic Vacuum Arc Deposition

Filtered cathodic vacuum arc deposition (FCVAD) is a metallurgical coating technique where a magnetic flux tube controls plasma generated from the cathode (target) in a curved duct to the deposition chamber. An overview of the filtered vacuum arc process and materials deposition has been reported by Martin and Bendavid [59,60]. The vacuum cathodic arc can carry large currents in a self-sustained discharge mechanism of electron emissions from the negative electrode. The macroparticles emitted from the cathode material are filtered by a 0–90° flexible plasma duct and are prevented from reaching the substrate surface and damaging the coating. The direction of the plasma is controlled by a set of electromagnetic coils governed by the power supplies. The ability to guide the plasma flow onto the substrate can enhance coating uniformity [61].

A typical cathodic arc source involves cathode material (target), an anode arrangement, and an igniter to confine the arc spot to the surface of the cathode. The cathode (titanium, aluminium, tantalum, or copper) is attached to a water-cooled copper housing; the anode is also water cooled and electrically isolated from the cylindrical plasma duct. A pneumatically controlled molybdenum trigger wire is used to ignite the arc in an automatic system. The trigger electrode is connected to the anode via a resistor with resistance of 2–10 Ω for arc initiation [62]. When the triggering electrode touches the cathode target, ions and atoms are released from the target. The plasma duct is 100 mm in diameter with 400 mm and 300 mm as outer and inner radii, respectively. The magnetic field varies between 0–100 mT, and is measured in the centre of the duct. The filtered beam is
connected to a diffusion pump in a high vacuum chamber with an isolated shutter that can be biased. The filtered beam can be scanned across the substrate using the magnetic coils mounted on the deposition chamber. The magnetic field in the scanning coils is between 0–10 mT. The substrate holder has a radiative heater in a rotating stage that can be biased for sputter cleaning the substrate by ion bombardment. Reactive gases flow through the gas inlet valve into the deposition chamber and reach the substrate [59].

The high degree of ionisation of arc produced vapour is an important parameter in enhancing the coating density and adhesion with processing conditions, and this cannot be achieved using conventional PVD methods such as electron beam evaporation, magnetron sputtering or ion plating. The ionised coating atoms are controlled by the deposition system using magnetic and electric fields. The cathodic arc generates ions with high kinetic energy between 20–200 eV, which increases the adatom surface mobility. Figure 1.2 shows a molecular scale where the variation between a high-energy coating (filtered arc deposition) is compared to a low-energy coating (electron beam evaporation). In low energy deposition (Figure 1.2 (a)), atoms arrive at the surface of the substrate at low mobility, leading to low coating density filled with voids and impurity atoms. As Figure 1.2 (b) shows, positive ions are attracted to the negatively charged substrate with enough energy to clean off surface atoms and diffuse to low energy sites producing a high density coating with less contamination [63]. Some of the main disadvantages of the arc process include the deposition of multilayer films and lack of uniformity over large areas [59].
1.2.3 Comparison between Plasma in Sputtering System and Cathodic Arc Deposition

Table 1.2 summarises the plasma and characteristics in a sputtering system and cathodic vacuum arc deposition. The parameters of the electrical characteristics in both deposition systems vary depending on the cathode material (target). A review which compared high power impulse magnetron sputtering and pulsed/filtered cathodic arcs has been reported by Anders [64].

Table 1.2 Comparison of plasma in a sputtering system and cathodic arc deposition [64–66]

<table>
<thead>
<tr>
<th>Feature</th>
<th>Sputtering</th>
<th>Cathodic Arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of plasma</td>
<td>Glow discharge induced in low pressure background working gas</td>
<td>Metal plasma discharge, cathode erosion species</td>
</tr>
<tr>
<td>Function of plasma</td>
<td>Bombardment of target by</td>
<td>Production of charged</td>
</tr>
</tbody>
</table>

Figure 1.2 Model showing a variation of atoms for low energy electron beam evaporation deposition and high energy cathodic arc coating [63].
plasma ions to eject particles (atoms/molecules) of material to be deposited onto a substrate

<table>
<thead>
<tr>
<th>Electrical characteristics</th>
<th>Low current (0.1−1 A)</th>
<th>High current (30−500 A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High voltage (200−1000 V)</td>
<td>Low voltage (10−50 V)</td>
<td></td>
</tr>
</tbody>
</table>

| Plasma density (m$^{-3}$) | 10$^{18}$ – 10$^{19}$ | 10$^{18}$ – 10$^{26}$ |
| Current density (A/m²)    | 10$^4$                | 10$^{12}$              |
| Ion velocity (m/s)        | (3−6)×10$^3$ (Ar ions) | (1−2)×10$^4$          |
| Ion energy (eV)           | 5−100                 | 20−200                 |

### 1.2.4 Linkage between Deposition Parameters and Film Properties

The surface properties of these films are determined principally by deposition parameters such as the arc current, substrate voltage bias, substrate temperature, substrate material, or a buffer layer and reactive gas pressure.

#### 1.2.4.1 Effect of Arc Current

For cathodic arc deposition, the current of a cathode spot ranges from a few to a few tens of amperes, depending on the cathode materials. The plasma generated by the vacuum arc contains a high concentration of metal ions, and the plasma ion current is a constant fraction of the arc current $I_{ion} = \varepsilon I_{arc}$, where $\varepsilon$ is between 0.06−0.12 [67]. A titanium target (a lighter element) normally consumes up to 100 A for a typical cathodic arc discharge [68], whereas for a heavy element metal like tantalum, an arc current of about ~200 A is used to stabilise plasma production [69]. When depositing tin oxide, some regions of the cathode surface may oxidise and cause a lower electrical conductivity due to the presence of oxygen in the deposition system; this destabilises the arc operation and leads to large fluctuations in the current. Figure 1.3 shows the video images of the cathode surface for different arc currents, and the threshold arc current to obtain a stable arc for the deposition of tin oxide is 30 A [70]. Increasing the arc current increases the number of cathode spots and causes spot splitting, as shown in Figure 1.3 (c) and (d), thus producing a poorly conductive film of tin oxide [70].
Figure 1.3 Video images of cathode surface during arcing for different arc currents. (a) 50 A, (b) 100 A, (c) 170 A, (d) 210 A [70].

The arc currents used in the deposition of tantalum films by cathodic arc deposition 120 A [71] and 90 A [72], but the stability of the arc varies with the optimum combination of arc current, gas pressure, magnetic fields, and the geometry of the deposition system.

1.2.4.2 Effect of Substrate Bias and Substrate Temperature

The two deposition parameters that influence the microstructures and properties of films are ion energy, which can be increased by applying substrate bias, and the substrate temperature [59]. Titanium nitride (TiN) films exhibit a high degree of preferred orientation when the substrate bias varies; they show a (200) orientation at low bias, (111) texture at a bias of −100 V, and (220) texture at a bias of −400 V [68]. The substrate voltage bias also has a strong influence on the intrinsic stress of films, while the microhardness and compressive stress of filtered-arc-deposition TiN films decreased with an increasing substrate bias [73], but when the substrate bias exceeds a certain level, internal stress in the film increases. The residual compressive stress of titanium aluminium nitride coatings increased from 7.67 to 11.8 GPa as the substrate bias varied from −50 to
−250 V [74], while the internal stress that develops in the film can affect the coating adhesion [75,76]. The shear stress at the coating/substrate interface is proportional to the thickness of the coating and to the internal stress in the coating [77]. The diamond-like carbon (DLC) coating with a thickness of 500 nm has a stronger adhesive strength than DLC films which are 300 nm and 650 nm thick [78]. It is therefore important to control the substrate bias and the thickness of the coating to produce film that is highly adherent.

Tantalum films have two crystalline phases, a body-centred cubic (α-Ta) phase and a tetragonal (β-Ta, a metastable phase) phase [79]. A lot of attention has been given to the fabrication of α-Ta because of its high toughness and ductility, low electrical resistivity (15–60 μΩ cm) and excellent corrosion resistance [80]. Hard and brittle β-Ta possesses high resistivity (170–210 μΩ cm), which is suitable for thin film resistors [81,82]. Ta grows in a body-centred cubic structure when the substrate is at ground potential (low ion bombardment energy). A mixture of α and β phases occurs when a negative voltage bias is applied (high ion bombardment energy). The growth of Ta structure depends on the energy of ion bombardment at the substrate during the sputtering process [83].

The structure of tantalum films changes from a metastable tetragonal (β-Ta) to a body-centred cubic (α-Ta) with help from substrate heating or post-deposition annealing. Figure 1.4 shows the variation of deposition time and thickness of the coating as a function of substrate temperature. Here the adatom surface mobility increases as the deposition time extends, leading to the formation of α-Ta. The β phase stops growing between 365–375 ºC (Figure 1.4) [84]. Knepper et al. [85] reported that α-Ta begins to form between 340–350 ºC and with a holding time of 10 min or longer. The sputtered tantalum oxide films has an amorphous phase with substrate temperature <400 ºC, while polycrystalline films with orthorhombic β-phase form at temperatures higher than 400 ºC [86].
Figure 1.4 The deposition time and thickness of the coating as a function of the substrate temperature of a tantalum coating deposited by modulated pulsed power [84].

The grain size in the coating is affected by the substrate temperature, so the grain size of the TaCN coatings increases with the substrate temperature (Figure 1.5). At a substrate temperature of 500 °C, grain formation is very uniform due to an increasing surface diffusion of the atomic species [87], but if the substrate is below 500 °C, the grain size is quite small because the mobility of the adatom is low. The adatoms increase in mobility with the substrate temperature, and this leads to the nucleation and agglomeration of crystallites and a subsequent increase in the grain size [88].
Figure 1.5 SEM micrographs of TaCN coatings grown at 4 cm$^3$/min of N$_2$ and 4 cm$^3$/min of CH$_4$ for three substrate temperatures (a) 23 ºC (room temperature), (b) 200 ºC and (c) 500 ºC [87].

1.2.4.3 Effect of Reactive Gas Pressure

For a reactive deposition, a coating with a different chemical composition can be produced in the presence of a gas or a mixture of gasses. Argon is the main gas used in reactive deposition and an amount of reactive gas is then introduced into the deposition chamber.
The reactive gasses most often used for industrial coating deposition are oxygen, nitrogen, carbon dioxide, acetylene, and methane. In gaseous arc deposition, the gas pressure is relatively low (~0.1 mbar) to avoid a gas phase nucleation of the vaporised material, and to allow the ions to accelerate from the plasma without collision and thermalisation. The pressure of the reactive gasses is controlled to deposit multi-component functional thin films such as tantalum nitride and tantalum oxide, so an increase in the nitrogen pressure from Figure 1.6 (b) to (f) caused a significant reduction in the high energy tail and a variation in the curve of ion energy distribution [89]. The collision processes of charge exchange and electron impact ionisation determine the ionic charge of an atom, so an increase in gas pressure may affect the composition of the plasma emitted from the cathode and also reduce the deposition efficiency [89].
Figure 1.6 Ion energy distributions for Ti⁺ as a function of background nitrogen gas pressure for pressures of (a) 3×10⁻⁷, (b) 1×10⁻⁴, (c) 5×10⁻⁷, (d) 5×10⁻⁴, (e) 1.5×10⁻³, and (f) 2×10⁻³ mbar [89].

The crystallographic properties of tantalum films deposited on Ti-Al-Nb and Co-Cr-Mo alloys using DC magnetron sputtering were investigated by Hallmann and Ulmer [90]. The α-Ta can be formed by changing the deposition parameters in a sputtering system such as the DC power, the substrate bias, and gas impurities. Oxygen was used to stabilise the α-Ta phase on Co-Cr-Mo substrate, whereas the amount of oxygen needed to stabilise the α-Ta phase on Ti-Al-Nb alloy substrate is insignificant. The results indicate that the structure of Ta film is affected by the substrate material [90].
Target poisoning is a common problem in reactive sputtering because oxides are formed when the oxygen impinges onto the surface of the target, and the amount of oxygen results in a variation of the sputter yield and coating uniformity [91]. Since target poisoning does not occur easily in cathodic arc deposition due to the high ionisation energy, it does produce more uniform films with fewer defects [64].

The adhesive strength between the sputtered TaN films and the substrate can be improved by optimising the pressure of the nitrogen gas and the temperature of the substrate. The hardness of the TaN films is influenced by the pressure of the nitrogen whereas the hardness of the film reached 40 GPa under an optimal combination of gas pressure and substrate temperature [53].

1.3 Characteristics of Ta and Ti Alloys/Compounds for Biomedical Applications

1.3.1 Biological Performance

Matsuno et al. [92] evaluates the biocompatibility of various refractory metals (tantalum, titanium, hafnium, niobium and rhenium); these metals did not dissolve in the soft tissue when implanted into the subcutaneous tissue of the abdominal region and in the femoral bone marrow of rats for 2 to 4 weeks, which indicates their good biocompatibility and osteoconductivity.

The in vitro biological performance of metallic implants can be examined by adsorption of protein on its surface because the implants are exposed to proteins that come from blood and tissue. The adsorption of fibrinogen on Ta oxide layer and hydroxyapatite coated surfaces increased compared to bare tantalum, suggests that the good biocompatibility of these modified surfaces [93].

An artificial heart valve is used to replace a diseased heart valve in patients with valvular heart disease. Pyrolytic carbon is the most common material used for artificial heart valves, but it is very brittle and its compatibility with blood is insufficient. Plasma surface modification is used to enhance the compatibility and mechanical durability of pyrolytic carbon. Figure 1.7 illustrates the blood clotting behaviour of Ta, TaN (tantalum nitride),
TiN (titanium nitride), and LTIC (low-temperature pyrolytic carbon). Ta absorbed the most hemolysed haemoglobin solution, thus indicating an improvement in thromboresistance. Clotting time is the time when absorbance is equal to 0.1, while a longer clotting time indicates that the materials have better blood compatibility. The result in Figure 1.7 shows that TaN had the best blood compatibility among the tested samples [53].

![Figure 1.7 Absorbance of a hemolysed haemoglobin solution as a function of time](image)

Tantalum and tantalum oxide films deposited by plasma immersion ion implantation and deposition followed by heat treatment had better adherence, growth, and the proliferation of endothelial cells than 316L stainless steel and commercially pure Ti. The endothelial cells increase the hemocompatibility of blood contacting devices, thus suggesting that Ta and tantalum oxide show some promise for use in artificial heart valves [94].

One essential requirement for a material to be bioactive is its ability to form a bone-like apatite layer in a human body [95]. When Ti metal surface is soaked in simulated biological fluid (SBF), a dense and uniform apatite layer is formed. This is attributed to the sodium ions in the surface layer replace the H3O+ ion to produce Ti−OH groups. The apatite layer consists of calcium deficient and nanosize hydroxyapatite that contains carbonate. The osteoblast (bone-producing cell) preferably proliferaes and differentiates to
produce apatite and collagen on the apatite layer while the surrounding bone comes into contact with the surface apatite of the titanium metal without the fibrous tissue intervening [96]. This bone-like apatite layer is also found in tantalum metal where its formation was accelerated by pre-treating the metal with a 0.2 M NaOH solution at 60 °C for 24 h. A sodium tantalite hydrogel layer forms Ta–OH groups with a reaction between the Na⁺ ions and H₃O⁺ ions in SBF. Apatite is then nucleated and grows onto the Ta metal in SBF [97], and then the Ta metal forms an apatite in SBF and bonds tightly to bone, as shown in Figure 1.8 [98].

![Figure 1.8: An SEM-EDX profile of the interface between the NaOH- and heat-treated tantalum metal and the tibial bone of a rabbit (8 weeks after implantation) [97].](image)

Tantalum oxide coatings were deposited onto pure Ta metal by micro-arc oxidation in electrolytic solutions containing calcium acetate and β-glycerophosphate disodium. A new phase of CaTa₄O₁₁ was formed after annealing at 800 °C for 3h; these annealed tantalum oxide coatings increase the ability of apatite formation [99].
Ta coated Co-Cr substrate demonstrated good apatite-forming ability after immersing in SBF for 4 weeks, suggesting its excellent in vitro bioactivity. Moreover, the Ta film significantly enhanced the in vitro biocompatibility of the Co-Cr substrate, which showed an increase in the proliferation and differentiation of pre-osteoblasts (MC3T3-E1) [100].

The adhesion of bacteria to an implant material is an important factor in the progress of clinical implant infection. Pure Ta has the lowest bacterial adherence of Staphylococcus aureus and Staphylococcus epidermidis compared to tantalum-coated stainless steel, titanium alloy, and polished stainless steel. A lower bacteria adherence of pure Ta is beneficial as an alternative material for orthopaedic implants [101].

The biological properties of plasma sprayed hydroxyapatite (HA) coatings and laser deposited Ta coatings on Ti substrates were compared by culturing the surfaces using osteoblast cell line hFOB. The HA and Ta coatings demonstrated excellent in vitro biocompatibility in terms of cellular adherence and growth. The Ta coating bonded metallurgically to the Ti substrate without a sharp interface, but there was a sharp interface for the HA coating on Ti substrate. The good in vitro biocompatibility of Ta coatings and the strong mechanical bonding between the Ta coating and Ti substrate interface, suggests that Ta coatings can be potential substitute for HA coatings on Ti implants [102].

1.3.2 Corrosion Performance

Human body fluid is a complicated chemical system that interacts with the metal surface after implantation into the human body. Ti alloys are subjected to corrosive species when they come into contact with a physiological medium consisting of organic acids, amino acids, and proteins in the human body [103]. The types of corrosion usually found in implants are fretting, crevices, and pitting. Fretting often happens in hip joint prostheses with corrosive damage at the contact interface due to small movements in the corrosive aqueous medium [104]. Surface degradation could limit the longevity of prostheses due to the reactions of tissue with corrosive products. Similarly, crevice corrosion occurred in a combined cobalt-alloy head on a titanium-alloy femoral hip stem. This crevice corrosion at the tapered connections between the head and stem leads to the release of metal ions and
the potential failure of stem fixation [104]. Many metals naturally form an oxide layer on their surface as they corrode and the surface will passivate if the oxide layer hinders further corrosion. In some cases, local areas of the passive film are damaged, allowing metal corrosion to occur in just a small part; this phenomenon is known as pitting corrosion [106].

Ta is extremely corrosion resistant in an in vivo environment because of the low solubility Ta oxide on its surface. The electrochemical behaviour of metallic implant materials was evaluated in both pure aerated physiological saline and deaerated saline with stable redox system containing K₄Fe(CN)₆ and K₃Fe(CN)₆. The results showed that pure Ta has the lowest corrosion current density of the metallic implant materials tested, such as stainless steel, cobalt-based alloy, and Ti6Al4V alloy. The stable oxide layer on the Ta metal inhibits a redox reaction that involves an exchange of electrons. The electrochemical corrosion of Ta metal in the redox processes involving tissue compound indicates the excellent biocompatibility of this metal [107].

Ta was deposited onto the surface of ZK60 Mg (Mg−5.04 wt% Zn−0.52 wt% Zr) alloy using reactive magnetron sputtering, and then electrochemical corrosion tests were carried out in simulated biological fluid at 37 °C. It was found that the stable and protective surface layer consisting of Ta₂O₅, Ta sub-oxides, and Ta had a huge improvement in corrosion resistance compared to uncoated ZK60 Mg alloy [106]. Similarly, a tantalum pentoxide (Ta₂O₅) coating synthesized by hydrolysis condensation improved the biocompatibility and corrosion resistance of Ti. An electrochemical corrosion test was carried out in simulated blood plasma (SBP) at 37 °C for 24 hours, and then the solution was analysed using inductively coupled plasma-mass spectrometry (ICP-MS) to measure the ions released. Bare Ti metal released Ti ions faster than the Ta₂O₅ coated sample, thus indicating the enhanced corrosion resistance of the coated sample. This means the inorganic compound Ta₂O₅ is chemically stable and possesses better corrosion resistance than Ti surfaces [107].

The corrosion performance of Ta coated cobalt-chromium modular necks and Ti6Al4V alloy modular necks were examined under dry conditions and wet conditions. Figure 1.9 shows the assembly in a dry condition, where the neck-stem taper junction is dry and clean.
and the trimodular hip prosthesis is surrounded by an air-filled container. Wet conditions means the neck-stem taper junction was contaminated with calf serum only, or with calf serum and cancellous bone particles. The titanium alloy modular neck showed no signs of corrosion in the dry assembly, but it was contaminated in both wet assemblies. The Ta coated cobalt-chromium modular necks showed no sign of corrosion or chemical reaction in all three environments, suggesting the highly protective effect of Ta coating [108].

![Figure 1.9 Trimodular hip prosthetic system [108].](image)

Reactive-sputtered-deposited β-Ta$_2$O$_5$ and TaON nanoceramic coatings improve the wear and corrosion resistance of Ti6Al4V alloy. The electrochemical corrosion of the two coatings was evaluated by potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) in a naturally aerated 5 wt.% HCl (hydrochloric acid) solution. The resistance of both coatings to corrosion was much higher than the Ti6Al4V alloy, thus providing good protection against corrosion. The TaON coating had a higher corrosion resistance than β-Ta$_2$O$_5$ due to the lower carrier density of the TaON coating. The donor density ($N_d$) of the tested samples was examined using Mott-Schottky analysis, the $N_d$ is the highest for the passive film formed on bare Ti6Al4V alloy (3.76×10$^{20}$ cm$^{-3}$), followed by the β-Ta$_2$O$_5$ (9.89×10$^{18}$ cm$^{-3}$) and TaON (7.19×10$^{18}$ cm$^{-3}$) coatings. This means that the
protective oxide film provided by the TaON coating is the most stable and offers more protection to Ti6Al4V alloy than the β-Ta2O5 coating [109].

1.3.3 Mechanical Properties and Wear Performance

Proper adhesion between the coating and the substrate interface is needed to protect Ti implant materials from corrosion due to mechanical wear. Good adhesion means a low residual stress in the interfacial region, a high fracture toughness of the materials in contact, and good atomic contact between the dissimilar materials. The adhesion of sputtered α-Ta and β-Ta films on steel was investigated using scratch testing. Figure 1.10 shows scanning electron micrographs of the tracks of α-Ta and β-Ta phase films; the 5 µm thick Ta films show a well adhering coating with high critical load for both phases, but the tetragonal β-Ta film has developed cracks under load and has begun to delaminate. An ultrasonic signal was detected whilst scratching the β phase film, possibly because the film was brittle, whereas the ductile α phase film had no cracks and no acoustic wave has been generated under stress [110].

![Figure 1.10 Traces of a diamond tip on the α-phase film (left) and the β-Ta phase film (right). The tip travelled from the bottom to the top of the figure. The arrows point to the cracks.](image-url)
exposed substrate under the tip at the critical loads of 29 N and 24 N for the α and β phases, respectively [110].

A multilayer coating of Ta and Ta oxide is able to resist plastic deformation by the 316L stainless steel without delamination, in fact the plastic deformation of 316L substrate induced by cracks is healed by repassivation of the Ta layer at the interface. This repassivation is attributed to the reaction of the Ta surface with the electrolyte (physiological saline solution) [111].

The mechanical properties (hardness and elastic modulus) of coatings are influenced by internal residual stresses, composition, the interatomic bonding state, the preferred orientation, the grain size, and the grain boundary conditions [112,113]. Tantalum nitride coatings synthesized onto Ti6Al4V substrates using plasma assisted bias sputtering deposition produce different phases by varying the nitrogen partial pressure. The structure of a tantalum nitride-based coating is transformed from hexagonal Ta2N to face-centred cubic (fcc) TaN with a strong (200) preferred orientation as the partial pressure of nitrogen increases. The hardness and elastic modulus of the Ta2N coating is higher than the fcc TaN coating, in fact the improved mechanical properties of the Ta2N coating has better damage resistance under nanoindentation and offers better protection to the underlying Ti6Al4V substrate under load-bearing conditions [113].

The Ti6Al4V alloy has poor wear resistance and accelerates its degradation when surrounded by corrosive body fluids. In dental implants, the contacting surfaces at the implant/abutment joints are exposed to sliding wear in the presence of saliva, food particles or tooth brushing [114], and in prosthesis, tribo-corrosion occurs at the stem/bone interface. The contacting surfaces in micro-motion can result in osteolysis and aseptic loosening, and release wear particles and metal ions. The resulting wear particles and metal ion release would cause toxicity, allergic reactions, inflammation of tissues, and subsequent early failure of the implant. The tribological testing of etched Ti6Al4V alloys was investigated in a phosphate buffer saline solution (PBS) containing proteins [115], and damage to the wear scar had reduced due to the formation of a tribolayer. The passive layer of TiO2 on the Ti6Al4V alloy produces two types of hydroxyl groups, i.e., a protonated base (Ti–OH2+ ↔ Ti–OH + H+) and acidic hydroxyl (−OH ↔ O− + H+) [116]. Proteins react with positively charged metal ions to create either an adsorbed film on the surface or
metal/proteins/hydroxylate compounds which transport the metal ions away from the interface. Therefore, oxygen diffusion from the surface is inhibited by the formation of these absorbed films, which also limit metal dissolution; this means the biotribolayer which forms at the metal surfaces is the contributing factor to enhanced wear resistance [115].

Cytotoxicity and biocompability of Ti particles was examined by mixing neutrophils in Hanks’ balanced salt solution containing 1–3 µm Ti particles. The 1–3 µm Ti particles excited neutrophil activity and produced super oxide anions, leading to inflammation (Figure 1.11). The macrophages and adjacent collage cause degenerative changes in morphology; the magnified image shows that Ti particles (the black dots) were phagocytized into the cytoplasm by a macrophage [117]. The 1–3 µm Ti particles are smaller than the 5 µm cells, leading to cytotoxicity.

Figure 1.11 Response of tissue to 1–3 µm Ti particles inserted in subcutaneous tissue for 8 weeks [117].

In porous tantalum implants, Ta nanoparticles deposited onto the surface of the porous Ta implants may release and interact with peri-implant osteoblast. The cell behaviour of peri-implant osteoblasts and implant stabilisation was investigated by culturing a mouse
osteoblast cell line (MC3T3-E1) with the Ta nanoparticles. Cell viability had increased (Figure 1.12), suggesting that Ta particles generated from the Ta implants promote cell proliferation and show good bioactivity and cell–implant interactions [118].

![Cell viability graph](image)

Figure 1.12 Cell viability of MC3T3-E1. MC3T3-E1 cells were cultured with tantalum nanoparticles at 1, 10, or 20 μg/mL for 24 h; cells cultured with α-MEM alone served as a control. The cell viability of all the tantalum nanoparticles-treated groups was higher than the control group, especially for the 10 and 20 μg/mL groups ($P<0.05$) [118].

Tantalum oxide (TaO$_2$) coating was deposited onto Ti6Al4V alloy substrate by magnetron sputtering [52], and then wear testing was carried out using pin-on-disk configuration under foetal bovine serum (FBS) lubrication at an applied load of 15 N and a speed of 1.09 m/s, at 37 °C (body temperature). The pins were made from Ti6Al4V alloy and the disks were uncoated and coated samples. The experimental conditions were chosen to simulate a hip joint condition [119,120]. Figure 1.13 compares the worn surface of uncoated Ti6Al4V alloy substrate and a TaO$_2$ coated surface. The TaO$_2$ coating has shallower and smoother grooves and rims along the sliding track than the uncoated surface, indicating an improvement in the wear resistance of the TaO$_2$ coated surfaces [52].
A Ta-based multilayer coating of tantalum carbides and metallic Ta was synthesized using thermal treatment molten salts onto a CoCrMo alloy substrate. Wear testing was via a ball-on-disk configuration, with an alumina ball as the pin material. The wear rate of Ta coated samples is about one order of magnitude lower than the untreated cobalt-chromium-molybdenum alloy, indicating enhanced wear resistance of the modified surface [121]. The implant cobalt alloy was thermally treated in molten salts containing K$_2$TaF$_7$ 52 wt.%, NaCl 47 wt.% and Ta 1 wt.% for 60−120 min at 800 ºC. The improved hardness of the tantalum enrichment coating has low coefficients of friction which serve as a barrier for ion release, as verified by atomic absorption spectroscopy [122].

The in vitro tribological performance of laser-processed Ta coatings on Ti, commercially pure (CP) Ti, and CoCrMo alloy was investigated. The Ta coatings reduced the wear rate of CP Ti substrate by one order of magnitude in the linear reciprocating wear tests rubbing against a hardened chrome steel ball in simulated biological fluid. However, the wear performance of the Ta coatings is inferior to the CoCrMo alloy because it is harder. The wear resistance of the Ta coatings is higher than Ti which reduces the micro-motion between the bone-implant interfaces and also reduces the generation of wear debris. A Ta coating combined with excellent bioactivity is suitable for load-bearing implant applications [123].
1.4 Chapter Summary
An overview of the characteristics of metallic implant materials, including stainless steel, cobalt-chromium alloys, and pure Ti or Ti alloys is presented. The use of Ti alloys as implant material has increased dramatically over the years, but its poor wear resistance and corrosive degradation in a human body limits the lifespan of Ti based alloys. Abrasion of the Ti surface can release particles into the surrounding tissues and cause an undesirable inflammatory response. The biocompatibility, corrosion, and wear resistance of Ti alloys is inferior to tantalum and its compounds. Ta and its compounds have been suggested by a number of researchers as a protective layer for metallic implant surfaces because Ta films can enhance the biocompatibility, mechanical properties, and the wear and corrosion resistance of Ti-based alloys. In consideration of the readiness of technology, the economic factors, and the availability of laboratory facilities, Ta films can be deposited using both magnetron sputtering and filtered cathodic vacuum arc deposition. The microstructure, mechanical properties, and corrosion performance of Ta films can be influenced by a mismatch between the film and substrate lattices, the substrate temperature and substrate bias, the nature of the film material and deposition geometry, and the thickness of the film. An understanding of the underlying mechanism for developing Ta films on the surfaces of Ti alloys in an in vitro environment is essential.
References


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Chapter 2. Experimental Methodology

This chapter describes the film synthesis and characterisation techniques needed to evaluate the mechanical properties, corrosion, and biocompatibility of tantalum films on titanium alloys. It also explains how to calculate the surface free energy of tantalum films and titanium alloy substrate.

2.1 Film Synthesis on Ti Alloys

2.1.1 Substrate Preparation

Titanium alloy substrates were purchased from Shaanxi Cxmet Technology Co. Ltd., as annealed at 700–785 ºC; their chemical composition is provided by the supplier, and is given in Table 2.1.

Table 2.1 Chemical composition of the titanium alloys used in the present study

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>5.8</td>
</tr>
<tr>
<td>Ti13Nb13Zr</td>
<td>-</td>
</tr>
</tbody>
</table>

The 20×20×2 mm³ substrates (materials characterisations) and 50 mm diameter disks (for wear testing) went through a series of grinding and polishing processes, as listed in Table 2.2. The polished substrates were ultrasonically cleaned with ethanol for 10 minutes and then distilled water to remove impurities.
Table 2.2 Grinding and polishing steps for titanium alloys

<table>
<thead>
<tr>
<th>Step</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>SiC paper #500</td>
<td>MD-Pan</td>
<td>MD-Chem</td>
</tr>
<tr>
<td>Lubricant</td>
<td>Water</td>
<td>9 µm diamond polycrystalline suspension, water based lubricant (Struers DP-red)</td>
<td>25 ml oxide polishing suspension (OP-S), 2 ml ammonia, 1 ml hydrogen peroxide.</td>
</tr>
<tr>
<td>Process time</td>
<td>5 min</td>
<td>5 min</td>
<td>6 min</td>
</tr>
<tr>
<td>Force</td>
<td>25 N</td>
<td>30 N</td>
<td>30 N</td>
</tr>
<tr>
<td>Disc rotation speed</td>
<td>150 rpm</td>
<td>150 rpm</td>
<td>150 rpm</td>
</tr>
<tr>
<td>Sample holder direction</td>
<td>Anti-clockwise</td>
<td>Anti-clockwise</td>
<td>Anti-clockwise</td>
</tr>
</tbody>
</table>

2.1.2 Film Deposition using Magnetron Sputtering

The multi-target magnetron sputtering facility is in-house built in the CSIRO Manufacturing Business Unit, Australia. The deposition chamber is connected to a turbo pump system where the base vacuum pressure reaches $10^{-5}$ Pa. Argon gas is introduced into the chamber at a pressure of 1.5 Pa and flow rate of 16 cm$^3$/min. A balanced DC magnetron source (75 mm diameter) is mounted directly above the substrate holder at a distance of 5 cm and is fitted with a high purity tantalum/titanium cathode (<0.015 Ω cm, n-type, low resistivity, Si wafer). The target faces the substrate and the substrate is kept stationary during deposition. The substrate holder is connected to a DC power supply and it could be biased negatively. The deposition rate is 30 nm min$^{-1}$.

2.1.3 Film Deposition using Filtered Cathodic Vacuum Arc Deposition

The deposition of tantalum was carried out using in-house built filtered cathodic vacuum arc deposition systems located at the CSIRO, Australia, and at the University of Wollongong. Figure 2.1 shows a schematic diagram of the deposition system. The polished substrates are mounted on a rotary sample stage. The arc cathode (the target) is made of
high purity tantalum (purity, 99.99 %), it is 58 mm in diameter, and it is mounted on a water cooled copper housing. The anode is electrically isolated from the plasma duct and is also water cooled. The flow rate of the water pump was maintained at 40 litres per minute. Pure argon gas (99.9 vol%) was introduced into the deposition chamber through a gas inlet near the cathode ion source. The arc was ignited using a pneumatically controlled molybdenum trigger wire 2 mm in diameter, and activated by an automatic system. The plasma duct is 100 mm in diameter, and the inner and outer radii are 400 mm and 300 mm respectively. The magnetic field in the centre of the duct varies from 0 to 100 mT. The substrate holder is electrically isolated from the chamber so that a substrate bias voltage can be applied. The temperature of the substrate was monitored by an Ircon Inc. infrared pyrometer. The gas pressure during deposition was measured with a MKS capacitor gauge.

![Schematic diagram of filtered cathodic vacuum arc deposition.](image)

Figure 2.1 Schematic diagram of filtered cathodic vacuum arc deposition.
2.2 Materials Characterisation Methods

2.2.1 X-ray Diffractometry

X-ray diffraction (XRD) at grazing incidence was used to control the depth of analysis and minimise the contribution related to the substrate. In this geometry, the angle of incidence was small and the angle between the incident beam and diffracted beam (2θ) was varied by only moving the detector arm. The incident beam went over a long way onto the surface of the film, reinforcing its diffraction pattern, and the depth of penetration decreased due to the small angle of incidence. The grazing incidence X-ray diffraction studies of the deposited films were carried out using a GBC MMA diffractometer equipped with monochromatic Cu-Kα (λ = 0.15418 nm) radiation. The operating voltage and current of the X-ray beam was set at 35 kV and 28.6 mA, respectively; the scan had a step size of 0.02°, a scan rate of 1°/min, and an incidence angle of 2–5°.

2.2.2 Atomic Force Microscopy

Surface roughness and topography of the films were examined by a Veeco Dimension™ 3100 atomic force microscope (AFM). The AFM cantilever was made of silicon nitride with a nominal tip radius of 20 nm. The surface measurement was performed in the contact mode using line-to-line scanning with a scanning rate of 1 Hz. The surface roughness profile was analysed using the Nanoscope SPM version 5.12b.

2.2.3 Focused Ion Beam Microscopy

An FEI xT Nova Nanolab 200 dual-beam workstation located at the University of New South Wales (UNSW) was used to characterise the surface morphology of the coating specimen after the nano-indentation test and prepare thin foil specimens for transmission electron microscopy (TEM) observation. As Figure 2.2 shows, this instrument combines a dual beam high resolution focused ion beam (FIB) miller with an energetic beam of gallium ions and a scanning electron microscope. The sample is tilted 52° towards the electron column and is perpendicular to the ion column to focus the electron and ion beams onto the same spot. Prior to milling, a platinum strap was deposited along the top of the region of interest, to be thinned. The ion beam removed successive slices of material, while
the electron beam captured a new image of the material after each sectioning. The milling and serial sectioning at 30 kV and 1.0 nA, and the voltage and current for imaging with the electron beam were 5 kV and 98 pA. The cross sectional specimens were then lifted out with a micromanipulator and transferred onto a TEM support grid.

Figure 2.2 Geometry of the dual-beam workstation.

### 2.2.4 Transmission Electron Microscopy

The FIB cross sections of the coating specimens were investigated with a JEOL JEM2011 TEM microscope equipped with a Gatan Orius CCD camera; it has a spatial resolution of 0.16 nm and an operating voltage of 200 kV. Selected area electron diffraction (SAED) patterns were recorded to obtain crystallographic information about the coatings.

### 2.2.5 Wettability Measurements

The surface wettability of the samples is obtained by measuring the contact angle with the sessile drop method at room temperature, using a Rame-Hart Instrument contact angle goniometer. Prior to taking the measurement, the surfaces are cleaned with isopropanol.
Five measurements are taken at different locations on each sample and then an average value is reported. In order to assess the compatibility and bonding of the modified surface in a human body that contains mainly water and protein, distilled water and foetal bovine serum (12003C, Sigma Aldrich) were implemented. Since the liquid surface tension and the contact angle are known the surface tension of the solid can be calculated, but since the dispersive and polar components of foetal bovine serum are not known, measurements were also made using glycerol and the values were used to help calculate the solid surface tension. The surface free energy is calculated with the Owens-Wendt method [1] based on the following equation.

\[ \gamma_l \cdot (1 + \cos(\theta)) = 2(\gamma_s^d \cdot \gamma_l^d)^{\frac{1}{2}} + 2(\gamma_s^p \cdot \gamma_l^p)^{\frac{1}{2}} \]

where \( \theta \) is the contact angle, \( \gamma_l \) is the surface tension of the liquid, and \( \gamma_s \) is the surface tension of the solid. The dispersive (\( \gamma_l^d \)) and polar (\( \gamma_l^p \)) components of distilled water are 29.1 mJ m\(^{-2}\) and 43.7 mJ m\(^{-2}\), respectively. The dispersive and polar components of glycerol are 37.4 mJ m\(^{-2}\) and 26.0 mJ m\(^{-2}\), respectively [2].

### 2.2.6 X-ray Photoelectron Spectroscopy

The chemical composition of the samples is examined with a Specs PHOIBOS 100 X-ray photoelectron spectroscopy (XPS) operating with an Al K\( \alpha \) X-ray source at 12 kV and 120 W or a Specs SAGE 150 XPS operating with Mg K\( \alpha \) X-ray source at 10 keV and 10 mA. XPS peak fitting was carried out using CasaXPS software. The data were calibrated to the adventitious C1s peak present at 284.8 eV to minimise sample charging.

### 2.3 Mechanical Property Measurements

#### 2.3.1 Hardness, Elastic Modulus and Fracture by Nano-indentation

The hardness and elastic modulus are measured with an IBIS/UMIS 2000 ultra-micro indentation fitted with a diamond Berkovich indenter. Incrementally controlled loading and unloading tests with a dwell time of 2s were carried out with the maximum load varying from 5 mN to 50 mN at room temperature. The hardness and modulus calculations are in accordance with the Oliver and Pharr method [3].
A 5 μm diameter spherical diamond indenter was used to test the fracture modes of the coatings because a spherical indenter can deliver a more uniform stress field beneath the contact area than pyramidal indenters [4]. The test loads were 300–400 mN with a loading-unloading rate of 200 μN/s.

2.3.2 Measurement of Film Cohesion by Scratch Testing

Film cohesion was studied with a Revetest Xpress scratch tester (CSM instruments SA, Switzerland) equipped with a Rockwell C type diamond stylus (cone apex angle 120°, tip radius 200 μm). The diamond tip is driven over the coated surface in a load range from 0.1 to 50 N to produce a scratch. A schematic diagram of the scratch testing is shown in Figure 2.3. The scratch tester has a piezoelectric accelerometer to monitor the acoustic emissions and detect the onset of fracture. The coefficient of friction is determined by dividing the frictional force by the applied normal load, and the critical load is determined by a sudden change in the coefficient of friction or acoustic emissions which represent fracture information of the coating. The scratch images were observed under a JEOL JSM-6490LV scanning electron microscope (SEM) equipped with an automated montage acquisition.
2.3.3 Sliding Wear Testing

Sliding wear tests of the uncoated and coated samples were via a CETR UMT2 multi-specimen test system. Figure 2.4 shows the ball-on-disk configuration for tribological testing where a 4 mm diameter alumina ball with a hardness of 16 GPa is used as the counter-face. The alumina ball has high wear resistance, ensuring that the principal wear occurred on the Ti alloys. The ball was slid at 10 cm/s against an uncoated and tantalum coated Ti13Nb13Zr alloy disk with a wear track diameter of 1.7 cm, a sliding distance of 360 m, and an applied force of 5 N to produce a Hertzian contact pressure of 1 GPa. The test ran for 1 hour at 37±1 °C, with 50% relative humidity and a simulated biological fluid (SBF) acting as a lubricant. The SBF was prepared by dissolving reagent-grade mixtures of NaCl, NaHCO₃, Na₂CO₃, KCl, K₂HPO₄·3H₂O, and MgCl₂·6H₂O in distilled water. The HEPES (4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid) was dissolved in 0.2 M NaOH solution in a separate volumetric flask before adding it into the mixture. Na₂SO₄ is
then added into the mixture until it had completely dissolved. The SBF solution is buffered at pH 7.4 with 1 M NaOH solution [5]. Detailed compositions of the simulated biological fluid are shown in Table 2.3. The operating conditions of the tribological test are based on a simulated hip joint and are defined in terms of contact pressure, speed, and lubrication [6,7]. Each test is repeated three times and an average of the replicated friction test results is reported. After the test the wear scars were dried in an a controlled humidity and temperature for 24hours, and then the samples were examined with the JEOL JSM-6490 scanning electron microscope. The elemental mapping and line scanning of the wear tracks were analysed using energy dispersive x-ray spectroscopy (EDS). The wear tracks were examined under a KEYENCE VK-X100 K 3D laser scanning microscope. The average wear volume of the disk is calculated by averaging the worn area measured at four positions at intervals of 90º and multiplying them by the length of the circumferential sliding path. The wear rates are calculated as the worn volume divided by the product of load and sliding distance (mm³/Nm) based on Archard’s equation [8]. The wear debris were washed thoroughly with distilled water, detergent and ethanol using an ultrasonic agitation device. A drop of lubricant was dropped onto Holey carbon film and dried for 24 hours at room temperature. The debris were observed via LEICA DMR optical microscope and JEOL JSM-6490 scanning electron microscope.
Table 2.3 Simulated biological fluid ingredients

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mass/volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5.403 g</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.504 g</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>0.426 g</td>
</tr>
<tr>
<td>KCl</td>
<td>0.225 g</td>
</tr>
<tr>
<td>K₂HPO₄·3H₂O</td>
<td>0.230 g</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>0.311 g</td>
</tr>
<tr>
<td>0.2 M NaOH</td>
<td>100 mL</td>
</tr>
<tr>
<td>HEPES (4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid)</td>
<td>17.892 g</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>0.293 g</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.072 g</td>
</tr>
</tbody>
</table>

2.4 Corrosion and Biocompatibility Measurements

2.4.1 Electrochemical Corrosion Characterisation Methods

The electrochemical corrosion measurements were measured with a CH Instrument potentiostat model 604D and Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). An electrochemical cell with three electrodes was used with a
platinum counter electrode and Ag/AgCl as the reference electrode. The working electrode was an uncoated and tantalum coated Ti alloy disk. A sample area of approximately 0.785 cm² was exposed to the electrolyte by confining the coated surface within a glass tube held on the surface by a pinch clamp. A schematic setup of the corrosion test is shown in Figure 2.5. 0.01 M phosphate buffered saline (PBS) aqueous solution (Sigma P-5368, pH 7.4) or simulated biological fluid (SBF) were used as an electrolyte. Samples were first exposed to electrolyte for 60 minutes at 37 ºC to establish the steady state potential, and then the electrochemical cell was placed in a Faraday cage to minimise interference from other electromagnetic devices.

The potentiodynamic polarisation tests were carried out at room temperature by sweeping the potential from −250 to +250 mV (vs. OCP) at different scan rates ranging from 0.3 mV/s, 0.5 mV/s, 1 mV/s, and 2 mV/s. The corrosion potential (E_corr), corrosion current density (I_corr), and polarisation resistance (R_p) were determined by extrapolating the cathodic and anodic Tafel slopes, using the Stern-Geary method [9].

Electrochemical frequency modulation (EFM) was used due to the non-destructive nature of the measurement, particularly when examining thin films. The frequencies of the perturbation signal of the electrochemical frequency modulation (EFM) technique were then measured using a base frequency of 0.1 Hz and integers of 2 and 5 for the multipliers A and B, respectively. A sinusoidal signal with 40 mV RMS amplitude was used to examine the current response with four cycles in each measurement. The corrosion rate is calculated based on non-linearity in the voltage-current response of the electrochemical interface. Causality factors with an acceptable range of around 2 and 3 were achieved to ensure the validity of the results [10,11]. The EFM measurement took 50 seconds for each test.

Electrochemical impedance spectroscopy (EIS) tests were carried out in an open circuit potential with an AC signal perturbation between 0.01 Hz to 100 kHz and amplitude of 10 mV. The impedance measurement of the samples was recorded after immersion with the electrolyte at durations ranging from 1 hour to 14 days. The experimental data were analysed and fitted to appropriate electrical equivalent circuits (EECs) using ZSimpWin
software package. EIS data were presented in the Nyquist and Bode plot forms with the raw data representing as dots and the simulation data from the equivalent circuit model as solid lines. The corroding surface was rinsed with distilled water and dried in an oven at 40 °C. The surface morphologies of the samples were examined using the JEOL model JSM-6490 SEM.

Figure 2.5 Schematic setup of the corrosion test.

2.4.2 Cell Culturing

Disk shape samples with 6 mm diameter and 2 mm thickness were sterilized by immersing in 75% ethanol for 2 hours prior to the experiment. The rat bone mesenchymal stem cells (rBMSCs, of the fourth passage) were provided by Stem Cell Bank, Chinese Academy of Science, Shanghai, China, with the cell count of $1 \times 10^4$ cells/ml. The cells were seeded on samples in 96-well plates with 200 μL α-MEM (with 10% fetal bovine serum, 1% antimicrobial of penicillin and streptomycin) in each well and cultured for 1, 4, and 7 days. For cell morphology observation, the cultured samples were rinsed in phosphate buffered saline (PBS) aqueous solution and then kept in 4 % (v/v) glutaraldehyde (in PBS) at 4 °C for 2 hours. The samples were then washed in PBS, dehydrated in graded ethanol solution (30, 50, 70, 80, 90, 95 and 100%), and observed via scanning electron microscope (SEM).
The cell proliferation was evaluated according to the alamarBlueTM assay (AbDSerotec Ltd., UK). The rBMSCs were seeded on the sterilized samples at $1 \times 10^4$ cells/ml and cultured for 1, 4, and 7 days. Then, after gently rinsing with PBS twice, the samples were cultured in refreshed α-MEM (with 10% alamarBlueTM) for another 2 hours. After that, the fluorescence intensity of the reduced alamarBlueTM was examined using a fluorescence microplate reader at an extinction wavelength of 560 nm and an emission wavelength of 590 nm. The fluorescence intensity was positively associated with the accumulation of reduced alamarBlueTM in the culture medium and viability of cells on each sample. The experimental procedures and calculation of cell proliferation followed the instruction of the alamarBlueTM assay. Triplicate samples were used to achieve accuracy and reproducibility.

The rBMSCs were cultured on the samples at a density of $1.0 \times 10^4$ cells/ml (for 7 days) or $0.5 \times 10^4$ cells/ml (for 14 days) to evaluate the changes in alkaline phosphatase activity (ALP) levels. After incubating for 7 and 14 days, the cells were rinsed twice with phosphate buffer saline, lysed at 4 °C, and incubated by p-nitrophenylphosphate at 37 °C for 30 min. Then, the optical density (OD) values (at 405 nm) of the resulting solutions were recorded. The data were normalized to a series of standard bovine serum albumin at an OD of 570 nm, and described as the relative ALP levels to the total proteins (μM/μg).
References


Chapter 3. Effect of the Titanium Buffer Layer on the Corrosion and Adhesion of Sputtered Tantalum Films on Ti6Al4V Substrate

3.1 Introduction

Pure tantalum (Ta) has been used to manufacture stents for endovascular surgery since the 1990s [1]. Ta is easily oxidised and passivated in air and in aqueous solutions, and the passive film (Ta$_2$O$_5$) that forms on its surface is very stable and corrosion resistant in a biological environment. The desirable properties of Ta (high hardness, moderate hardness to elastic modulus ratio and excellent biocompatibility) can sustain load bearing, facilitate natural bone growth [2,3] and help with occasional multinucleated macrophage [4]. The Ta surfaces exhibit better cell activity\-interactions between human mesenchymal stem cells (MSCs) than other surfaces such as titanium (Ti) and chromium [5].

Ta film grows as either body-centred cubic (α-Ta) and tetragonal (β-Ta) crystal structures whose structure depends on the type of substrate, the position of the substrate towards the target, and substrate bias and gas pressure [6]. The use of aluminium substrate and a niobium underlayer leads to α-Ta due to the close lattice match between the underlayer material and α-Ta [7]. β-Ta is commonly formed on silicon substrates with the native oxide intact, while α-Ta is found on untreated silicon substrates with an inclination angle of the substrate and a high target voltage of 1000 V; this is because the number of neutral deposition atoms reaching the substrate decreases as the angle of inclination increases. As a result, an increased bombardment of ions relative to the deposition rate can be achieved while the negative substrate bias maintains a flux of ions onto the substrate [8]. With a sputter gas pressure of 1.3 Pa and lower, a β-Ta with a strong (002) fibre textured is formed and more random beta oriented Ta is deposited at a gas pressure of 2.6 Pa or higher [9].

Ti6Al4V alloy is widely used in metal implants due to its high specific strength, excellent corrosion resistance, enhanced osseointegration and biocompatibility [10,11]; however, Ti alloys have poor wear resistance and generate wear debris in load bearing applications. The production of wear debris can contaminate the surrounding tissue and also lead to
bone resorption, loosening, and failure [12]. As the demand for orthopaedic implants for younger patients grows there is a requirement to reduce the need for repeat surgery later in life. Ceramic coatings such as bioactive calcium phosphate, silicon nitride or diamond-like carbon coatings on metal implants have been explored as a means to enhance bone on implant contact, but cracking, delamination, decomposition in long term implementation, and the low fracture toughness of ceramic coatings are huge obstacles to their widespread application [13,14]. Hence, further advancements in load bearing metal implants with excellent mechanical and electrochemical performance are still required.

To combine the good properties of Ta and Ti6Al4V alloy, Ta coatings on Ti6Al4V substrates are being investigated. While the corrosion resistance of Ta film coated onto Ti6Al4V is still inadequate, localised corrosion of Ta film did occur and showed that it might be less resistant to corrosive attack [1]. However, the corrosive behaviour of NiTi alloy with a thin layer of Ta coating has improved to give a wider passive region and a higher breakdown potential [15]. Understanding the corrosive mechanism of a Ta coating in physiological environments is important to diminish the risk of metal degradation in the human body. In this chapter Ta coatings were deposited onto Ti6Al4V substrates by magnetron sputtering, and Ti buffer layer was applied onto a Ti6Al4V substrate to reduce the compressive stress and improve adhesion between the Ta coatings and the Ti6Al4V substrate.

3.2 Experimental Details

3.2.1 Tantalum Deposition by Magnetron Sputtering

Ti6Al4V plates (20×20×2 mm³) were ground and polished with a Struers Abramin polisher, as described in Chapter 2. The average surface roughness of the Ti6Al4V substrates after polishing is 0.05 µm, as measured by contact profilometry (Hommel Tester T1000). The substrates were ultrasonically cleaned in ethanol and distilled water, and then blow dried at room temperature ready for film deposition. Details of Ta coating deposition are described in Chapter 2. Two coating depositions were prepared: pure Ta (Ta) and Ta with Ti buffer layer (Ta/Ti). The titanium buffer layer was deposited for 3 minutes followed by one hour deposition of Ta for the Ta/Ti sample.
3.2.2 Surface Characterisations

The surface topography of the Ta films was examined using an atomic force microscope (AFM) in contact mode. The images were acquired on a scanning area of 5×5 μm² and 1×1 μm² at a scan rate of 1.0 Hz. The surface roughness of the films was measured by scanning the tested samples at five different positions and the average value was reported. The contact angle was measured via the sessile drop method using a Rame-Hart Instrument contact angle goniometer. Two types of media with different polarities, namely distilled water and foetal bovine serum (FBS), were dropped onto the sample surface at 25 °C. These measurements were repeated 5 times at different locations on the samples and an average value was reported. The phase structure was identified by grazing incidence X-ray diffraction (GIXRD) analysis with a GBC MMA diffractometer. The scan was carried out with a step size of 0.02° at a scan rate of 1°/min using a grazing angle of 5°. Quantitative phase analysis was carried out using Rietveld refinement in the Maud Program. The hardness and elastic modulus were measured using an ultra-micro indentation system (UMIS). Incrementally controlled loading and unloading tests with a dwell time of 2s were carried out with maximum load from 5 mN to 50 mN at room temperature. 25 indentations with an applied load of 10 mN were made to obtain an average value for each sample. A spherical diamond indenter with a 5 μm diameter was used to test the fracture modes of the coatings. The test loads were 300 mN with a loading-unloading rate of 200 μN/s. The cross section of the indentations was prepared by milling the sample with a focused ion beam (FIB) microscope. The thin foil specimens of the cross section were then examined with the JEOL 2011 transmission electron microscope (TEM). Film cohesion was examined using a Revetest express scratch tester. Here the probe was drawn across the surface of the coating for a scratch length of 5 mm at a rate of 10 mm/min with an increasing load from 0 to 50 N. The scratch tracks were then examined by an scanning electron microscope (SEM).

Stress measurements of the Ta coatings were measured using the traditional $\sin^2\psi$ analysis. The scan at $2\theta = 114^\circ$ corresponded to the reflection from Ti α-(114) and was initially conducted. There was no peak which means the signal is from the coating itself with minimal contribution from the substrate material. The residual stress of the coatings corresponds to the slope of the plot of strain $\varepsilon = \Delta d/d_0$ versus $\sin^2\psi$ using equation (1).
\[ \varepsilon = \frac{(1-\nu)\sigma \sin^2 \psi}{E} \]  
(1)

where \( E \) is the elastic modulus, \( \nu \) is Poisson’s ratio, and \( \sigma \) is the stress coefficient [16]. d-spacing measurements were carried out on the \( \alpha \)-Ta (110) and \( \alpha \)-Ta (321) planes. The \( \alpha \)-Ta (321) plane was specifically chosen to produce a precise stress analysis and avoid the overlap of stress coming from the tetragonal \( \beta \) phase. The residual stress was calculated using equation (2)

\[ \sigma = \frac{m E}{d_0(1+\nu)} \]  
(2)

where \( m \) is the slope of the line when \( \Delta d \)-spacing is plotted against \( \sin^2 \psi \) [17].

### 3.2.3 Electrochemical Corrosion Measurements

A potentiodynamic polarisation measurement was carried out at room temperature (25±1 °C) in a phosphate buffered saline (PBS) aqueous solution, by utilising platinum mesh and Ag/AgCl as a counter electrode and reference electrode, respectively. A CH Instrument potentiostat model 604D was used for corrosion testing. Two different scan rates, 2 mV/s and 0.3 mV/s were used to obtain accurate results; the 0.3 mV/s scan rate was to reduce disturbance of the charging current which corrodes Ti6Al4V alloy [18]. The initial and final potential was ±0.25 V from the OCP (open circuit potential). The current–voltage data were plotted as Tafel plots in the form of log (i) versus potential, and the corrosion potential \( (E_{\text{corr}}) \) and corrosion current \( (I_{\text{corr}}) \) were calculated from the Tafel plot. The samples were immersed in a PBS aqueous solution for 2 weeks and the potentiodynamic polarisation measurements were recorded every 2 days to monitor surface stability and corrosion over the long term.

### 3.3 Results and Discussion

#### 3.3.1 Surface Roughness

Figure 3.1 shows the atomic force micrographs of two coatings; the average roughness \( (R_a) \) and root mean square roughness \( (R_q) \) of pure Ta and Ta/Ti are between 4–7 nm. Both surfaces had homogeneous coatings and a faceted shape which indicates a smooth facet growth mechanism of the Ta grains in the films. The 3D images in Figure 3.1 show the magnified structure of Ta coatings on a scanning area of 1×1 \( \mu \text{m}^2 \). The nano-sized surface
facets seem slightly more compact and densely packed for Ta/Ti, which implies a smoother surface than pure Ta. The film growth phenomenon is affected by the working pressure so at high pressure the electron temperature decreases and the bombardment of energized species is less effective, thus producing less compact structures [19]. The standard surface roughness of the femoral heads and femoral knee components are between 5–40 nm [20], so increasing the roughness of the counter face may dramatically accelerate abrasive polyethylene wear [21]. Although the wear rates decrease slower with decreased roughness for R\(_a\) values below 50 nm, a femoral head roughness below 10 nm R\(_a\) is preferred to maintain low frictional forces between the articulating surfaces and to achieve full fluid-film lubrication.
Figure 3.1 Atomic force microscope (AFM) images of (a) Ta coating and (b) Ta/Ti.
3.3.2 Surface Wettability

Figure 3.2 shows variations in contact angle for uncoated and coated samples in contact with water and foetal bovine serum. The increased contact angle of water and bovine serum indicates that the coated surfaces became more hydrophobic; a hydrophobic surface is the result of low surface energy which provides less attraction to water molecules and thus improves the absorption of protein [22,23]. A Ta surface with high surface energy and wettability is better for cell and material interactions [24], and in this study there was an increase in the contact angle with water and FBS for Ta coated surfaces, unlike the uncoated surface. While the contact angle of water with the bare substrate is less than with FBS, the contact angle of water with Ta coated substrates is higher than with FBS which suggests that while a Ta coating imparts significant hydrophobicity, it does not inhibit the affinity between the FBS and surface as much. The surface dipole moment (k) plays an important role in hydrophobic surfaces, where the dipole moment decreases with an increase in the contact angle [25]. Water molecules have one OH vector pointing towards the hydrophobic surface whereas water molecules in contact with the hydroxylated silica (hydrophilic surface) have one electron lone pair pointing outwards from the surface. The orientation of the water molecule changed from hydrophobic to hydrophilic profiles when the hydrophobic surface was tuned persistently to the hydroxylated silica. This means that the orientation of the water molecule, the surface polarity and the contact angle are corresponding to one another [25]. The Ta coated surfaces have a higher contact angle of water and bovine serum which indicates that the surface polarity (dipole moment) is low and the surface hydrophobicity can promote the adsorption of protein. In a human body, where water and protein compete to absorb and interact with the metal surface, the Ta coating would probably promote the absorption of protein on the surface rather than water because protein can form a stable layer that improves its lubricating ability [26]. The adsorption of protein depends on the nanoscale chemistry and topography of the interface because nano rough tantalum oxide surfaces with an increasing rigidity of adsorbed fibronectin layers, promote additional changes to the protein [27], such that the absorption of proteins such as albumin and globulin is higher on the hydrophobic surfaces than the hydrophilic surface. Bovine serum film is mainly formed due to the aggregations and hydrodynamic effect of protein, whereas the formation of a lubricant film depends on the conformity of contacting surfaces and kinematic conditions, such as temperature, and the velocity of body fluid around the surface [28].
3.3.3 Structural and Mechanical Properties

Figure 3.3 shows the XRD patterns of the bare substrate and sputtered Ta coatings. Two phases were identified: (i) a stable body centred cubic (bcc) phase (α-Ta) and (ii) a metastable tetragonal phase (β-Ta). The peak located at 38.5°/38.2° with the reflections of (110) or (202) can be attributed to α-Ta (JCPDS-04-0788) or β-Ta (JCPDS-25-1280), respectively. Nonetheless, a strong broadening peak located at 95.0° of α-Ta (310) diffraction confirms that the Ta/Ti buffered structure favours α-Ta growth.
In Figure 3.4 the quantitative phase analysis in Rietveld refinement shows that the Ti buffer layer increased the amount of alpha phase, whereas the (002)-preferred orientation became weaker in favouring α-Ta growth when the Ti buffer layer was introduced. One possible reason for this mechanism is an epitaxial relationship between the α-Ti buffer layer and the α-Ta coating, where the increased α-Ta phase in the Ta/Ti buffered film is probably linked to favourable lattice matching between α-Ta and the α-Ti buffer-layer phase. The detailed crystallographic mechanism of α-Ta and underlaying Ti has been proven by Chen et al [29]. The α-Ta (110) planes have an irregular hexagonal mesh with a side length (2.876 Å) that matches the underlying titanium to constitute a regular hexagonal mesh with a side length of 2.890 Å. By contrast, the pure Ta coating is highly (002)-textured, which indicates a predominant formation of β-Ta. The formation of (002)-texture is usually found in sputtered Ta film and is consistent with the work reported by a number of researchers [8,30]. For wear and corrosion resistant applications α-Ta is preferred but it is very difficult to deposit without heating the substrate or post-annealing.
treatment [31]. The deployment of a thin Ti buffer layer in this study produced a higher α-Ta phase formation.

The hardness values as a function of the depth of indentation are shown in Figure 3.5, and Table 3.1 indicates that the hardness had increased to 13–14 GPa for Ta coated samples at a load of 10 mN. This result is comparable to literature where typical hardness values for α-Ta and β-Ta are from 8–12 GPa and 16–20 GPa, respectively [32]. Note that the hardness of the deposited films is affected by the thickness of the coating, the grain size, residual stresses, and the texture of the material [33,34]. Both deposited Ta coatings had a
high elastic recovery rate and a high H/E ratio compared to uncoated Ti6Al4V. Since the H/E ratio (elastic strain to failure) is the main contributing factor in wear performance, a high H/E ratio will result in materials with high wear resistance [35].

The area function was calibrated by performing a series of tests on a fused silica specimen that covers the force range of the instrument. With the known value of modulus for fused silica (72.5 GPa), the actual area of contact was calculated and compared with the area that would have been found if the indenter was of perfect geometry. The measured elastic modulus of the Ti6Al4V is 155 GPa after calibration of the area function. This is still higher than reported bulk elastic modulus of Ti6Al4V (110 GPa). It is not uncommon that the elastic modulus measured by nanoindentation is systematically different from the bulk value. This can be due to a variety of contributing factors, such as thermal effect, residual stress in shallow surface of the sample, change of the exact geometry of the indentation tip over usage, and uncontrolled elastic change in the elastic deformation in the indenter rig. According to this new calibration, the calibrated elastic modulus of Ta coating and Ta/Ti is 165 GPa and 204 GPa, respectively. All values are obtained by taking 25 indentations on each sample.
Figure 3.5 Hardness measured using nano-indentation plotted as a function of the depth of indentation for Ti6Al4V substrate and coated surfaces.

Table 3.1 Mechanical properties of uncoated and coated surfaces at an applied load of 10 mN.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness (GPa)</th>
<th>Elastic modulus (GPa)</th>
<th>H/E ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Ti6Al4V</td>
<td>6.8 ± 0.6</td>
<td>155 ± 16</td>
<td>0.044</td>
</tr>
<tr>
<td>Ta</td>
<td>14 ± 1.2</td>
<td>165 ± 15</td>
<td>0.084</td>
</tr>
<tr>
<td>Ta/Ti</td>
<td>13 ± 0.8</td>
<td>204 ± 12</td>
<td>0.063</td>
</tr>
</tbody>
</table>

3.3.4 Indentation Behaviour

Figure 3.6 shows cross sections of the tested sample under an indentation load of 300 mN, where the Ta and Ta/Ti coatings are approximately 1.6 μm and 1.5 μm thick, respectively, and the adhesive Ti layer is around 90 nm thick. After indentation, the region directly
beneath the indenter has been deformed by downward pressure with no evidence of cracking, a result which indicates that Ta coatings possess excellent mechanical performance with strong bonding between the coating and the substrate. Under the same applied load of 300 mN, the sliding deformation (3.1 µm deep) for a pure Ta coating had decreased. Further study on shear induced deformability is discussed in the next section. There are shear bands in the pure Ta coating (Figure 3.6 (c)) that are similar to the shear bands of aluminium-based amorphous alloys induced by bending [36]. Here bending deformation dissipates the localised concentration of stress beneath the indenter at the substrate (arrow indicator). As shown in the inset of Figure 3.6 (d), the selected area electron diffraction pattern (SAED) of the sputtered Ta coating has an disoriented polycrystalline structure.

Figure 3.6 Cross sectional images of (a, c) Ta coating (b, d) Ta/Ti after indentation test with 300 mN load acquired by (a, b) SEM and (c, d) TEM methods.
3.3.5 Stress Analysis

The stress analysis of the two coatings is presented in Table 3.2, here the scans at $\alpha$-Ta (110) and $\alpha$-Ta (321) plane diffraction ($2\theta = 38.5^\circ$ and 121.5$^\circ$, respectively) for the Ta/Ti coating has the same residual compressive stress of ~0.9 GPa, whereas the slightly higher compressive stress of ~1.2 GPa confirms that the Ta coating had a $\beta$ phase which caused poor surface adhesion which can lead to early delamination of coated materials under friction at high load. Thin films are often mechanically and elastically anisotropic due to a crystalline texture and/or direction-dependent grain interaction [37]. A compressive in-plane residual stress is good because it tends to enhance the mechanical resistance and hardness of the coatings, but exceptionally high compression can have a negative impact because it can hinder protective layers from adhering to the underlying substrate. The residual stress of a Ta coating with Ti buffer layer decreased by 38 % compared to a pure Ta coating, this will probably help the coatings to adhere. Texture has a different effect in polycrystalline materials, as has been proven by the anisotropic nature of mechanical properties [38]; for example the (002)-textured pure Ta coating induced a higher compressive stress. The shear stress based on the lattice parameter of a crystallographic direction for Ta/Ti decreased considerably (Table 3.2) compared to the sole Ta film, which suggests that the Ti buffer layer relaxes the residual shear stress and favours film bonding.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Plane</th>
<th>Phase</th>
<th>Residual stress (GPa)</th>
<th>Shear stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>110</td>
<td>$\alpha$, $\beta$</td>
<td>$-1.2 \pm 0.2$</td>
<td>$-0.65 \pm 0.2$</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>$\alpha$</td>
<td>$-1.2 \pm 0.08$</td>
<td>$-0.084 \pm 0.09$</td>
</tr>
<tr>
<td>Ta/Ti</td>
<td>110</td>
<td>$\alpha$, $\beta$</td>
<td>$-0.87 \pm 0.08$</td>
<td>$-0.28 \pm 0.07$</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>$\alpha$</td>
<td>$-0.94 \pm 0.05$</td>
<td>$-0.059 \pm 0.05$</td>
</tr>
</tbody>
</table>

3.3.6 Film Cohesion

Scratch testing is used to evaluate the adhesive and cohesive properties of a coating. A diamond indenter is drawn across the coated surface under a progressive load until the coating fails. An abrupt change of acoustic emissions and the coefficient of friction is the determining factor for each scratch mechanism. In this study the acoustic emission signal
has a low average value of about 1.7, probably due to the ductile Ti6Al4V substrate, so the critical load is mainly determined by a change in the coefficient of friction and failure of the scratch track image. The scratch test result in Figure 3.7 shows that wedging commenced at a critical load of 2.5 N for Ta coating, which indicates a low adhesive strength without a Ti interlayer. The second critical load was at 19 N where the coating continued to perforate and detach itself from the substrate. It was noted that the adhesive strength of the Ta coating was low, with evidence of total penetration at the end of the scratch track image at higher magnification.
Figure 3.7 Coefficient of friction and acoustic emission signals with the scratch track images obtained for Ta coating.

The higher adhesive strength of the Ta/Ti layer, compared to the Ta coating, was indicated by the higher critical load of 7 N. The micrograph in Figure 3.8 shows the crack began as the load increased. A second critical load began at 23 N with evidence of the coating detaching; this means the Ta film with a Ti interlayer can withstand a higher load with strong bonding between the coating and the substrate. This result corresponds to the scratch track image shown at higher magnification, where the coating is attached to the substrate at an excessive load of 50 N. The α phase Ta has excellent cohesion and
adhesion, although cracks and disbanding occur more frequently in the β phase Ta [39]. The diamond like coating on the Ti substrate with an interlayer of α-Ta, has excellent cohesive and adhesive properties as well as less damage to the coating than the coating with a brittle β-Ta interlayer [40]. Similarly, the incorporation of Ti as an interlayer helps in α growth and forms a strong bond between the coating and the substrate. Triode sputtered Ta with an interface layer of niobium produced sole α phase Ta coatings on steel cylinders but with poor adhesion at the interface due to brittle fractures on the surface of niobium and a high surface residual stress which caused the coating to separate from the substrate [31]. The decreasing residual stress and indentation behaviour of the Ta/Ti layer are the main reasons why the film cohesion improved.
At high pressures (>0.6 Pa), sputter deposited films generally have anisotropic tensile stresses [41] because the sputtered ions lose their dynamic energy after many collisions with working gas molecules. In low pressure sputter deposition, energetic particle bombardment induces highly compressive stresses and high film density due to a lower probability of collisions in the gas phase, but excess compressive stress can lead to adhesive failure and other undesirable effects [42]. The use of 1.5 Pa as the sputtering
pressure in this study controls the intrinsic film stress, leads to preferential orientation and high hardness, and also improves the adhesive and cohesive properties.

3.3.7 Corrosion Testing by Potentiodynamic Polarisation

The corrosion potentials, corrosion current density, and polarisation resistance extracted from the polarisation curves with scan rates of 2 mV/s and 0.3 mV/s are given in Table 3.3. Figure 3.9 (a) shows the markedly lower current density of both coated samples, compared to uncoated Ti6Al4V, in the cathodic branch using a scan rate of 2 mV/s, but at a scan rate of 0.3 mV/s, in Figure 3.9 (b), the bare substrate has a lower current density than the coated samples. Disturbance of the charging current in potentiodynamic polarisation for Ti6Al4V is reduced when a scan rate of 0.3 mV/s [18] is used; a low scan rate reduces any errors introduced into the values of kinetic parameters when the charging current is disturbed, followed by a decrease in the corrosion current density. The low-scan-rate potentiodynamic scan curve shown in Figure 3.9 (b) reveals that Ti6Al4V has excellent corrosion resistance due to a natural and cohesive passive film which forms spontaneously when it is exposed to oxidising media (air, water). However, both Ta-coated surfaces had similar corrosion current density (at the level of middle 10⁻⁹ A) at the scan rates of 2 and 0.3 mV/s, thus implying the formation of a stable surface layer with insignificant capacitive behaviour. Apparently the anodic oxide that forms on a Ta surface is like an effective dielectric layer but the oxide film on Ta that was studied here did not show typical dielectric behaviour. The Ta coated surface (by ion implantation) reduced anodic dissolution at the active regions, unlike the bare Ti in a chloride solution [43]. Moreover, the β-phase of the Ta coating reportedly stabilises the surface and reduces the dissolution of Ti [44]. The corrosion current densities of bare Ti6Al4V (1.95×10⁻⁸ A.cm⁻² at 2 mV/s and 2.43×10⁻⁹ A.cm⁻² at 0.3 mV/s) presents a one order of magnitude difference between the scan rates of 2 mV/s and 0.3 mV/s; possibly due to the relatively high dielectric constant of titanium oxide [45] which results in a stronger capacitive behaviour of the surface layer and requires a longer time to reach equilibrium during a polarisation scan. Note that the scan was within ±0.25 V relative to the pre-measured OCP and with the direction of the scan going from a negative potential to a positive potential. So the corrosion potential close to the starting scan potential (note the direction of scan shown by arrows in Figure 3.9) indicates a non-equilibrium state for the Ti6Al4V sample. Interfacial
capacitance is more pronounced as the scan rate increase, whereas the dielectric constant of the surface layer is high due to the formation of insulating oxide [18]. A negligible capacitive behaviour by the Ta coatings in the polarisation test suggests a relatively oxide free and stable surface with minimal tendency for oxidation compared to untreated Ti6Al4V.

Table 3.3 Corrosion potential, corrosion current density, and polarisation resistance of bare Ti6Al4V and coated surfaces at different scan rates after one hour.

<table>
<thead>
<tr>
<th>Scan rate</th>
<th>2 mV/s</th>
<th>0.3 mV/s</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>E$_{corr}$ (mV)</td>
<td>i$_{corr}$ (A cm$^{-2}$)</td>
<td>R$_p$ (Ω cm$^2$)</td>
<td>E$_{corr}$ (mV)</td>
<td>i$_{corr}$ (A cm$^{-2}$)</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>−192</td>
<td>1.95×10$^{-8}$</td>
<td>3.03×10$^5$</td>
<td>−173</td>
<td>2.43×10$^{-9}$</td>
</tr>
<tr>
<td>Ta</td>
<td>−172</td>
<td>3.41×10$^{-9}$</td>
<td>8.86×10$^6$</td>
<td>−89</td>
<td>2.85×10$^{-9}$</td>
</tr>
<tr>
<td>Ta/Ti</td>
<td>−296</td>
<td>6.42×10$^{-9}$</td>
<td>5.57×10$^6$</td>
<td>−121</td>
<td>4.76×10$^{-9}$</td>
</tr>
</tbody>
</table>

Figure 3.9 Potentiodynamic polarisation curves for bare and Ta coated Ti6Al4V substrates at scan rates of (a) 2 mV/s and (b) 0.3 mV/s.

The polarisation curve for both Ta coated surfaces had a large positive shift in corrosion potential when the scan was carried out at 0.3 mV/s, as Figure 3.9 (b) shows. The R$_p$ values of Ta coated films are higher than with bare Ti6Al4V, which indicates a reduced dissolution of metal in PBS. The uncoated surface is more susceptible to corrosion when exposed to solutions containing aggressive ions such as chloride. Moreover, the R$_p$ value of a Ta coating is higher than Ta/Ti, implying that a pure Ta coating is more resistant to corrosive attack. After being immersed in electrolyte for 14 days, the bare substrate and Ta
coated substrates show similar polarisation results (Table 3.4), indicating no major chemical changes occur on the surfaces.

Table 3.4 Corrosion potential, corrosion current density, and polarisation resistance of bare Ti6Al4V and coated surfaces at different scan rate after 14 days.

<table>
<thead>
<tr>
<th>Scan rate</th>
<th>2 mV/s</th>
<th>0.3 mV/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E$_{corr}$ (mV)</td>
<td>i$_{corr}$ (A cm$^{-2}$)</td>
</tr>
<tr>
<td>Sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>−215</td>
<td>1.63×10$^{-8}$</td>
</tr>
<tr>
<td>Ta</td>
<td>−133</td>
<td>2.60×10$^{-9}$</td>
</tr>
<tr>
<td>Ta/Ti</td>
<td>−179</td>
<td>8.24×10$^{-9}$</td>
</tr>
</tbody>
</table>

Micrographs of uncoated and coated surfaces submitted to corrosion testing are shown in Figure 3.10. A comparison of Ti6Al4V substrate before corrosion testing [Figure 3.10 (a)] and Ti6Al4V substrate after corrosion testing [Figure 3.10 (b)], reveals inhomogeneous corrosion of Ti6Al4V in micro scale which might have occurred due to the formation of micro-galvanic cells within the multi-phase structure of the metal. Conversely, surface degradation is much reduced for Ta coated surfaces compared to uncoated Ti6Al4V substrate. Some of the corrosion pits shown in Figure 3.10 (c), were found beneath an O-ring used to seal the glass tube on the surface during the corrosion test. The surface within the O-ring region does not show extensive signs of corrosion or corrosion pits, but a discontinuous corrosion product was found on the Ta/Ti surface, and is visible as slightly lighter domains in the inset micrograph of Figure 3.10 (d). This could be due to a diffusion of corrosive ions through the intrinsic defects of Ta coating (e.g. phase boundaries) to the Ti/Ta interface causing under film corrosion. The corrosion obviously produced an expansion force which flaked off the Ta coating, and which is visible as darker domains.
3.4 Summary

Ta films with α-β dual-phase structure were successfully deposited by magnetron sputtering. The surfaces deposited with Ta were harder and had a high H/E ratio compared to the uncoated Ti6Al4V substrate. Moreover, Ta film with a Ti buffer layer has a lower compressive residual stress which improved the film cohesion. The passive films on bare Ti6Al4V caused a decrease of one order of magnitude in the corrosion current density, reaching $2.4 \times 10^{-9}$ A·cm$^{-2}$ at a slower scan rate, whereas the coated films had a similar low corrosion current density at high and low scan rates. Ta coatings improved the corrosion resistance of the bare Ti6Al4V substrate.
References


A. Leyland, A. Matthews, On the significance of the H/E ratio in wear control: a


Chapter 4. Corrosion and Microstructure of Tantalum Film on Ti6Al4V Substrate by Filtered Cathodic Vacuum Arc Deposition

4.1 Introduction

Ti6Al4V alloy has been widely used in biomedical implants due to its high strength-to-weight ratio, corrosion resistance, and good biocompatibility [1,2]. However, this alloy does not have enough wear properties so the surface tends to degrade in sliding contact with similar or other metals, and moreover, the release of vanadium and aluminium at elevated levels of friction could result in cytotoxicity [3,4]. Further research is needed to improve the wear and corrosion resistance of this implant material to achieve better bone tissue integration. Although ceramic (alumina/zirconia) and diamond-like-coatings have a low wear rate, their high elastic modulus, brittle nature and potential for catastrophic fracture associated with ceramics restricts their clinical use [5]. Similarly, diamond-like-coatings have a high internal compressive stress that can reach several gigapascals [6], which can also result in a weak adhesion between the coatings and the substrate and expose the metal substrate to aggressive media. To overcome these problems, tantalum (Ta) has been suggested as coating material to impart high hardness, a moderate elastic modulus, and high wear resistance for orthopaedic implants [6].

Ta appears to be a promising material for biomedical applications because of its superior mechanical properties and outstanding in vitro and in vivo biocompatibility [7–9]. Ta bonds strongly with carbon, nitrogen, and oxygen atoms and readily forms a stable protective layer. This protective film of stable pentoxide Ta2O5 which forms on the surface of Ta films has an outstanding ability to protect against corrosion [10]. Ceramic tantalum oxide thin film has also improved the mechanical properties and corrosion resistance of Ti6Al4V substrate [11,12]. Although tantalum has already been used for medical devices such as endovascular stents and neurosurgical implants [13], the use of tantalum implants in orthopaedics and dentistry has been limited because its high hardness makes it difficult to machine and Ta metal is expensive. Alloying Ta with Ti (titanium) is a possible solution to this problem. A number of researchers have demonstrated the outstanding corrosion resistance of Ti-Ta alloys [14,15], but fabricating Ti-Ta alloys by conventional
arc melting is difficult due to the large difference in the melting point (Ti: 1953 K, Ta 3273 K) and density (Ti: 4.51 g/cm³, Ta: 16.6 g/cm³) [16]. This is why applying a layer of Ta film as surface coating onto a Ti6Al4V substrate may be a desirable combination of properties, including corrosion and wear resistance.

A number of different techniques for fabricating Ta films has been reported, including magnetron sputtering [17–19], chemical vapour deposition [20,21], double glow plasma [22,23], and ion beam assisted deposition [24]. In fact Ta film has been deposited by filtered cathodic vacuum arc deposition (FCVAD) but as a commonly adopted industrial coating method, the preparation of Ta film by FCVAD has not been explored enough [25–27]. The effect of substrate bias on the deposition of metals, alloys, and compounds such as TiN, TiC, TiO₂ and ZrO₂ by filtered cathodic arc are reported in Ref. [28–30]. In this chapter we will investigate the deposition of Ta films on Ti6Al4V alloy substrate using FCVAD. The deposition system has been modified to accommodate the high melting point and low plasma stability of the Ta target. Two deposition conditions, i.e., Ta/0 V (zero substrate voltage bias) and Ta/~100 V (with a negative substrate voltage bias of 100 V) were used to compare the structure and mechanical properties of Ta films. The passivity and stability of the surface films were examined using potentiodynamic polarisation and electrochemical impedance spectroscopy in a phosphate buffered media to simulate the corrosion in a human body.

4.2 Experimental Details

4.2.1 Film Deposition using Filtered Cathodic Vacuum Arc Deposition

Prior to deposition, Ti6Al4V plates (20×20×2 mm³) were mechanically ground with SiC sandpaper #500, and then mechanically polished to an average surface roughness of 0.05±0.01 µm, as determined by a stylus type Hommel Tester T1000 profilometer. The substrates were then washed with ethanol and distilled water to remove residual particles. Deposition was carried out using an FCVAD made at the CSIRO, Australia. A schematic diagram of the deposition system is shown in chapter 2. The arc cathode (the target) is a high purity tantalum rod (purity, 99.99 %) of 58 mm diameter. The chamber in the deposition system reached a base pressure of 1.5×10⁻³ Pa. Prior to deposition, argon gas
was introduced into the chamber near the cathode to reach a deposition pressure of 0.32 Pa. The DC arc current was set at 200 A, which was the lowest stable arc current required to maintain a plasma state during deposition. The substrate holder was electrically isolated from the chamber so that a substrate voltage bias could be applied. The substrate voltage bias varied between 0 V and −100 V and deposition was set for 5 minutes. The Ta ion beam current was set at 200 mA and was measured in the centre of the chamber with an isolated shutter. The deposition rate was about 20 nm min$^{-1}$.

### 4.2.2 Structure and Surface Characterisations

The deposited films were inspected with grazing-incidence X-ray diffraction (XRD) using a GBC MMA diffractometer equipped with the Cu Kα incident radiation. The XRD scan operated in the 2 theta mode between 20º and 100º in steps of 0.02º. The angle of incidence was fixed at 2º.

A FEI xT Nova Nanolab 200 dual-beam work station with scanning electron microscopy (SEM) and focused ion beam (FIB) navigation and milling capabilities was used to prepare the cross section of the deposited films for transmission electron microscopy (TEM) observation. The surface roughness and topography of the films were examined using a Veeco Dimension™ 3100 atomic force microscope (AFM) operating in contact mode over a scanning area of 5×5 μm$^2$ at a scanning rate of 1 Hz.

The surface wettability of the samples was obtained by measuring the contact angle with the sessile drop method at room temperature, using a Rame-Hart Instrument contact angle goniometer. The surface free energy of the samples is presented in Chapter 2.

Film cohesion was evaluated with a Revetest Xpress scratch tester (CSM instruments SA, Switzerland); the diamond tip was driven over the coated surface in a load ranging from 0.1 to 50 N to produce a scratch which was then observed using a JEOL JSM-6490LV scanning electron microscope (SEM) equipped with automated montage acquisition.
4.2.3 Measurements of Electrochemical Corrosion

An electrochemical examination was carried out with a CH Instrument potentiostat model 604D with a three-electrode cell arrangement in phosphate buffered saline (PBS) aqueous solution (Sigma P-5368, pH 7.4). The sample, platinum, and Ag/AgCl were used as a working electrode, and auxiliary and reference electrodes, respectively. A sample area of 0.8 cm² was exposed to the electrolyte by confining the coated surface within a glass tube held on the surface with an O-ring (1 cm) and a pinch clamp. The samples were exposed to electrolyte for 60 minutes under open circuit potential (OCP) prior to being measured. The potentiodynamic polarisation tests were carried out at room temperature by sweeping the potential from −250 to +250 mV (vs. OCP) at a scan rate of 0.3 mVs⁻¹. A scan rate of 0.3 mVs⁻¹ was chosen based on the work reported by Zhang et al [31], where minimum disturbance of the charging current occurred for a corrosion system of Ti6Al4V alloy. Electrochemical impedance spectroscopy (EIS) tests were carried out in open circuit potential with an AC signal perturbation in a frequency between 0.01 Hz to 100 kHz and amplitude of 10 mV. All the tests were repeated at least three times to check for reproducibility.

An X-ray photoelectron spectroscopy (XPS) analysis of the samples after corrosion testing was carried out with a Specs PHOIBOS 100 analyser operating at 12 kV and 120 W with an Al Kα X-ray source. The XPS peak fitting was carried out using CasaXPS software. The data were calibrated to the C1s peak present at 284.8 eV to minimise shifts caused by the sample surface charging.

4.3 Results and Discussion

4.3.1 Film Structure by X-ray Diffraction

Figure 4.1 shows the XRD patterns of the uncoated surface and Ta films deposited at a substrate voltage bias of 0 V and −100 V. β-Ta (JCPDS-25-1280) was identified for the peaks located at 33.7° and 71.1° with a reflection of (002) and (513), respectively. Broad peaks located at 82.5° and 93.5° from the (220) and (310) planes, respectively, were attributed to α-Ta (JCPDS-04-0788) in the −100 V biased film, indicating the formation of a bcc (body-centred cubic) structure as the substrate voltage bias increased from 0 V to −100 V. The formation of α-Ta was probably due to an increase in the energy of the
depositing atoms at the substrate when a negative bias was applied. In experiments with titanium dioxide coatings, it was found that TiO\textsubscript{2} with an anatase structure was formed at zero substrate bias, and rutile diffraction peaks occurred at −100 V bias. The high concentration of ionic species and high energy of particles impinging on the substrate were the main reasons why the rutile phase formed in FCVAD deposition [29]. Similarly, applying a substrate bias during Ta deposition increased the ion energy and led to the formation of α-Ta; α-Ta has superior chemical, thermal, and mechanical properties as well as ductility, formability and corrosion resistance [33,34], whereas β-Ta is hard, brittle, and thermally unstable [34]. It is therefore anticipated that the formation of α-Ta in Ta/−100 V would improve the wear and corrosion resistance in a biological environment.

Figure 4.1 X-ray diffraction (XRD) patterns of the Ti6Al4V substrate and the Ta films.

As shown in Figure 4.2 (a) and Figure 4.3 (a), the deposited films were almost 88 nm and 110 nm thick when Ta was deposited at a voltage bias of 0 V and −100 V, respectively. To understand the structural characteristics of these deposited films, the corresponding
selected area electron diffraction (SAED) patterns were recorded at several places along the surface. The diffraction patterns indicate that film deposited at zero substrate bias consists of pure β-Ta (metastable tetragonal structure). The β-Ta films is a family of topologically close packed structures with different SAED patterns across the surface, indicating that the crystallographic orientations of the deposited films are random. The α-Ta (body centred cubic structure) consists of distinguishable rings with indexes that agree with the bcc structure shown in Figure 4.3 (d). Moreover when the α phase is small grained and there is only a small amount, some of the β phase may be mixed in the diffraction pattern. The strong diffractive intensity of α-Ta phase in the SAED of Ta coating deposited at −100 V bias, as shown in Figure 4.3 (d), provides evidence for the existence of α-Ta. Ta coatings revealed a pure β phase at zero substrate bias, and a mixture of α + β phase with a substrate bias of −100 V. This result agrees with the work reported by Alami et al. [19], where α-Ta was formed using a substrate voltage bias of more than 50 V in magnetron sputtering.

Figure 4.2 Cross section image of Ta deposited at 0 V voltage bias (a) and the corresponding selected area electron diffraction patterns (b, c, d) across the film.
Figure 4.3 Cross section image of Ta deposited at −100 V voltage bias (a) and the corresponding selected area electron diffraction patterns (b, c, d) across the film.

4.3.2 Surface Roughness and Wettability

Figure 4.4 shows the atomic force micrographs of the deposited Ta films. The topography in Figure 4.4 (a) is composed of islands protruding from the surface which are typical features of physical vapour deposited films due to the impact of ions [35]. Figure 4.4 (b) shows that Ta/−100 V has surface ridges which is the surface topography of the crystalline phases of the film. The shallow potholes in the Ta/−100 V film are possibly due to the shading effect of temporary surface droplets. The root mean square roughness (Rq) and average roughness (Ra) of the film deposited at −100 V substrate bias are higher than the roughness of film with zero substrate bias. The films became rougher as the substrate bias increased due to the re-sputtering effect which is the result of competition between the negative ion bombardment of an evolving thin film and etching the deposited material [36]. With a substrate bias of −150 V, the excessive energy of ions bombarding...
the film leads to an increase in surface roughness and poor adhesion of the carbon nitride film [37].

![Atomic force micrographs of Ta films deposited at the substrate bias of (a) 0 V and (b) −100 V. ± indicates standard deviation.](image)

Figure 4.4 Atomic force micrographs of Ta films deposited at the substrate bias of (a) 0 V and (b) −100 V. ± indicates standard deviation.

The wettability and surface energy of materials is important to determine the cell adhesion and proliferation on implant materials [38]. Table 4.1 summarises the contact angles and surface free energy of Ti6Al4V substrate and Ta films. The contact angles of the Ta films

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in contact with the tested liquids are much higher than those of the bare Ti6Al4V substrate. High contact angles indicate a surface with low wettability (hydrophobic surface). The solid surface free energy of the Ti6Al4V substrate is approximately 68 mJ m$^{-2}$, which can be separated into its two main components; the polar component with a low value of 0.48 mJ m$^{-2}$, and the dispersive component with a relatively high value of 67 mJ m$^{-2}$. The surface free energy of Ti6Al4V substrate is mainly contributed by the dispersive component, which is caused by the van der Waals and other non-site-specific interactions [39]. The surface energy of Ti6Al4V is higher than those reported in the literature (34 mJ m$^{-2}$ [40] and 51 mJ m$^{-2}$ [41]). This difference in the surface energy may be due to surface roughness or the procedure used to prepare the liquids and the cleaning protocols [42]. Ta films have a lower surface energy than uncoated Ti6Al4V substrate because the surface energy of Ta films is governed by the polar component, which implies an increase in the surface polarity of the metal. This lower surface energy reduces the attraction between the surface and the water molecules and promotes the adsorption of protein. This increase in the hydrophobicity of the surface enhances the absorption of β-Lg (β-lactoglobulin) on the surface [43]; the competition between the adsorption of water and proteins is endothermic where the surface interaction with proteins is established by exposure to either the hydrophobic or hydrophilic domains through the surface. Therefore, the repulsion of water from the hydrophobic surface induces protein-surface interaction [44] and the adsorbed protein can also form a stable layer that can enhance the lubrication of prosthetic implants [45,46]. Ta films reduce the interaction (bonding) with protein because the contact angle is increased, so the bonding forces (either electrostatic or van der Waals) between the protein and surface are weaker; water follows the same trend. Ta/−100 V film shows a hydrophobic characteristic with a contact angle of ~100º. The hydrophobic property of Ta films is consistent with the result of Ta sputtered films [47]. In the interaction between protein and surface, other surface forces also contribute so they might not be present in the case of water. The angle of Ta/−100 V film in contact with water and bovine serum is higher than the film of zero substrate bias because of the enhanced inertness of the film. The mechanism of an inert surface is explained in Section 4.3.4.
Table 4.1 The contact angle and surface energy of the uncoated substrate and Ta films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact angle (°)</th>
<th>Surface Energy (mJ m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Distilled water</td>
<td>Foetal bovine serum</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>70 ± 2</td>
<td>77 ± 2</td>
</tr>
<tr>
<td>Ta/0 V</td>
<td>99 ± 2</td>
<td>79 ± 4</td>
</tr>
<tr>
<td>Ta/−100 V</td>
<td>102 ± 2</td>
<td>91 ± 3</td>
</tr>
</tbody>
</table>

Note: ± indicates standard deviation. Standard deviations for the polar and dispersion surface energy are not available, because it was determined through least squares fitting of the equation proposed by Owen-Wendt.

### 4.3.3 Scratch Behaviour

Scratch testing is a quantitative technique to evaluate the adhesive and cohesive properties of a coating [48,49] where its failure corresponds to the film-to-substrate critical load and their corresponding failure modes. Figure 4.5 (a) shows the coefficient of friction, and the acoustic emissions and normal load as a function of the scratch length for film deposited at zero bias. The critical load is defined by abrupt changes in the coefficient of friction as the acoustic emission is weak and non-indicative of film failure due to a soft substrate. The film at zero substrate bias appears to have failed at the start with evidence of continuous perforation in the magnified inset of Figure 4.5 (b). The fluctuation in the coefficient of friction of the load vs scratch length profile may be due to local film cracking and shifting, indicating a weak interfacial cohesion. A sudden change in the coefficient of friction is observed at 5 N, possibly due to the small build-up of Ta film on the track. The Ta film was accumulating at the end of the scratch track, exposing the Ti6Al4V substrate along the track, as shown in Figure 4.5 (c).
Figure 4.5 (a) Coefficient of friction, acoustic emission and normal load as a function of scratch length for Ta/0 V; (b) is where the scratch started; (c) is where the scratch ended.

Figure 4.6 shows the scratch on the Ta film at −100 V and the magnified image where the scratch began at the first critical load of 10 N. Buckling is seen in Figure 4.6 (b) and the coating was removed completely at the second critical load of 44 N, as shown in Figure 4.6 (c), this detachment is accompanied by an abrupt increase in the coefficient of friction. Ta film deposited at −100 V resisted scratching more than Ta/0 V due to a change in the surface microstructure because filtered arc deposition produces highly ionised, high-density plasma [50], so when the substrate bias increased to −100 V, the ionised particles have more energy. Energised atoms are attracted by the negatively charged substrate with enough energy to sputter the surface atoms clean and then diffuse to low energy sites which produce high density film with less contamination. The high energy of the
condensing species using a substrate bias of \(-100\) V improves film cohesion and increases the critical load more than film deposited without a substrate bias.

Figure 4.6 (a) Coefficient of friction, acoustic emission, and normal load as a function of scratch length for Ta/\(-100\) V; (b) is where the scratch started; (c) is where the coating was completely removed.

4.3.4 Analysis of Electrochemical Corrosion

The potentiodynamic polarisation curves of the non-coated Ti6Al4V surface, the Ta/0 V, and the Ta/\(-100\) V after one hour of electrolytic immersion are shown in Figure 4.7. Table 4.2 lists the electrochemical parameters of the Ti6Al4V substrate and Ta coated surfaces treated in the PBS solution. Polarisation resistance \((R_p)\) is inversely proportional to the corrosion current density \((I_{corr})\) according to the Stern-Geary equation, both of which are
measures of the protection afforded by the passive layer on the surface. The polarisation resistance of Ta/−100 V is about one order of magnitude higher than the uncoated surface, thus implying improved corrosion resistance, and it also has more positive electrode potential, implying a less reactive/more inert surface that is also consistent with the contact angle measurement. The anodic Tafel slope \( \beta_a \) and cathodic Tafel slope \( \beta_c \) of Ta/−100 V shifts towards the low current density region and more positive values, indicating an increased passivation effect on the anodic reaction of the protective oxide film. The Ta/−100 V film has much lower \( I_{corr} \) than the uncoated and Ta/0 V samples. The density of film could help to reduce the corrosion current or increasing the polarisation resistance (kinetic), but it is unlikely to affect the corrosion potential (thermodynamic) because thermodynamic is influenced more by the chemical nature of oxide film on the surface and the reactivity or stability of the oxide film. The formation of a dense film of Ta_2O_3 with a passive nature on the surface has enhanced corrosion resistance. Ta coated Ti6Al4V prepared by FCVAD at a substrate bias of −100 V has improved corrosion resistance, as indicated by corrosion current density of about one order of magnitude lower than the uncoated surface. Similar protective properties were reported for Ta coatings prepared by atmospheric pressure chemical vapour deposition [51] and double glow plasma surface tantalumising [22], by enhancing the corrosion resistance of Ti6Al4V substrate.
Figure 4.7 Potentiodynamic polarisation curves of the samples after one hour of electrode immersion.

Table 4.2 Electrochemical parameters of Ti6Al4V substrate and Ta coated surfaces treated in a phosphate buffered saline solution after one hour of electrode immersion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$I_{\text{corr}}$ (µA cm$^{-2}$)</th>
<th>$\beta_a$ (mV dec$^{-1}$)</th>
<th>$\beta_c$ (mV dec$^{-1}$)</th>
<th>$R_p$ (kΩ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V substrate</td>
<td>−163 ± 1</td>
<td>0.109 ± 0.01</td>
<td>260 ± 12</td>
<td>133 ± 7</td>
<td>352 ± 15</td>
</tr>
<tr>
<td>Ta/0 V</td>
<td>−168 ± 1</td>
<td>0.042 ± 0.002</td>
<td>269 ± 13</td>
<td>125 ± 6</td>
<td>881 ± 20</td>
</tr>
<tr>
<td>Ta/−100 V</td>
<td>−45 ± 0.1</td>
<td>0.009 ± 0.001</td>
<td>221 ± 15</td>
<td>188 ± 9</td>
<td>4570 ± 87</td>
</tr>
</tbody>
</table>

Data are shown in mean ± standard deviation.
The results of the electrochemical impedance test in the PBS solution are shown in Figure 4.8 in the form of Nyquist and Bode plots, where the Nyquist plots (Figure 4.8 (a)) show that the real impedance of Ta films is much higher than for Ti6Al4V substrate, which is in accordance with the results of potentiodynamic polarisation. As Figure 4.8 (b), the maximum phase angle for Ta/−100 V film is close to π/2, which implies a surface with a strong capacitive response.

![Nyquist and Bode plots](image)

**Figure 4.8** (a) Nyquist plot and (b) Bode plot of uncoated and coated surfaces in a phosphate buffer saline solution after one hour of electrode immersion.
Table 4.3 summarises the quantitative analysis of EIS results by fitting the appropriate electrical equivalent circuit (EEC) onto the EIS data. Figure 4.9 (a) shows the EEC used for modelling EIS result from Ti6Al4V and Ta/0 V, while Figure 4.9 (b) shows the EEC used for the EIS result from Ta/−100 V. The $Q_{\text{oxide film}}$ and $R_{\text{oxide film}}$ represent the constant phase element (CPE) and resistance associated with oxide film on the surface. $Q_{\text{dl}}$ and $R_{\text{ct}}$ are the CPE and resistance associated with the electrical double layer and charge transfer resistance, respectively. The exponent $n$ indicates the variation from ideal capacitor/resistor where 1 is an ideal capacitor and 0 is the ideal resistor. The simple circuit with a one loop element, i.e. Figure 4.9 (b), that produced a successful fit for the Ta/−100 V data indicates the presence of a uniform layer without defects. However, the need for a more complex EEC with two loop elements, i.e. Figure 4.9 (a), for a close fit on the EIS results of Ti6Al4V and Ta/0 V suggests a heterogeneous surface with potential defects in the surface film. This is also reflected by exponent $n$ which is higher for Ta/−100 V surface treatment. The charge transfer resistance is also consistent with the polarisation resistance and indicates the enhanced insulation and corrosion protection offered by the Ta/−100 V surface.

Table 4.3 Electrical components calculated by fitting an equivalent electrical circuit on the EIS data.

<table>
<thead>
<tr>
<th>Electrical component</th>
<th>Ti6Al4V</th>
<th>Ta/0 V</th>
<th>Ta/−100 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{oxide film}}$ ($\mu \Omega^{-1} s^{n} \text{cm}^{-2}$)</td>
<td>25.6 ± 1</td>
<td>71.7 ± 3</td>
<td></td>
</tr>
<tr>
<td>$n_1$</td>
<td>0.90 ± 0.01</td>
<td>0.89 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{oxide film}}$ (kΩ cm$^2$)</td>
<td>158 ± 5</td>
<td>195 ± 5</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{dl}}$ ($\mu \Omega^{-1} s^{n} \text{cm}^{-2}$)</td>
<td>36.1 ± 0.1</td>
<td>35.2 ± 0.1</td>
<td>11.2 ± 0.1</td>
</tr>
<tr>
<td>$n_2$</td>
<td>0.90 ± 0.01</td>
<td>0.89 ± 0.01</td>
<td>0.92 ± 0.01</td>
</tr>
<tr>
<td>$R_{\text{ct}}$ (kΩ cm$^2$)</td>
<td>38.2 ± 2</td>
<td>29.7 ± 1</td>
<td>2520 ± 10</td>
</tr>
</tbody>
</table>
The high resistance of Ta against corrosion in sodium chloride is attributed to the very stable passive oxide layer [52–54]. Figure 4.10 shows the high resolution XPS spectra for Ta 4f and O 1s of the Ta/−100 V film before and after corrosion testing. The Ta 4f spectra is divided to four energy doublets which consist of the most stable form of pentavalent state (Ta$_2$O$_5$), sub-oxides (TaO$_2$, TaO) and metallic tantalum (Ta$^0$). Note that the peak fitting of all the energy doublets of 4f$_{7/2}$ – 4f$_{5/2}$ should be constrained to the condition of a fixed area ratio of 4:3 and an energy separation of 1.91 eV [55,56]. The Ta 4f$_{7/2}$ and Ta 4f$_{5/2}$ peaks located at 26.3 eV and 28.2 eV are assigned to Ta$_2$O$_5$ [57]; the doublets at 25.0 eV and 26.9 eV are attributed to a lower state of oxidation (TaO$_2$), while the peaks located at 23.5 eV and 25.4 eV are categorised to the TaO [58], and the binding energies of the low energy-doublets (21.9 eV and 23.8 eV) are attributed to metallic tantalum, Ta$^0$ [59,60]. The amount of Ta sub-oxides and Ta metal decreased significantly after corrosion testing (Figure 4.10 (b)), which indicates the formation of a passive oxide layer on the surface.
Figure 4.10 (c) and (d) shows that the O 1s spectra has resolved into two peaks. The binding energy located at 530.0 eV is assigned to Ta-O bonds in tantalum oxides [61] and the higher binding energy peaks at 530.9 eV and 531.5 eV are attributed to either oxygen in the form of hydroxide or other adsorbed species of oxygen [62]. A comparison between Figure 4.10 (a) and (b), and Figure 4.10 (c) and (d) shows that after the corrosion test the surface has transformed from a mixture of valent status of Ta and hydro-oxide domination to a more corrosion inhibiting Ta$_2$O$_5$ domination.

Figure 4.10 X-ray spectroscopy spectra of the Ta/$-100$ V (a) Ta 4f before corrosion test; (b) Ta 4f after corrosion test; (c) O 1s before corrosion test; (d) O 1s after corrosion test.
4.4 Summary

Ta films ~100 nm thick were deposited successfully onto Ti6Al4V substrate using the filtered cathodic vacuum arc deposition system. The Ta film deposited at zero substrate voltage bias has a purely tetragonal phase (β-Ta), and the amount of α phase increases as the substrate bias increased to −100 V. This increase in the flux of depositing ions onto the substrate contributes to collisional intermixing and increased film cohesion. The strong bond between the Ta film and the Ti6Al4V substrate presents a surface with high chemical stability (inert), as confirmed by the wettability and electrochemical measurements. The XPS results verify a shift to a Ta2O5 surface dominance on the surface of Ta film during corrosion and therefore the fundamental mechanism of corrosion resistance is offered by a cohesive Ta/−100 V film for the Ti6Al4V substrate.
References


5.1 Introduction

Prosthetic implants made of titanium alloys are widely used because of their high strength-to-weight ratio and superior biocompatibility [1]. The thin oxide surface layer (1.5−10 nm) that forms naturally on titanium metal exposed to air at room temperature actually improves the surface stability [2], but unfortunately, titanium implants have poor wear resistance and the generated wear debris accelerates the rate of electrochemical reactions between the surface of the implant and the surrounding physiological environment [3]. Therefore, further development is needed to extend the longevity of these implants and decrease the risk of an agonising repeat implantation procedure. Over the past few decades transition metal nitride and oxide films have been utilised to improve the corrosion and mechanical properties of biomedical components due to their excellent resistance to wear and corrosion [4]. The metal nitride and oxide coatings have a strong covalent bonding which leads to high hardness and chemical stability, attributes which and make them suitable candidates for bioactive coatings. Several studies have shown that Ta-N films can promote cell proliferation [5], enhance corrosion resistance [6,7], have good blood compatibility, and they are suitable for fabricating artificial heart valves commercially [8].

Tantalum oxide and oxynitride (TaON) have a better corrosion resistance than the native oxide film on uncoated Ti6Al4V [9–11]. These stable TaON coatings are attributed to the release of ammonia (NH4+) or nitrate ions which consume protons and increase the overall pH [12], and possible acidification caused by the dissolution of metal is then neutralised by the ammonia. The NH4+ ions then undergo a further reaction to form stable compounds of nitrate and nitrites which are either corrosion inhibitors or they stabilise the passive films and improve resistance to pitting corrosion [13,14].

Despite the promising chemical and mechanical properties of metal nitrides, investigations into the tantalum nitrides prepared by filtered cathodic vacuum arc deposition (FCVAD) are limited. In this chapter we will evaluate the performance of Ta and Ta-N films deposited on Ti6Al4V substrate for biomedical applications. The N2/Ar gas ratio during
film deposition was varied to study its effect on the structure and electrochemical properties of the films. Morphological characterisation was carried out using atomic force microscopy and scanning electron microscopy. In order to simulate and examine the performance of this coating in a human body, and understand the reaction mechanisms, Ta and Ta-N films were tested in simulated biological fluid using electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM).

5.2 Experimental Details

5.2.1 Deposition Conditions

Ti6Al4V sheet substrates of 20×20×2 mm³ were ground and polished with 9 µm diamond polycrystalline suspension and then polished with an oxide polishing suspension consisting of 2 ml ammonia and 1 ml hydrogen peroxide. This deposition was carried out with filtered cathodic vacuum arc deposition built at the University of Wollongong. The parameters of this deposition are summarised in Table 5.1. The arc cathode (the target) was made from high purity tantalum (purity, 99.99 %) with a diameter of 58 mm. The chamber in the deposition system reached a base pressure of 1.0×10⁻² Pa prior to deposition, and the DC arc current and substrate voltage bias were set to 200 A and −100 V, respectively for all the samples. The N₂/Ar gas flow rate varied from 0–0.75, and is defined as the ratio of mass flow rate of nitrogen to the total mass flow rate of argon and nitrogen. Gas pressure during deposition was between 0.35–0.40 Pa, as measured with a MKS capacitor gauge. To investigate the influence of film thickness on the adhesion and electrochemical performance, two samples with N₂/Ar gas ratio of 0 and 0.5 were prepared using a longer deposition time of 30 min.
Table 5.1 Deposition parameters of the Ta and Ta-N films.

<table>
<thead>
<tr>
<th>N₂/Ar gas ratio</th>
<th>Mass flow rate</th>
<th>Average ion beam current (A)</th>
<th>Deposition time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂ (sccm*)</td>
<td>Ar (sccm*)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>20</td>
<td>0.04</td>
</tr>
<tr>
<td>0.25</td>
<td>5</td>
<td>15</td>
<td>0.06</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>0.08</td>
</tr>
<tr>
<td>0.75</td>
<td>15</td>
<td>5</td>
<td>0.10</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>20</td>
<td>0.04</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>0.08</td>
</tr>
</tbody>
</table>

*sccm (standard cubic centimetre per minute)

5.2.2 Surface Analysis

Grazing-incidence X-ray diffraction (XRD) tests of the deposited films were carried out with a GBC MMA diffractometer equipped with Cu Kα incident radiation. The XRD scan was in the 2θ mode at a glancing angle of 5° and from 30° to 80° in 0.02° steps. The contact angle of the surface was measured by the sessile drop method in a contact angle goniometer (Rame-Hart Instrument). 2 µL of the testing liquid, i.e. deionised water and fetal bovine serum (FBS) was used to measure the contact angle on the surface; these measures were repeated five times and an average value is reported. The thickness of the films was examined by cross-sectioning the surface in an FEI XT Nova Nanolab 200 work station equipped with a dual beam focused ion beam (FIB) and a field emission scanning electron microscope (FESEM). Film cohesion was studied using a Revetest Xpress scratch tester (CSM Instruments) with a 200 µm radius diamond indenter. The diamond tip was driven over the coated surface in the load range from 0.1 to 10 N to produce a scratch; the length of the scratch and the loading rate were 3 mm and 10 N/min, respectively. Scanning electron microscope (SEM) observations of the scratch were via a JEOL JSM-6490 SEM.

5.2.3 Measurements of Electrochemical Corrosion

Measurements of Electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) were taken with a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). Details of the electrochemical measurements are depicted in Chapter 2. A simulated biological fluid (SBF) solution was used as the test
solution because its ionic composition is similar to human blood plasma. Details of the compositions and method of preparing the SBF are described in Chapter 2. The pH of the SBF solution was 7.4±0.5. X-ray photoelectron spectroscopy spectrometer (XPS) was performed using a Specs SAGE 150 XPS that operated with Mg Kα X-ray source at 10 keV and 10 mA. The data were calibrated to the adventitious C1s peak present at 284.8 eV to minimise sample charging. CasaXPS was used to analyse the XPS data and curve fitting was displayed with a linear background.

5.3 Results and Discussion

5.3.1 Structure and Morphology of Ta-N Films

Figure 5.1 shows the XRD patterns of Ta and Ta-N films prepared at various N₂/Ar gas ratios. The deposited films exhibit peak broadening from 33º to 38º, which is attributed to a mixture of Ti6Al4V substrate and Ta-N film. The use of glancing angle XRD at 5º incident angle penetrate more than the film thickness 300 nm and therefore reflects the substrate peaks. At pure Ar gas pressure the film has a tetragonal β-Ta structure (JCPDS-25-1280), but as the N₂/Ar gas ratio increased to 0.25, 0.5, and 0.75, minor peaks which correspond to hexagonal Ta-N (JCPDS-39-1485) appeared, as did tetragonal β-Ta. This result is consistent with the work reported by Kim and Cha [15], except that orthorhombic Ta₃N₅ was not found in this work. The structure of tantalum nitrides is formed by the closely packed Ta atoms with N atoms inserted in interstitial sites [16]. A wide range of nitrogen-rich compounds (Ta₅N₆, Ta₄N₅, Ta₃N₅) may form as the amount of nitrogen increases. The complexity of Ta-N compounds is well reported in Ref. [17]. The equilibrium and metastable phases formed depend on the deposition procedures and conditions.
Figure 5.1 X-ray diffraction patterns of the Ta and Ta-N films prepared at various N$_2$/Ar gas ratios.

Figure 5.2 shows the AFM deflection images of Ta-N films at different nitrogen to argon gas ratios, with a Z-range of 30 mV. Pure Ta film (0 N$_2$/Ar gas ratio) has a very smooth surface with an average roughness of 3 nm; the smooth surface of pure Ta film is attributed to the growth of an amorphous film, as shown by the XRD result. As the nitrogen to argon gas ratio increases the surface topography exhibits island style growth of about 100 nm (Figure 5.2 (b)). The surface of film with a 0.5 N$_2$/Ar gas ratio, as shown in Figure 5.2 (c), tends to disintegrate between the colonies of the islands and makes the surface rougher, a result attributable to the reduced surface mobility of the atoms added by the formation of Ta-N bonding during deposition. The average surface roughness of the TaN film is 25 nm and 17 nm for 0.25 and 0.5 N$_2$/Ar gas ratio, respectively. The surface has become smoother ($R_a=10$ nm) in the Ta-N film with a 0.75 N$_2$/Ar gas ratio, probably due to the prolonged time for the migration of surface atoms due to a very low growth rate.
Figure 5.2 AFM deflection images of Ta-N films at nitrogen to argon gas ratios of (a) 0 (b) 0.25 (c) 0.5 (d) 0.75 with a Z-range of 30 mV.
5.3.2 Wettability Test of the Ta and Ta-N Film Surfaces

Surface wettability and surface biocompatibility are important parameters which influence cell growth. The average contact angle of water and fetal bovine serum is reported in Table 5.2. The contact angles of water and bovine serum in the Ta-N coated samples are higher than the contact angle of uncoated sample; however the sample deposited at a pure Ar gas pressure (0 N₂/Ar gas ratio) has a high water contact angle and a low contact angle when the sample is exposed to the FBS. This means that while the pure Ta surface presents hydrophobicity, it does not restrain the affinity between FBS and the film surface as much. The Ta-N films (N₂/Ar gas ratio of 0.25, 0.5 and 0.75) has similar contact angles for water and FBS from 81°–88°, indicating little change in the contact angle in relation to the presence of Ta-N phase in the films. Literature suggests that cell proliferation increases with increasing surface wettability [18,19]. Here, a contact angle less than 90° for Ta and Ta-N films indicates a less hydrophobic surface that is expected to promote cell adhesion and proliferation.

Table 5.2 Contact angles of each sample; note the N₂/Ar gas ratio of 0 indicates that the Ta coating was deposited in a pure argon atmosphere.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti6Al4V substrate</th>
<th>N₂/Ar gas ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Water contact angle (°)</td>
<td>70.3 ± 1</td>
<td>89.1 ± 1</td>
</tr>
<tr>
<td>Fetal bovine serum contact</td>
<td>77.2 ± 1</td>
<td>73.7 ± 1</td>
</tr>
<tr>
<td>angle (°)</td>
<td></td>
<td>(°)</td>
</tr>
</tbody>
</table>

5.3.3 Scratch Behaviour

The adhesion of the film was examined using a progressive load of up to 10 N. The critical load as a result of coating failure was determined by a sudden change in the coefficient of friction and the scratch track image. The acoustic emissions signal remains constant and is not indicative of film failure, due to the thin Ta film and ductile Ti6Al4V substrate. As Figure 5.3 (a) shows, the film began to fail at the first critical load of 1.8 N. Both tensile cracking and conformal cracking (white semi-circular lines) are shown in Figure 5.3 (b) at the start of the track. Tensile cracks opened in the direction of the scratch due to tensile frictional stresses as the tip of the stylus moved across the surface. These micro-cracks...
formed as a result of tensile bending within the coating as the tip of the stylus deformed the coating and the underlying substrate [20].

The scratches on the Ta-N film deposited at 0.25 N₂/Ar gas ratio are shown in Figure 5.4. The first critical load is shown at 2.6 N, followed by a sudden increase in the frictional force. As Figure 5.4 (b) and Figure 5.5 (b) show, there is buckling and spalling on the Ta-N films deposited at 0.25 and 0.5 N₂/Ar gas ratios; the main reason these coating failed is because the compressive stress field preceded the moving stylus [21]. Figure 5.5 shows the Ta-N film deposited at 0.5 N₂/Ar gas ratio; the first critical load was at 5.2 N, indicating a
significant improvement in the film-substrate adhesion, and the bond between the film and substrate improves as the N₂/Ar gas ratio increases. However, at 0.75 N₂/Ar gas ratio, the first critical load of 1.8 N is less than the critical load obtained for Ta-N film at 0.5 N₂/Ar gas ratio. Tensile cracks appeared in Figure 5.6 (b). The tensile frictional stresses in the film generated defects in the surface and resulted in low adhesion.

Figure 5.4 (a) Micrograph of failure after scratch test for Ta-N film at 0.25 N₂/Ar gas ratio; (b) is where buckling occurred, (c) is where gross spallation occurred.
Figure 5.5 (a) Micrograph of failure after scratch test for Ta-N film at 0.5 N$_2$/Ar gas ratio; (b) is where buckling occurred, (d) is where gross spallation occurred.
Figure 5.6 (a) Micrograph of failure after scratch test for Ta-N film at 0.75 N₂/Ar gas ratio; (b) is where the tensile cracks started, (c) is where gross spallation occurred.

To compare the coating adhesion with a thicker film, pure Ta and Ta-N film with 0.5 N₂/Ar gas ratio were prepared at a deposition time of 30 minutes. The films deposited in 5 minutes varied in thickness between 233–365 nm, while the films deposited for 30 minutes at 0 and 0.5 N₂/Ar gas ratio were 0.7 µm and 1 µm thick, respectively. Figure 5.7 shows the relationship between the length of the scratch, the normal force, the coefficient of friction, and the acoustic emissions for Ta-N film deposited for 30 minutes at 0.5 N₂/Ar gas ratio. The first critical load appeared at 1.1 N accompanied by a sudden increase in the acoustic emissions and the coefficient of friction. The SEM image and X-ray mapping of the corresponding scratch track image are shown in Figure 5.8. An energy dispersive X-ray
(EDX) spectroscopy analysis shows that the coating peeled off mainly at the start of the track due to the weak bond between film and substrate; this is followed by complete detachment of the film after a certain distance which is consistent with the results shown in Figure 5.7. It does suggest that a thicker film does not help adhesion because the critical load for spallation is proportional to the thickness of the coating [22], so as the thickness increases, the tensile stress normal to the interface increases due to the action of the stress in the plane of the surface. An increase in the residual stress of a thicker film can contribute to poor adhesion between the film and the substrate. The SEM and scratch (Figure 5.7) results for thick film indicate relatively poor adhesion compared to the 5 minute film. Three scratch experiments were carried out for each sample and the results of the critical load obtained at which failure modes occurred are reproducible. However, a conical indenter with a tip radius of a few microns is preferable for sub-micron coatings, whereas the Rockwell ‘C’ stylus is appropriate for industrial hard coatings with a thickness >1 µm [23].

Figure 5.7 Result of scratch test for Ta-N film at 0.5 N_2/Ar gas ratio for deposition time of 30 min.
5.3.4 Analysis of Electrochemical Corrosion

The impedance spectra of Ta-N films at 10 mV amplitude produced at different N₂/Ar gas ratios after exposure to SBF for 1 hour are shown in Figure 5.9. The Nyquist plot, Figure 5.9 (a), shows a relatively larger semi-circle for the coated samples at 0 and 0.25 N₂/Ar gas ratios, which indicates an increased resistance of the surface layer with the most capacitive
behaviour for the sample prepared at 0.25 N₂/Ar gas ratio. Figure 5.9 (b) shows a magnified section of the Nyquist plot in the lower range of values in Figure 5.9 (a). In Figure 5.9 (b) & 5.9 (c), it is evident that the Ta and Ta-N coated samples have much higher impedances than the uncoated Ti6Al4V substrate, which implies that the passive film formed on the coated surfaces is more protective than for the uncoated Ti6Al4V in SBF. Figures 5.9(b) & 5.9(c) also suggest there is a threshold for N₂/Ar gas ratio after which impedance begins to decrease. Low frequency (<1 Hz) impedance is lower in the thick 30 minute Ta film with 0 N₂/Ar gas ratio, whereas the thick 30 minute Ta film with 0.5 N₂/Ar gas ratio has a higher impedance than the thinner 5 minute film. The mid-frequency region of the Bode plots can be used to characterise local surface defects, while the reactions on the surface, e.g. charge transfer, are indicated by the low frequency region (<1 Hz) [24]. As Figure 5.9 (d) shows, there is a significant change in the phase angle in the low frequency region for samples of 0.5 N₂/Ar gas ratio+5 min and 0.75 N₂/Ar gas ratio+5 min, showing that the surface was acting like a non-ideal or leaking capacitor. This is possibly due to the passive film of the sample becoming unstable and defective after immersion in SBF, causing a large variation in the phase angle. While the phase shift reached 85° for the sample of 0.25 N₂/Ar gas ratio+5 min, implying a passive film present on the surface with highly capacitive response, the Ti6Al4V substrate has the lowest phase shift in the low frequency range of the Bode plot, as shown in Figure 5.9 (c). However, the passivating layer on top of the Ta-N films acts like an insulating layer that offers corrosion protection in a buffered biological environment. Similar protective properties of Ta-N films on 316L stainless steel attributable to the formation of a protective surface layer, were recently reported by Alishahi et al [25].
Figure 5.9 Nyquist and Bode impedance spectra of Ta-N films at different N\textsubscript{2}/Ar gas ratios.

Table 5.3 presents a quantitative analysis of EIS data by fitting the appropriate electrical equivalent circuit (EEC). The impedance data of Ti6Al4V substrate fit the EEC with two loop elements, as shown in Figure 5.10 (a). In the circuit $R_s$ represents the resistance of the solution between the working and reference electrodes, $Q_{\text{oxide film}}$ and $R_{\text{oxide film}}$ are the constant phase element (CPE) and resistance associated with the oxide film on the surface. The constant phase element (CPE) is indicative of the capacitive contribution and its deviation from ideal dielectric behaviour due to surface heterogeneities such as roughness, inhomogeneous surface, absorption of ions, or possible variations in the physical properties of the covering film [26]. The exponent $n$ indicates a variation from ideal capacitor/resistor where $n = 1$ for the pure capacitor, and $n = 0$ for the pure resistor. $Q_{dl}$ and $R_{ct}$ are the CPE and resistance associated with the electrical double layer and charge transfer resistance, respectively. The EEC model with one time constant (loop element), Figure 5.10 (b), produced a good fit on the impedance data for the samples with 0.25 N\textsubscript{2}/Ar gas ratio+5 min, whereas the impedance data of Ti6Al4V substrate and other coated samples fit the
EEC model best with two time constants [Figure 5.10 (a)]. The simulation model with one time constant for the 0.25 N$_2$/Ar gas ratio+5 min indicates the formation of a uniform oxide layer without defects. The 0.25 N$_2$/Ar gas ratio+5 min has the highest charge transfer resistance of 3607 kΩ cm$^2$ of the tested samples. This indicates that the surface itself affords the best corrosion protection due to the stability of passive film.

The corrosion seen in Figure 5.12 (a) and (e) and the EDS analysis in Figure 5.13 confirms the formation of a surface layer of calcium phosphate on the pure Ta films with deposition of 5 minutes and 30 minutes. The pure Ta film exhibits a somewhat protective effect because the pores are sealed by the precipitation of calcium phosphate in the electrolyte. Hydrated oxide film (Ta-OH group) was formed by a slow hydration of the tantalum oxide layer in the SBF solution. This Ta hydroxide reacts with calcium ion and phosphate ion on the metal surface and build up a layer of calcium phosphate [27,28]. Similar results were reported by Valero Vidal and Igual Munoz [29], on the protective effect that phosphate had on stainless steel in a phosphate buffered saline solution that improves the passive behaviour by increasing the charge transfer resistance. In Ta-N coated Ti6Al4V substrate, passive film forms and protects the substrate from degradation and generates a capacitive response.
Table 5.3 Electrical components calculated by fitting an equivalent electrical circuit on the EIS data.

<table>
<thead>
<tr>
<th></th>
<th>( Q_{\text{oxide film}} ) (µΩ⁻¹ sⁿ cm⁻²)</th>
<th>( n_1 )</th>
<th>( R_{\text{oxide film}} ) (kΩ cm²)</th>
<th>( Q_{dl} ) (µΩ⁻¹ sⁿ cm⁻²)</th>
<th>( n_2 )</th>
<th>( R_{ct} ) (kΩ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V substrate</td>
<td>31.3</td>
<td>0.90</td>
<td>18.3</td>
<td>855</td>
<td>0.91</td>
<td>9.58</td>
</tr>
<tr>
<td>0 N(_2)/Ar gas ratio+5 min</td>
<td>14.1</td>
<td>0.94</td>
<td>133</td>
<td>2.28</td>
<td>0.84</td>
<td>336</td>
</tr>
<tr>
<td>0.25 N(_2)/Ar gas ratio+5 min</td>
<td></td>
<td></td>
<td>12.2</td>
<td>0.95</td>
<td>3607</td>
<td></td>
</tr>
<tr>
<td>0.5 N(_2)/Ar gas ratio+5 min</td>
<td>12.4</td>
<td>0.80</td>
<td>36.7</td>
<td>58.3</td>
<td>0.80</td>
<td>604</td>
</tr>
<tr>
<td>0.75 N(_2)/Ar gas ratio+5 min</td>
<td>13.2</td>
<td>0.95</td>
<td>13.6</td>
<td>18.9</td>
<td>0.73</td>
<td>282</td>
</tr>
<tr>
<td>0 N(_2)/Ar gas ratio+30 min</td>
<td>29.0</td>
<td>0.87</td>
<td>733</td>
<td>47.5</td>
<td>0.87</td>
<td>903</td>
</tr>
<tr>
<td>0.5 N(_2)/Ar gas ratio+30 min</td>
<td>21.9</td>
<td>0.89</td>
<td>43.1</td>
<td>10.7</td>
<td>0.89</td>
<td>494</td>
</tr>
</tbody>
</table>
Figure 5.10 Electronic equivalent circuits (EEC) used in the fitting procedure of the EIS experimental data.

Table 5.4 summarises the results from an electrochemical frequency modulation (EFM) that was used because this measurement is non-destructive, particularly when examining thin films. The rate of corrosion was derived from non-linearity in the voltage-current response of the electrochemical interface [30], while the corrosion parameters and causality factors were calculated in a single measurement using the data analysis software package provided by Gamry. Ta-N films deposited at 0 and 0.25 N\textsubscript{2}/Ar gas ratios at a deposition time of 5 minutes show a corrosion current density of $10^{-7}$ A/cm\textsuperscript{2}. This result is consistent with the EIS results when identifying Ta-N films at low N\textsubscript{2}/Ar gas ratio with protective characteristics for the Ti6Al4V substrate. The sample prepared at 0.25 N\textsubscript{2}/Ar gas ratio with 5 minute deposition time, i.e. 0.25 N\textsubscript{2}/Ar gas ratio+5 min, has the lowest corrosion rate of 0.25 mpy. The polarisation resistance of 0.25 N\textsubscript{2}/Ar gas ratio+5 min is an order of magnitude higher than the value of the uncoated Ti6Al4V substrate. We attributed
a TaON layer on the deposited Ta-N film (will be depicted in section 5.3.5 XPS results) to the enhanced corrosion resistance, with the TaON layer acting as a charge transfer barrier. The causality factors with an acceptable range of 2 and 3 were achieved to ensure the validity of the EFM results [31,32]. In this current work a sinusoidal signal with amplitude of 40 mV was used to examine the response of current relating to pitting corrosion. As Figure 5.11 shows, current fluctuations increased with an increasing N\textsubscript{2}/Ar gas ratio, possibly due to localised corrosion such as the formation of corrosion pits in the high N\textsubscript{2}/Ar gas ratio samples after exposure to solutions containing chloride. A large current response at inter-modulating frequencies indicates the formation of pitting [30].

Table 5.4 Corrosion parameters calculated from electrochemical frequency modulation (EFM).

<table>
<thead>
<tr>
<th>N\textsubscript{2}/Ar gas ratio + deposition time</th>
<th>Corrosion current density, I\textsubscript{corr} (µA/cm\textsuperscript{2})</th>
<th>Corrosion rate (mpy)</th>
<th>Polarisation resistance, R\textsubscript{p} (Ωcm\textsuperscript{2})</th>
<th>Causality factor 2</th>
<th>Causality factor 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 N\textsubscript{2}/Ar gas ratio + 5 min</td>
<td>0.714</td>
<td>0.646</td>
<td>8.78 × 10\textsuperscript{4}</td>
<td>2.13</td>
<td>2.73</td>
</tr>
<tr>
<td>0.25 N\textsubscript{2}/Ar gas ratio + 5 min</td>
<td>0.276</td>
<td>0.250</td>
<td>2.43 × 10\textsuperscript{5}</td>
<td>1.69</td>
<td>2.73</td>
</tr>
<tr>
<td>0.5 N\textsubscript{2}/Ar gas ratio + 5 min</td>
<td>1.78</td>
<td>1.61</td>
<td>1.05 × 10\textsuperscript{5}</td>
<td>2.05</td>
<td>2.50</td>
</tr>
<tr>
<td>0.75 N\textsubscript{2}/Ar gas ratio + 5 min</td>
<td>3.20</td>
<td>2.89</td>
<td>3.00 × 10\textsuperscript{4}</td>
<td>1.63</td>
<td>3.37</td>
</tr>
<tr>
<td>0 N\textsubscript{2}/Ar gas ratio + 30 min</td>
<td>1.98</td>
<td>1.79</td>
<td>3.31 × 10\textsuperscript{4}</td>
<td>1.85</td>
<td>2.71</td>
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<tr>
<td>0.5 N\textsubscript{2}/Ar gas ratio + 30 min</td>
<td>2.69</td>
<td>2.43</td>
<td>3.30 × 10\textsuperscript{4}</td>
<td>1.95</td>
<td>1.65</td>
</tr>
<tr>
<td>Ti6Al4V substrate</td>
<td>6.51</td>
<td>2.89</td>
<td>1.72 × 10\textsuperscript{4}</td>
<td>1.80</td>
<td>2.77</td>
</tr>
</tbody>
</table>
Figure 5.11 Non-linear behaviour of the current response in the frequency domain.

Figure 5.12 shows SEM images of the specimens after one hour immersion in SBF and then 20 minutes of EIS testing. There is a layer of corrosion on the pure Ta film after EIS testing, as shown in Figure 5.12 (a). An EDS analysis of the corroded surface shown in Figure 5.13 confirmed the presence of oxygen, tantalum, titanium, aluminium, vanadium, chlorine, sodium, calcium and potassium; the calcium, sodium, chlorine and potassium came from the SBF. According to XPS analysis, tantalum oxide is formed when Ta corrodes in aqueous environments by an electrochemical reaction. Figure 5.12 (b), (c) & (d) show the SEM images of Ta-N films at 0.25 N₂/Ar gas ratio+5 min, 0.5 N₂/Ar gas ratio+5 min and 0.75 N₂/Ar gas ratio+5 min, respectively. Under the same magnification, the formation of small pits was more obvious as the N₂/Ar gas ratio increased. In a reactive position, the deposition rate reduces with increase in reactive gas and there were chances of increase in pin holes formed. The reduced thickness of Ta film with 0.75 N₂/Ar gas ratio allows easier penetration by the SBF solution through defects. Figure 5.14 (a) shows the corroded surface at other regions on the 0.5 N₂+5 min Ta-N. It is apparent that Ta-N film is susceptible to pitting corrosion, where cracks occur and the corrosive liquid diffuses into the coating, as shown in Figure 5.14 (b) at a magnification of ×1000. With the Ta-N films
at a deposition time of 30 minutes, i.e. Figure 5.12 (e) & (f), film detachment was clearly evident. The corrosion current density of Ta-N film at 0.5 N₂/Ar gas ratio+30 min increased to 2.69×10⁻⁶ A/cm² from 1.78×10⁻⁶ A/cm² thus corresponding to Ta-N film at 0.5 N₂/Ar gas ratio+5 min. Although the difference in the current density is not large, the corroded surface of the thicker film is prone to the formation of micro cracks [Figure 5.12 (e) & (f)]. Coating adhesion is an important factor for protecting biomedical coatings from corrosion, and the thicker Ta-N film has relatively poor adhesion, as discussed in section 5.3.3. There is also the possibility of a more distinct difference in reactivity between the grain boundaries and the rest of the surface in the thicker film compared to the thinner film. In the micro-arc oxidation process, a thicker coating requires a higher breakdown voltage and allows more energy to accumulate than a thinner coating. The larger stresses in a thicker coating also create more local defects such as micro-fractures. Those defects reportedly allow more eroding ions to enter into the coating and worsen the corrosion resistance of the oxide coating [33]. Similarly, the thicker Ta-N films in this study had poor coating adhesion and coating defects which expedited the formation of micro cracks after immersion in SBF.
Figure 5.12 SEM images of Ta and Ta-N films after electrochemical measurement (a) 0 N$_2$/Ar gas ratio+5 min (b) 0.25 N$_2$/Ar gas ratio+5 min (c) 0.5 N$_2$/Ar gas ratio+5 min (d) 0.75 N$_2$/Ar gas ratio+5 min (e) 0 N$_2$/Ar gas ratio+30 min (f) 0.5 N$_2$/Ar gas ratio+30 min.
Figure 5.13 Energy dispersive X-ray spectrum of the sample 0 N$_2$/Ar gas ratio+5 min. Data is associated with the area shown in Figure 5.12 (a).

Figure 5.14 SEM images of 0.5 N$_2$/Ar gas ratio+5 min Ta-N film after electrochemical measurement at magnification of (a) ×50 (b) ×1000.
5.3.5 X-ray Photoelectron Spectroscopy Analysis

Figure 5.15 (a) shows the full XPS spectrum of Ti6Al4V substrate after EIS corrosion testing (1 hour soaking in SBF and 20 minutes EIS scanning at 10 mV amplitude). The spectrum shows signals from Ti, O, Ca and C elements, which suggests the presence of TiO$_2$ and small amounts of calcium on the surface. The high resolution Ti 2p core level spectrum (Figure 5.15 (b)) shows that the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ doublet was located at 458.5 eV and 464.2 eV, respectively. The splitting of the doublet is 5.7 eV, which indicates that TiO$_2$ was a main component in the surface layer of the uncoated sample. The Ti 2p peaks were in good agreement with the pure TiO$_2$ reported in the literature [34,35]. As shown in Figure 5.15 (c), the O 1s peak can be de-convoluted into two peaks at 530.6 eV and 531.9 eV, and assigned to the TiO$_2$ and carbonyl C=O peaks, respectively. The layer of Ca 2p with the binding energies recorded at 350.8 eV (calcium phosphate) and 346.9 eV (calcium carbonate) was also present on the uncoated surface after EIS testing in SBF (Figure 5.15 (d)). Ca and P are the result of a reaction between the Ti6Al4V substrate and SBF solution. This result is consistent with the work reported by De Sena et al. [36], where a calcium phosphate layer formed spontaneously on the titanium surface when it was immersed in SBF solution.
Figure 5.15 X-ray spectroscopy spectra of the Ti6Al4V substrate after corrosion test (a) full spectrum (b) Ti 2p (c) O 1s (d) Ca 2p.

Figure 5.16 compares the Ta 4f core-level spectra of pure Ta film and Ta-N film at 0.25 N2/Ar gas ratio+5 min before and after corrosion tests. The deconvolution of all four Ta 4f spectra was carried out with a constraining condition where all the 4f7/2 – 4f5/2 doublets have a fixed area ratio of 4:3 and an energy separation of 1.91 eV [37,38]. As Figure 5.16 (a) shows, the Ta 4f spectrum is de-convoluted into four doublets consisting of Ta2O5, Ta sub-oxides with lower oxidation states (TaO2 and TaO), and metallic Ta0. The Ta 4f7/2 and Ta 4f5/2 peaks located at 26.3 eV and 28.2 eV are attributed to the most stable form of pentavalent state, Ta2O5, as reported in the literature [39]. The Ta 4f7/2 and Ta 4f5/2 peaks located at 25.0 eV and 26.9 eV correspond to the TaO2, peaks located at 23.5 eV and 25.4 eV, and are categorised to the TaO. The binding energies of the sub-oxides are close to the values reported by Moo et al [40]; these sub-oxides may exist in the surface layer or they may occur due to a reduction of the oxide by the preferential removal of oxygen during Ar etching before XPS scanning [40]. The binding energies of the low energy-doublet (22.0 eV and 23.9 eV) are attributed to metallic tantalum, Ta0 [35]. Note that a Ta 4f spectrum of
pure Ta film has a relatively large shoulder at the low energy doublet, which implies the deposited film contains mainly metallic Ta. After a corrosion test, the peak width (Figure 5.16 (b)) at the low energy doublet decreased significantly and the spectrum shows two primary peaks of Ta 4f\(_{7/2}\) and Ta 4f\(_{5/2}\) peaks located at 26.3 eV and 28.2 eV; this result indicates the formation of a passive layer of Ta\(_2\)O\(_5\).

For Ta-N film at 0.25 N\(_2\)/Ar gas ratio+5 min, the deconvolution of Ta 4f spectrum is shown in Figure 5.16 (c), where the Ta 4f\(_{7/2}\) and Ta 4f\(_{5/2}\) peaks positioned at 26.3 eV and 28.2 eV correspond to Ta\(_2\)O\(_5\); there are also small peaks corresponding to TaO\(_2\) (25.0 eV and 26.9 eV). The doublet with the Ta 4f\(_{7/2}\) and Ta 4f\(_{5/2}\) peaks is in close agreement with the values of 25.6 eV and 23.7 eV reported for hexagonal TaN [41]. The TaN peaks are consistent with the result obtained for XRD, where a hexagonal TaN phase is observed as the N\(_2\)/Ar gas ratio increased. Representative peaks of metallic Ta\(^0\) are also observed in the surface. After the corrosion test, the Ta 4f peaks of Ta\(_2\)O\(_5\) were shifted to lower binding energies by 0.5 eV to 25.8 eV and 27.7 eV for the 4f\(_{7/2}\) and Ta 4f\(_{5/2}\) peaks, respectively (Figure 5.16 (d)). This implies the formation of a TaON layer on the surface. This result is consistent with the work reported by Xu et al [13], where the binding energies of the Ta 4f peaks for pure Ta\(_2\)O\(_5\) coating shift to a lower energy of 0.6 eV for pure TaON coating. This shift in the binding energies is caused by covalency between Ta and N that is greater than between Ta and O where the oxygen is more electro-negative than nitrogen. The peak intensity and peak width of the 4f\(_{5/2}\) and Ta 4f\(_{7/2}\) peaks (21.4 eV and 23.3 eV) at low-energy doublet corresponding to metallic Ta\(^0\) decreased after the corrosion test. The TaO\(_x\) phase on the surface layer generally acts like a charge barrier layer that protects the substrate from corrosion. As reported by Xu et al. [9], a TaON coating with a lower carrier density had higher corrosion resistance than β-Ta\(_2\)O\(_5\). The charge donor density (N\(_d\)) is highest for the passive film formed on bare Ti6Al4V alloy (3.76 × 10\(^{20}\) cm\(^{-3}\)), followed by the β-Ta\(_2\)O\(_5\) (9.89 × 10\(^{18}\) cm\(^{-3}\)) and TaON (7.19 × 10\(^{18}\) cm\(^{-3}\)) coatings as calculated from Mott-Schottky plots. This means that the protective oxide film provided by the TaON coating is the most stable and insulating, therefore offers more protection to Ti6Al4V alloy than the β-Ta\(_2\)O\(_5\) coating. In fact the Ta-N film at 0.25 N\(_2\)/Ar gas ratio+5 min had higher corrosion resistance than pure Ta film in this work because of good passivation by TaON due to its lower carrier density. The XPS results confirmed the passive surface oxide and TaON on the surfaces of pure Ta film and Ta-N film at 0.25 N\(_2\)/Ar gas ratio +5 min after corrosion.
respectively. The formation of TaON could be attributed to electrochemical reactivity of TaN in aqueous media due to its low isoelectric point of 1.0 [42] and presence of negative charge on TaN surface at pH 7.4. This promotes absorption and interaction with the electronegative species thus formation of oxide or hydrated oxide TaN, i.e. TaON or TaON,xH2O. Similar mechanism has been proposed elsewhere [43] for formation of TaOxNy upon exposure of TaN film to SBF. TaON layer would intrinsically exhibit higher inertness compared to TaN and therefore will afford more effective passivation. We believe that the TaON in the surface provided satisfactory resistance to corrosion and leads to a significant improvement in the corrosion resistance of Ta-N film with a proper thickness of 300 nm and with mechanical integrity.

Figure 5.16 X-ray spectroscopy spectra of the (a) pure Ta film before corrosion test; (b) pure Ta film after corrosion test; (c) Ta-N film at 0.25 N2/Ar gas ratio+5 min before corrosion test (d) Ta-N film at 0.25 N2/Ar gas ratio+5 min after corrosion test.
5.4 Summary

Ta-N films were successfully deposited onto Ti6Al4V substrates using filtered cathodic vacuum arc deposition. A hexagonal Ta-N phase in the resultant films was identified with an increase in the N2/Ar gas ratio. The ~300 nm Ta-N film prepared at 0.5 N2/Ar gas ratio exhibited good adhesion to the Ti6Al4V substrate but this adhesion deteriorated as the thickness of the coating increased to ~1 μm. Ta-N films enhanced the corrosion resistance of Ti6Al4V substrates due to the stability of the layers of passive oxide and oxy-nitride. The low charge carrier density of the TaON layer was verified by XPS results and the high electrochemical impedance. An increase in the N2/Ar gas ratio weakens the adhesion of the film and increases its susceptibility to pitting corrosion. These results show that Ta-N film prepared by filtered-cathodic-arc deposition technique in an optimised atmosphere and thickness showed improved corrosion resistance and strong bonding to Ti6Al4V surface.
References


Chapter 6. Tribo-corrosion Performance of Filtered-arc-deposited Tantalum Coatings on Ti13Nb13Zr Alloy for Bio-implants Applications

6.1 Introduction
Titanium and its alloys are widely used as metallic materials in orthopaedics due to their lower elastic modulus, enhanced biocompatibility, better corrosion resistance in comparison with cobalt-based alloys and conventional stainless steels [1–3]. Thin oxide layer that forms naturally on the titanium surface contributes to excellent corrosion resistance [4]. However, titanium alloys exhibit poor wear resistance and increases its degradation when surrounded by corrosive body fluids. The release of metallic ions from the articulating bearing surfaces would cause toxicity, allergic reactions, inflammation of tissues, and failure of implants [5,6]. Ti6Al4V alloy loses its biocompatibility if vanadium or aluminium ions are introduced into human tissues, where vanadium ions have cytotoxic effects, and aluminium ions can cause neurological disorder [7]. Therefore, Ti13Nb13Zr alloy which has a relatively low elastic modulus (E= 79 GPa), is developed to improve load transfer to the bone and reduce the incidence of loosening in total hip replacement [8,9]. Nb and Zr substitute does not cause adverse tissue reaction while the strength and toughness of the metal are comparable to the existing implant metal Ti6Al4V alloy [10,11].

Tantalum (Ta) attracts considerable attention due to its good mechanical properties, biocompatibility and outstanding corrosion resistance [12–14]. The formation of Ta-OH groups on its surface, when exposed to simulated biological fluid, promotes apatite nucleation and helps with the bone-bonding ability [15]. The use of Ta has been limited to suture wire, wire mesh, cranial plates and fixation plates for surgical purposes since the 1940s [16]. The high density and cost of manufacture restrict the widespread acceptance of bulk Ta metal for implant applications. Therefore, Ta coatings have been investigated to combine the desirable bulk properties of the substrate and excellent surface properties of the coating [17,18]. The refractory metal, Ta renowned for its high melting point, presents in three different natures; (1) body-centred cubic (2) tetragonal (3) amorphous. β-Ta with tetragonal structure is hard and brittle, and generally found in most magnetron sputtered
films [19], and double cathode glow discharge plasma technique [20]. The soft and ductile nature of α-Ta with body-centred cubic structure is formed by manipulating the deposition conditions, such as sputtering gas [21], the thickness of the layer, energetic ion bombardment [22], bias voltage [23], substrate temperature [24], substrate material and buffer layers [25,26]. Amorphous tantalum film exhibits characteristic of high-resistivity metallic behaviour, can be produced by pulsed laser deposition [27] and electron-beam evaporators [28].

In this chapter the tribo-corrosion performance of Ta coatings on Ti13Nb13Zr alloy substrate is evaluated using a ball-on-disk tribometer in simulated biological fluid. Although the medical device industry has expended a lot of resources trying to develop clinically correlated test methods for implants, including dynamic loading, multi-directional sliding, and long run capacity, a ball-on-disk configuration is a simplified and reliable method for a first stage tribological/corrosion assessment of the coating, the substrate materials, and the coating condition [29]. Only a few studies of the wear performance of Ta coatings have been reported, and they focused on the wear performance of a tantalum based multilayer coating on cobalt chromium molybdenum alloy in a dilute bovine serum [30,31]. A ceramic tantalum oxide (TaO₂) coating deposited by magnetron sputtering improved the wear and corrosion resistance of Ti-6Al-4V alloy [32], but the analysis of sliding wear debris is inadequate in the literature. This study therefore seeks to investigate the corrosion and wear resistance of a Ta coating deposited by filtered cathodic vacuum arc deposition, which is intended for use as protective films for orthopaedic implants. The wear debris generated from uncoated and coated surfaces is characterised by scanning electron microscopy, and the corrosion performance of the samples was examined by electrochemical impedance spectroscopy and potentiodynamic polarisation. The microstructure of the coatings and adhesion between the coating and substrate interface were correlated to their response to corrosion. The effect of substrate heating on the microstructure and film cohesion of the filtered-arc-deposited coatings was also investigated.

6.2 Details of Experiments
Ti13Nb13Zr alloy disks 25 mm in diameter (for structure characterisation) and 50 mm in diameter (for tribological testing) were mechanically ground and polished. These
substrates were ultrasonically cleaned in ethanol, distilled water and acetone, and then dried prior to deposition. The average surface roughness of the polished substrates was 0.05 µm, as measured by a Keyence VK-X100 laser scanning microscope. Deposition was carried out using FCVAD (filtered cathodic vacuum arc deposition) made at the University of Wollongong. The arc cathode (target) was high purity tantalum (purity, 99.99 %) with a diameter of 58 mm. The chamber was pumped out to a base pressure of 1.0×10⁻² Pa, and then pure argon was introduced into the deposition chamber through a mass flow controller at 5 cm³/min. The substrates were cleaned by argon ion etching at a high substrate bias of −850 V using Ta ions generated from the arc source for 2 minutes. Ta coatings were deposited for about 30 min using a substrate voltage bias of −100 V and an arc current of 200 A. The operating pressure was stabilised at 0.4 Pa during deposition. There were two depositions, (a) Ta coating on the non-heated substrate, and (b) Ta coating with the substrate heated to 300 ºC during deposition.

The phase compositions of the deposited films were assessed by grazing incidence X-ray diffraction (XRD) analysis with a GBC MMA diffractometer equipped with the Cu Kα incident radiation. The scan was between 25°–80° with a step size of 0.02°, scan rate of 1°/min, and a grazing angle of 5°. Nano-indentation was made on the coated samples using a UMIS-2000 (Ultra-Micro Indentation System). The hardness and elastic modulus were determined with incremental controlled loading and unloading tests in a range of maximum loads from 5 mN to 50 mN. Scratch tests on the deposited films were carried out with a Revetest Xpress Scratch Tester. A progressive load from 0.1 N to 50 N over a length of 5 mm was made to characterise the critical load where failure occurs. Three scratch experiments were carried out on each sample to verify the reproducibility of the results. The thickness of the coating was examined by an FEI XT Nova Nanolab 200 workstation. Tribological tests were via a ball-on-disc tribometer (UMT2 multi-specimen testing system). The experimental setup of the tribological tests is presented in chapter 2.

An electrochemical impedance spectroscopy (EIS) analysis was carried out using a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). The experimental setup for the electrochemical measurements is illustrated in Chapter 2. A simulated biological fluid (SBF) was used as the test solution. Samples were exposed to electrolyte for 60 minutes under open circuit potential (OCP) prior to taking measurements. The
samples were immersed in the SBF solution for 14 days at 37 °C and the SBF solution was periodically replaced after every 24 hours. Impedance measurements were taken at the interval of 1 hour, 7 days, and 14 days using an amplitude of 10 mV RMS between 10 mHz – 10 kHz. The experimental data were analysed and fitted to appropriate electrical equivalent circuits (EECs) using ZSimpWin software package. A potentiodynamic polarisation test was carried out on the samples immersed in electrolyte for 14 days, and the corroded surface was examined with a JEOL JSM-6490 scanning electron microscope.

6.3 Results and Discussion

6.3.1 Structural Analysis

Figure 6.1 shows the XRD patterns of the Ti13Nb13Zr substrate and the Ta coatings. The Ti13Nb13Zr alloy substrate has two strong peaks at 38° and 40° with reflections of (002) and (101) planes; they correspond to the hexagonal closed-packed (JCPDS card no 00-044-1294) [33]. There is a large broad hump in the 2θ range of 30–38°, which indicates the Ta coating has an amorphous structure on the non-heated substrate. This amorphous layer could be due to an insufficient energy flux which destabilised the interfacial reaction between tantalum and the substrate material. Small charged clusters that nucleated in the gas phase and did not adapt to the surface structure of the substrate resulted in an amorphous, non-crystalline film [34]. There are similar results in the literature, where thin, non-crystalline Ta was created in the sputtered Ta films [24,35]. With the Ta coating on the heated substrate, a diffraction of (002) at 33.7° and a diffraction of (110) at 38.5° correspond to the metastable tetragonal phase (β-Ta) and stable body-centred cubic phase (α-Ta), respectively [36]. When the substrate temperature is heated to 300 °C, the high temperature surface charged clusters result in less agglomeration and offer the possibility of a good crystalline structure [37]. Similarly, the nucleation of α-Ta was achieved by heating the substrate in a magnetron sputtering system. The driving force towards the nucleation of α-Ta increased as the substrate temperature increased, with a mixture of α-Ta and β-Ta phases from 450–600 K, while the film is 100% pure α-Ta above 600 K [24].
Figure 6.1 XRD patterns of the Ti13Nb13Zr substrate and Ta coatings.

Figure 6.2 shows cross sectional images of Ta coatings on the non-heated and heated substrates. These Ta coatings are 1.1 µm and 0.64 µm thick on the non-heated substrate and the heated substrate, respectively. Note that the temperature of the substrate has little influence on the growth rate of the film [38], however, the suppression of the deposition rate of about 40% for the Ta coating on heated substrate may be due to re-sputtering effect as a result of competition between deposition and etching by the surface material [39]. Increasing the substrate temperature generates high-energy atoms, hence the re-sputtering effect by high energy gas atoms increases.
6.3.2 Mechanical and Tribological Properties

Figure 6.3 shows the hardness and elastic modulus vs. the depth of indentation of the samples. Hardness increases as the indentation depth decreases because the effect of the substrate decreases and the hardness value mainly reflects the hardness of the coatings. The hardness of the Ta coating on the non-heated substrate is significantly higher than the Ta coating on the heated substrate, which is attributed to the thicker film (1.08 µm) of the Ta coating on the non-heated substrate. The hardness of the coating is < 15 GPa which agrees with the hardness of the Ta films concomitant of the α and β phases [26,40]. The elastic modulus of the Ta coating on the heated substrate is much lower than the value of the Ta coating on the non-heated substrate. This transformation of the Ta coating on the heated substrate from an amorphous to a crystalline structure leads to a decrease in the elastic modulus. When the substrate is heated to 300 °C, the coating has a relatively high hardness and low elastic modulus, giving a high hardness to modulus ratio of ~ 0.1. A high hardness to modulus ratio is a good indicator of the wear performance of a coating [41].
Figure 6.3 The curves plotted (a) hardness, (b) elastic modulus as a function of the indentation depth of the samples.

Figure 6.4 shows the scratch behaviour of the Ta coating on the unheated substrate. The SEM images representative of the scratch track at different levels of loading (increasing from (b) to (d)) are shown in Figure 6.4, and indicate that the coefficient of friction and acoustic emissions undergo an abrupt change at the first critical load of 3.5 N due to tensile cracking [Figure 6.4 (b)] as a result of tensile bending within the coating as the tip of the stylus deformed the coating and the underlying substrate [42]. Figure 6.4 (c) shows buckling at a second critical load of 17 N, followed by complete exposure of the substrate material; this result indicates that the coating has clearly broken, as shown in Figure 6.4 (d), exposing the Ti13Nb13Zr substrate and the Ta coating that accumulated at the end of the track.
Figure 6.4 Scratch result of Ta coating and the corresponding micrographs.

Figure 6.5 shows the scratch test of the Ta coating on the heated substrate; here the coating shows a weak adhesion with the film peeling off at the first critical load of 1.5 N, as shown in Figure 6.5 (b). The second critical load is recorded at 7.5 N accompanied with an increasing coefficient of friction and fluctuating acoustic emissions which indicate the film has been removed. Figure 6.5 (c) shows that the coating was detached at both sides of the track, signifying that the Ta coating failed. The rapid increase in the amount of acoustic emission for the Ta coating on the heated substrate revealed that the coating is brittle [43]. Increasing the temperature of the substrate accelerates the energy of the bombardment ions, and changes the surface morphology of the film nucleation. This result is consistent with the work reported by Li et al [33], where a TiN coating on Ti13Nb13Zr alloy substrates was heat treated to a higher hardness, and the limited deformation in the substrates improved considerably but had little influence on coating adhesion. It is obvious that heating the substrate slows the solidification rate of impinging particles, thus allowing better contact of particles to the substrate and consequently, enhanced film adhesion. Conversely, our result reveals that heating the substrate reduces the adhesive strength
between the coating and the substrate. Surface oxidation by heating can be ruled out due to two minutes of etching at −850 V before deposition; here the increased oxygen content after heating the substrate can cause poor coating/substrate adherence. Post heat treatment generally increases the crystallinity of films, whereas post heat treatment may reduce the bonding strength between the substrate and coating due to their different thermal expansion coefficients [44]. The thermal expansion coefficient of Ti is \((8.4−8.8)\times10^{-6} \text{ K}^{-1}\) at 20 °C [2] and it increased to \(10.5\times10^{-6} \text{ K}^{-1}\) for 200–700 °C [45]. The thermal expansion coefficients of Ta ranged from \((6.0−6.9)\times10^{-6} \text{ K}^{-1}\) for 30–200 °C, depending on the structure of the film [46]. The low bonding strength between the Ta coating and the heated Ti substrate is attributed to the high thermal expansion mismatch between the two materials; in other words, the heating temperature may not increase diffusion between Ta and Ti.

Figure 6.5 Result of scratch on Ta coating on heated substrate and the corresponding micrographs.
Figure 6.6 shows variations of the coefficient of friction with sliding time and the number of cycles for Ti13Nb13Zr substrate and Ta coatings; note that the coefficient of friction of the Ti13Nb13Zr substrate fluctuates severely, whereas the coefficient of friction of the Ta coated samples remained around 0.35 at a relatively steady stage. The coefficient of friction of the Ta coated samples is approximately 27% lower than the uncoated sample. This reduction in the coefficient of friction is probably due to the ratio between the increased hardness and the elastic modulus of the Ta coated surfaces (~0.1), unlike the H/E ratio of 0.04 for bare Ti alloy substrate where the coefficient of friction suddenly increased at the beginning of the test, especially for the uncoated sample. This is attributable to the running-in period resulting from the severe friction between the ball and the disk during the transition from sliding to ploughing [47,48]. The curve of the coefficient of friction decreases with time and reaches a stable stage where the ball slides gently on a uniform worn track. There is no significant difference in the coefficient of friction of the Ta coatings on the non-heated and heated substrates which suggests that the amorphous and crystalline phases of the Ta coatings are protecting the surface from wear.
Figure 6.6 The graph of coefficient of friction determined in wear tests for Ti13Nb13Zr substrate and Ta coatings.

Figure 6.7 compares the wear scar and the corresponding wear profile of the rubbing ball surfaces in contact with (a) Ti13Nb13Zr substrate; (b) Ta coating, and (c) Ta coating on the heated substrate. The alumina ball sliding against the bare Ti13Nb13Zr disk has the lowest wear rate ($7.6 \times 10^{-6}$ mm$^3$/Nm) compared to other contacting pairs, and is commensurate to a smaller and deeper plough mark found on the counter surface (Figure 6.7 (a)). The extent of wear on the ball in contact with the Ta coated disks is severe, probably due to the enhanced wear resistance of the Ta coating which caused more material to be removed from the counter surface.
Figure 6.7 Wear profile of the rubbing ball surfaces in contact with (a) Ti13Nb13Zr substrate; (b) Ta coating, and (c) Ta coating on the heated substrate.

The optical micrographs of the wear track and its corresponding wear profile are shown in Figure 6.8. The wear track of the Ta coated disks in Figure 6.8 (b) & (c) is much wider than the bare Ti13Nb13Zr disk, possibly due to surface irregularity when the load is high, when the debris spread on the sample surface enlarges the trace. The wear rate of the Ta coated disks is slightly lower than the bare Ti13Nb13Zr disk, and although the wear track of the bare Ti13Nb13Zr disk is not as wide, the track is deeper than the track on the Ta coated disks. In a ball-on-disk configuration, the wear rate of the ball dominates the disk because while the ball and disk are the same hardness, the ball is slightly harder than the disc at room temperature, the wear rate of the ball becomes dominant [49]. Here, the hardness of the alumina ball and Ta coated disk is 16 GPa and 15 GPa, respectively, and since there is no significant difference in the wear loss of the disk, the wear is caused by the ball.
Figure 6.8 Wear profiles of the disks (a) Ti13Nb13Zr substrate; (b) Ta coating; (c) Ta coating on the heated substrate.

Figure 6.9 shows the SEM image of the wear scar of the ball sliding against Ta coating disk and its corresponding EDS point analysis. The EDS analysis confirmed the adhesive effect where material transferred from the Ti alloy and attached to the counterpart surface (spectrum 2), however the Ta film has peeled off and adhered to the counter-face, as shown at point 003.
Figure 6.9 SEM image of wear damage for a ball sliding against Ta coating disk and its corresponding EDS point analysis.

Figure 6.10 shows the EDS line scan of the wear track on the disc with Ta coating; here the coating has progressively burnished along the track, showing the high peak intensity of titanium. The peak intensity of Al and O can be seen on the track due to a transfer of material from the counterpart surface. Small amounts of Ta are visible along the wear track which suggests that the layer of debris consists of Al, O, Ti and Ta. The Ta coating was fragmented and incorporated into a debris layer as shown in the proposed physical model in Figure 6.11 (b). The Ta wear particles served as hard secondary phase inside the track and accelerated the wear damage of counterface ball. With the contact pair of alumina ball onto bare Ti alloy substrate shown in Figure 6.11 (a), debris has accumulated on the wear track and also adhered to the articular surface; it can be categorised as adhesive and abrasive wear.
Figure 6.10 The worn surface of the Ta coating disk surface and its corresponding EDS line scanning element analysis.

Figure 6.11 A schematic of the wear mechanism showing the formation of debris layer for (a) the contacting pair of alumina ball on the Ti13Nb13Zr substrate; (b) the contacting pair of alumina ball on the Ta coated Ti13Nb13Zr substrate.
Figure 6.12 shows the typical shape of the wear debris generated from the contact interfaces. The optical micrograph (Figure 6.12 (a)) and scanning electron micrograph (Figure 6.12 (b)) show the wear debris obtained from the sliding pair of alumina ball and uncoated Ti13Nb13Zr substrate. The particles are made of sheet and flake at an average size of 5 µm. This particle size is calculated by measuring the diameters of 100 particles, and the size distribution of the wear particles is shown in the inset picture in Figure 6.12 (a). Figure 6.12 (b) shows the wear particles are irregular in shape and with fibres in various lengths. The wear particles are smaller for the sliding pairs of alumina ball against Ta coated surfaces (Figure 6.12 (c)) than the debris generated from uncoated substrate (Figure 6.12 (b)). As shown in Fig. 12 (d), Ta coating was flaked off as a result of the severe sliding. The wear debris produced in this experiment is significant larger than the wear debris produced by metal-on-metal couples using hip simulator (<0.1 µm) [50]. The wear particles generated by the sliding pair between the alumina ball and Ta coated surface can induce inflammatory reactions and cause aseptic loosening. Preliminary ball-on-disk assessment in this study revealed that the wear characteristic of Ta coatings did not show significant improvement over the uncoated Ti-13Nb-13Zr substrate. More research is needed to establish the suitability of using such coating as implant materials such as the coating thickness, metal ion concentration, in vitro testing of Ta wear particles and greater range of test conditions.
Figure 6.12(a) Optical micrograph and size distribution of the wear debris generated from the contact pair of alumina ball on Ti13Nb13Zr alloy disk; scanning electron micrographs of wear debris generated from (b) alumina ball on Ti13Nb13Zr alloy disk; (c) alumina ball on Ta coating; (d) alumina ball on Ta coating on the heated substrate.

6.3.3  Electrochemical Corrosion Analysis

Figure 6.13 shows the Nyquist and Bode plots of samples after immersion with the electrolyte for one hour, 7 days, and 14 days. The Nyquist plots show that the Ta coatings have a larger diameter of the capacitive semicircle than the bare Ti13Nb13Zr substrate, which suggests that Ta coatings offer good insulation and corrosion protection with enhanced capacitive response for a solid/liquid interface. Figure 6.13 (d) & (f) show that Ta coatings have high values for the modulus of impedance and phase angle maximum of ~84° in a frequency range of −1 Hz to 1 Hz, this implies that the passive film formed on the Ta coating offers more protection than the uncoated Ti13Nb13Zr alloy. The samples show similar impedance spectra after immersion with the electrolyte for 7 days and 14 days, which indicates there is no major chemical change and the passive film on the surfaces is stable.
Figure 6.13 Effect of immersion time on the impedance spectra of (a) Nyquist plot (b) Bode plot of Ti13Nb13Zr substrate; (c) Nyquist plot (d) Bode plot of Ta coating; (e) Nyquist plot (f) Bode plot of Ta coating on the heated substrate.
To better understand the electrochemical behaviour of the substrate and tantalum coatings, two equivalent electrical circuits (EECs) are proposed to simulate the EIS plots. Table 6.1 summarises the quantitative analysis of the EIS data by fitting the appropriate electrical equivalent circuit (EEC). The EEC in Figure 6.14 (a) consists of a solution resistance between the working and reference electrodes $R_s$, a constant phase element of the oxide film $Q_{oxide\ film}$, resistance associated with the oxide film $R_{oxide\ film}$, a constant phase element of the electrical double layer $Q_{dl}$, and charge transfer resistance $R_{ct}$. The exponent $n$ is the variation from an ideal capacitor/resistor where $n = 1$ for the pure capacitor, and $n = 0$ for the pure resistor. The EEC model consists of one time constant (Figure 6.14 (b)) which produces a good fit on the impedance spectra of the tantalum coatings. Ta coatings increase the charge transfer resistance by one order of magnitude higher than the value of uncoated Ti13Nb13Zr substrate (Table 6.1). This result is consistent with the polarisation resistance and indicate the enhanced insulation and corrosion protection of the Ta coated surfaces.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ti13Nb13Zr substrate</th>
<th>Ta coating</th>
<th>Ta coating on the heated substrate</th>
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</thead>
<tbody>
<tr>
<td>$Q_{oxide\ film}$ (µΩ$^{-1}$ s$^n$ cm$^{-2}$)</td>
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<td></td>
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<tr>
<td>$n_1$</td>
<td>0.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{oxide\ film}$ (kΩ cm$^2$)</td>
<td>38.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{dl}$ (µΩ$^{-1}$ s$^n$ cm$^{-2}$)</td>
<td>2.97</td>
<td>12.6</td>
<td>9.81</td>
</tr>
<tr>
<td>$n_2$</td>
<td>0.60</td>
<td>0.93</td>
<td>0.94</td>
</tr>
<tr>
<td>$R_{ct}$ (kΩ cm$^2$)</td>
<td>2330</td>
<td>12380</td>
<td>30620</td>
</tr>
</tbody>
</table>
Figure 6.14 Electronic equivalent circuits (EEC) used in the fitting procedure of the EIS experimental data.

Figure 6.15 shows a comparison of the potentiodynamic polarisation curves of the samples after exposure to SBF for 14 days at 37 °C. The corresponding polarisation parameters determined from the extrapolation of the polarisation curves are given in Table 6.2. Note that the corrosion current densities for both Ta coatings are less than the bare Ti13Nb13Zr substrate. The Ta coating on the heated substrate has the highest polarisation resistance, which is consistent with the EIS results. A high polarisation resistance indicates a low electrochemical activity and means the surface is more resistant to corrosion, a result that suggests the Ta coatings will protect the Ti13Nb13Zr substrate from corrosion.
Figure 6.15 Polarisation curves of the samples immersed in SBF solution for 14 days.

Table 6.2 Electrochemical parameters extracted from potentiodynamic curves of the samples after immersion with electrolyte for 14 days.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ti13Nb13Zr substrate</th>
<th>Ta coating</th>
<th>Ta coating on the heated substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_a$ (mV/decade)</td>
<td>627.6</td>
<td>739.7</td>
<td>246.4</td>
</tr>
<tr>
<td>$-\beta_c$ (mV/decade)</td>
<td>255.2</td>
<td>297.5</td>
<td>148.1</td>
</tr>
<tr>
<td>$E_{corr}$ (V vs SCE)</td>
<td>$-0.14$</td>
<td>$-0.16$</td>
<td>$-0.18$</td>
</tr>
<tr>
<td>$I_{corr}$ (A cm$^{-2}$)</td>
<td>$4.76\times10^{-8}$</td>
<td>$9.87\times10^{-9}$</td>
<td>$1.84\times10^{-9}$</td>
</tr>
<tr>
<td>$R_p$ (Ω cm$^2$)</td>
<td>$9.12\times10^6$</td>
<td>$9.33\times10^6$</td>
<td>$2.18\times10^7$</td>
</tr>
</tbody>
</table>

Figure 6.16 show scanning electron micrographs of the samples before and after the corrosion tests. There is a very thin layer of inhomogeneous corrosion on the corroded surface of Ti13Nb13Zr substrate, as shown in Figure 6.16 (b); this surface degradation
might be due to the formation of micro-galvanic cells within the multi-phase structure of the metal. Figure 6.16 (d) shows that the Ta coating on the non-heated substrate after corrosion testing has less degradation (compared to Ti13Nb13Zr surface) but with some discontinuous corrosion. The corroded surface in Figure 6.16 (f) suggests that the corrosive media has diffused beneath the coating and led to pitting corrosion and film detachment. This phenomenon is denoted as filiform corrosion, where oxygen and water reach the corrosion site by diffusing through the porous filiform tail [51]. The scratch test results (Figure 6.5) indicated poor adhesion of the Ta film on heated substrate which is a major contributing factor to the ingress of electrolyte at the coating-substrate interface and initiation of under-film corrosion. The crystalline phases of the samples induced corrosion, unlike the amorphous structure of the Ta coating on the non-heated substrate. The hypothesis here is that the Ta coating on the heated substrate, despite showing inferior adhesion and stability after exposure to corrosive media (Figure 6.16 (f)), has superior integrity and fewer defects due to heating during deposition. This is evidenced by Figure 6.16 (c) (Ta coating on the non-heated sample before the corrosion test) which shows defective sites in the coating that are reflected by the lower impedance (Figure 6.13) and higher corrosion current density (Figure 6.15) than the heated sample. Micro defects can impact on the electrochemical response of the sample, but overall, the superior coating-substrate adhesion and stability of the coating on non-heated surface affords better protection against corrosion.
Figure 6.16 Scanning electron micrographs of (a) Ti13Nb13Zr substrate before corrosion; (b) Ti13Nb13Zr substrate after corrosion for 14 days; (d) Ta coating on non-heated substrate before corrosion; (d) Ta coating on non-heated substrate after corrosion for 14 days; (e) Ta coating on heated substrate before corrosion; (f) Ta coating on heated substrate after corrosion for 14 days.
6.4 Summary

The structure of the Ta coating changed from amorphous to a mixture of (α+β) crystalline when the substrate was heated to 300 °C in filtered cathodic vacuum arc deposition. Heating the substrate during deposition does not help in the bonding between the coating and substrate interface. The Ta coatings reduced the coefficient of friction of the Ti13Nb13Zr substrate, however, the wear performance of the Ta coatings did not show significant improvement over the uncoated surface, which therefore not suitable for implant applications. The 1 µm thick Ta coating wear through quickly and produced wear debris which may increase the risk of aseptic loosening. Electrochemical measurements showed that the Ta coating with (α+β) phase had the highest charge transfer resistance and polarisation resistance, thus providing high corrosion protection to the Ti13Nb13Zr substrate.
References


7.1 Introduction

The Ti6Al4V alloy is the most common material used for medical implants because of its high corrosion resistance and excellent biocompatibility [1–4]. The use of Ti6Al4V alloy for implant applications include artificial hip joints, artificial knee joints, bone plates, screws for fracture fixation, cardiac valve prostheses, pacemakers, and artificial hearts [5]. However, titanium (Ti) based alloys have low wear resistance and the generation of wear debris causes adverse tissue reactions [6]. In addition, the mismatch between different elastic modulus of bone tissues and titanium implants leads to bone resorption [7]. Efforts have been made to improve surface properties of Ti-based metals. For example, bioceramic coatings such as hydroxyapatite [8], calcium silicate [9], and nanoclays [10] are used to improve osteoconductivity (promote bonding to bone) and osteoinductivity (induce osteogenic differentiation of cells and generate new bone) of titanium implants. However, these coatings have low fracture toughness and show insufficient strength for load-bearing orthopaedic implants [11,12]. To overcome this problem, tantalum (Ta) coatings have been suggested as biomedical coatings because of their chemical stability, biocompatibility, and excellent mechanical properties [13–16].

Ta metal possesses high corrosion resistance due to its ability to form a self-passivating surface oxide layer [17]. Since the 1940s, applications of Ta has been applied to suture wire, wire mesh, cranial plates and fixation plates for surgical purposes [18]. Its high density and cost of manufacturing restricts the widespread acceptance of bulk Ta metal for implant applications. Thus applying a layer of Ta film as a surface coating onto a Ti6Al4V substrate has been proposed to achieve a desirable combination of properties, including corrosion and wear resistance. A ceramic tantalum oxide (TaO₂) coating deposited by magnetron sputtering was shown to improve the wear and corrosion resistance of Ti6Al4V substrate [19]. A β-Ta nanocrystalline coating deposited by double glow discharge plasma technique enhanced the corrosion resistance of Ti6Al4V [20]. Tantalum oxide and nitride...
deposited by physical vapour deposition methods exhibit haemocompatible properties, which is a potential candidate for cardiac and vascular devices [21–23].

Filtered cathodic vacuum arc deposition (FCVAD) is widely known for its effective source of energetic, ionized material to produce dense and adherent thin films at high deposition rates [24–27]. Despite this unique capability, FCVAD has not been fully exploited for fabrication of Ta films and a literature survey returns only a few published works in this area. In our previous study, sputtered (α+β)-Ta coatings was shown to improve mechanical and anticorrosion properties of the Ti6Al4V substrate [28]. In this study, Ta films were grown on Ti6Al4V substrates using FCVAD and then the effect of substrate bias on the microstructure, mechanical and corrosion properties of the Ta films was investigated. The in-vitro cytocompatibility of the coatings was examined using rat bone mesenchymal stem cells (rBMSCs).

7.2 Experimental Details

7.2.1 Film Deposition using Filtered Cathodic Vacuum Arc Deposition

Ti6Al4V sheet substrates 20×20×2 mm³ were prepared to characterise the physical properties of Ta films, and 30 pieces of Ti6Al4V disks (6 mm in diameter by 2 mm thick) were also prepared for the deposition to examine the cytocompatibility of Ta film. The substrates were ground and polished and the samples were mounted on a rotary sample holder inside the vacuum chamber. Deposition was by filtered cathodic vacuum arc deposition at the University of Wollongong and it is described in Chapter 2. The 58 mm diameter arc cathode (target) is made of high purity tantalum (purity, 99.99 %). The chamber was pumped down to a base pressure of 3×10⁻² Pa before deposition, and the substrates were cleaned by Ar ion etching at a high substrate bias of −850 V using Ta ions generated from the arc source for 2 minutes. The substrates were heated to 350 °C during deposition, and the arc operated at 200 A. High purity (99.9 vol%) Ar gas was introduced into the deposition chamber through a hollow filament cathode ion source; deposition pressure was maintained at 0.27 Pa and the substrate bias was kept at −100 V and −200 V with a deposition time of 30 minutes. The Ta ion beam current ranged between 70–100 mA, and it was measured in the centre of chamber with an isolated shutter.
7.2.2 Characterisation of Physical Properties

The crystallographic structure of the films was examined using grazing-incidence X-ray diffraction (GBC MMA diffractometer) equipped with the Cu Kα incident radiation. The incident angle was fixed at 5° to evaluate the phase of the thin films. The adhesion of the coatings was studied with a Revetest Xpress scratch tester (CSM Instruments) with a 200 µm radius diamond indenter. The diamond tip was driven over the coated surface in a load range from 0.1 to 50 N at 5 mm/min to produce a 5 mm long scratch. To verify reproducible results, three scratch tests were carried out on the samples. Scanning electron microscope (SEM) observations of the scratch were via a JEOL model JSM-6490 SEM. The thickness of the films was measured using the cross-sectional transmission electron microscope (TEM) specimens prepared using an FEI xT Nova Nanolab 200 work station. The nanoindentation test was performed by using a UMIS-2000 (Ultra-Micro Indentation System). A 5 µm diameter spherical diamond indenter was used to test the fracture modes of the films, and indentation took place with an applied load of 400 mN at a loading-unloading rate of 200 µN/s.

7.2.3 Measuring Electrochemical Corrosion

Electrochemical impedance spectroscopy was performed using a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). The experimental setup of the electrochemical measurements is described in Chapter 2. The sample was kept in the SBF solution for 60 min at 37 ºC prior to electrochemical testing to establish the steady state potential. Impedance measurements were taken between 10 mHz–10 kHz with a data density of 10 points per decade. The electrochemical cell was placed in a Faraday cage to minimise interference from other electromagnetic devices. The corroded samples were rinsed with distilled water, and dried in an oven at 40 ºC. The surface morphologies of the samples were examined with the JEOL model JSM-6490 SEM. X-ray photoelectron spectroscopy spectrometer (XPS) was with a Specs PHOIBOS 100 Analyzer operated with Al Kα X-ray source at 12 kV and 120 W. XPS peak fitting was carried out using CasaXPS software. The data were calibrated to the adventitious C1s peak present at 284.8 eV to minimise sample charging.
7.2.4 Cell Culturing

The rat bone mesenchymal stem cells (rBMSCs, of the fourth passage) provided by Stem Cell Bank, Chinese Academy of Science, Shanghai, China were cultured on sterilised samples in 96-well plates with 200 μL α-MEM (with 10% foetal bovine serum, 1% antimicrobial of penicillin and streptomycin). The experimental procedures of cell culturing are described in detail in Chapter 2.

7.3 Results and Discussion

7.3.1 Physical Properties of the Tantalum Films

Figure 7.1 shows the XRD patterns of uncoated Ti6Al4V substrate and Ta films deposited with a substrate bias of −100 V and −200 V. Ta/−100 V exhibits peak broadening in the 2θ range of 35−40º, which is attributed to a mixture of Ti6Al4V substrate and Ta film due to its small thickness, 0.5 µm. The diffractions lines of Ta/−200 V reveals the substrate peaks more clearly due to its smaller thickness of 0.23 µm. Small peaks corresponding to tetragonal β-Ta (JCPDS-25-1280) were observed, as were two peaks at 2θ = 38º and 56º which correspond to (110) and (200) orientations of the body-centered cubic α-Ta phase (JCPDS-04-0788). Ta films deposited at −100 V and −200 V exhibit a mixture of predominantly β-Ta and minority of α-Ta.

It was mentioned in Chapter 4 that the crystalline (α+β) phases were identified in the cathodic-arc-deposited Ta film deposited at −100 V, but here a broad hump with predominantly β-Ta were observed in the Ta film at −100 V bias. This is due to a lower Ta ion beam current of 70−100 mA compared to the ion beam current of 200 mA for Ta deposition in Chapter 4; both of which have similar plasma beam size and identical arc current. The kinetic energy intensity of the depositing adatoms increases with the density of plasma beam current. The vaporised Ta in this chapter (in the UOW FCVAD) is less ionized than that of Chapter 4 (CSIRO FCVAD), resulting in a decrease in energy of the particles which impinged on the substrate and lowered the surface mobility of the adatoms, and eventually resulted in the formation of predominantly β-Ta. The phase formation in FCVAD depends on the energy level of Ta atoms. The amount of α-Ta phase increased
with an increasingly energetic Ar\(^+\) ion bombardment of Ta films deposited by filtered arc deposition.

![XRD pattern of the Ti6Al4V substrate and the Ta films at substrate bias of −100 V and −200 V.](image)

Figure 7.1 XRD pattern of the Ti6Al4V substrate and the Ta films at substrate bias of −100 V and −200 V.

Figure 7.2 shows the typical scratch results for Ta film at −100 V. The scanning electron micrographs show the scratch track at different levels of loading. Note that the film has relatively poor adhesion with the first critical load recorded at 2.5 N, followed by an abrupt increase and fluctuation in the coefficient of friction; this indicates that the film is detaching from the substrate. Figure 7.2 (a) shows that the film is being removed laterally from the edges of the scratch, denoting the mechanism of chipping [29]. A series of nested micro-cracks within the scratch groove can be seen in Figure 7.2 (b); these ring cracks are classified as Hertz cracking [30] which leads to partial spallation of the film extending to the side of the track, as shown in Figure 7.2 (b). This behaviour and the fluctuation in the coefficient of friction also indicate that the film is quite brittle. The second critical load occurred at 20 N, which corresponds to cohesive failure and subsequent intermittent
exposure of the substrate. Figure 7.2 (c) shows that the film detached at the end of the track and Hertz cracks are more prevalent.

Figure 7.2 Scratch behaviour and the corresponding scanning electron micrographs of Ta/–100 V film.
The scratch behaviour of Ta/−200 V film is shown in Figure 7.3; here the crack began at the first critical load around 4 N with a small increase in the coefficient of friction. The cracks can be seen in Figure 7.3 (a) where the film adhered to the surface, thus indicating improved adhesion. The second critical load is recorded at 37 N and exposes the Ti6Al4V substrate, as shown in Figure 7.3 (b). Figure 7.3 (c) shows that Hertz cracking is finer and the film adheres to the cracks.

![Scratch behaviour and the corresponding scanning electron micrographs of Ta/−200 V film.](image)

Figure 7.3 Scratch behaviour and the corresponding scanning electron micrographs of Ta/−200 V film.

Figure 7.4 shows the damage to the Ta films under an indentation load of 400 mN. The impression of the indent appears to be more pronounced in the film at −100 V than the film at −200 V; this result indicates that the films are prone to detach under a high applied load. The cross-sectional images of the tested samples under an indentation of 400 mN are shown in Figure 7.4 (c) & (d); there is a cohesive fracture in the Ta film at −200 V, as shown in the Figure 7.4 (d). It appears that a certain thickness has sufficient adhesion to
the substrate and there is no apparent detachment, which is consistent with the scratch test result, whereas in the Ta/−100 V sample there is detachment at the Ti/Ta interface. The Ta films were 0.5 µm and 0.23 µm thick when deposited at −100 V and −200 V, respectively.

Figure 7.4 (a) & (b) SEM images of indentation made at 400 mN; (c & d) cross-sectional images of the Ta films after an indentation test with an applied load of 400 mN, as obtained by TEM method.

Figure 7.5 shows SEM surface morphology of Ta/−200 V film where the surface of the film is uniform and homogeneous (Figure 7.5 (a)) and delamination is seen in Figure 7.5 (b). However, some particles protruding from the surface can be seen at 5000X magnification, as shown in Figure 7.5 (c). These growth defects are caused by impinging atoms induced by high kinetic energy during deposition.
Figure 7.5 (a) Low, (b) medium and (c) high magnification scanning electron micrographs showing growth defects of the Ta/−200 V film.
7.3.2 Analysis of Electrochemical Corrosion

Figure 7.6 shows the impedance spectra (Nyquist and Bode plots) of bare Ti4Al4V substrate and Ta films recorded after 1 hour, 4 days, and 7 days in SBF solution. The Ta/−100 V film has higher impedance values than the Ti6Al4V substrate and the Ta/−200 V film, which indicates that this surface has the highest electrochemical resistance. The phase angles of the coated samples are higher than the uncoated sample, indicating that the Ta films have a stronger capacitive behaviour, however the phase angle of the Ta/−200 V shifted towards smaller values at a low frequency range (log(f)≤ 1). This could be due to defects on the surface that exposes the substrate to the electrolyte and manifests itself as leaking capacitor behaviour with a lower phase angle.
Figure 7.6 Effect of immersion time on the impedance spectra of (a) Nyquist plot (b) Bode plot of Ti6Al4V substrate; (c) Nyquist plot (d) Bode plot of Ta/−100 V; (e) Nyquist plot (f) Bode plot of Ta/−200 V in simulated biological fluid.
Figure 7.7 shows the equivalent electrical circuits (EECs) used to model the experimental EIS data. Table 7.1 summarises the values for each electrical element in the EEC. The proposed EEC model shown in Figure 7.7 (a) is used to fit the EIS data for the uncoated Ti6Al4V substrate. In this circuit, $R_s$ corresponds to the resistance of the solution, and $Q_{oxide\,film}$ and $R_{oxide\,film}$ are ascribed to the constant phase element (CPE) and resistance of the passive film. The exponent $n$ indicates the variation from an ideal capacitor/resistor where 1 is pure capacitor and 0 is pure resistor. The circuit consists of $Q_{dl}$ and $R_{ct}$, which are the CPE and resistance attributed to the electrical double layer and charge transfer resistance, respectively. The EIS spectra of the Ta/−100 V film can be fitted well using the simple EEC model shown in Figure 7.7 (b). The EEC model with two time constants (Figure 7.7 (a)) is used to fit the experimental EIS data for the Ta/−200 V film. The Ta/−100 V film has relatively high values of charge transfer resistance (4644 kΩ cm²) and the exponent $n$ of 0.95. This result suggests the surface provides the best protection against corrosion by presenting a high capacitive behaviour. The EEC model with one time constants produces a good fit for the experimental EIS data for Ta/−100 V film, thus indicating the presence of a uniform layer without defects. The use of more complex EEC models (two time constants) for the Ti6Al4V substrate and the Ta/−200 V film suggests the covering film deviates from ideal behaviour due to surface heterogeneities.
Figure 7.7 Electronic equivalent circuits (EEC) used in the fitting procedure of the EIS experimental data.
Table 7.1 Electrical components calculated by fitting an equivalent electrical circuit on the EIS data after 14 days.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ti6Al4V substrate</th>
<th>Ta/−100 V</th>
<th>Ta/−200 V</th>
</tr>
</thead>
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<tr>
<td>$Q_{oxide\ film}$ (µΩ$^{-1}$ s$^n$ cm$^{-2}$)</td>
<td>28.2</td>
<td>14.2</td>
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<tr>
<td>$n_1$</td>
<td>0.87</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>$R_{oxide\ film}$ (kΩ cm$^2$)</td>
<td>55.6</td>
<td>104</td>
<td></td>
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<tr>
<td>$Q_{dl}$ (µΩ$^{-1}$ s$^n$ cm$^{-2}$)</td>
<td>10.3</td>
<td>10.7</td>
<td>21.2</td>
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<tr>
<td>$n_2$</td>
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<td>0.95</td>
<td>0.69</td>
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<tr>
<td>$R_{ct}$ (kΩ cm$^2$)</td>
<td>1456</td>
<td>4644</td>
<td>2396</td>
</tr>
</tbody>
</table>

Figure 7.8 shows the surface morphology of the samples after immersion in SBF for 7 days, and the electrochemical measurements. Figure 7.8 (a) & (b) shows that the Ti6Al4V substrate is covered by a layer of corrosive product, while the surface of Ta/−100 V film [Figure 7.8 (c) & (d)] shows no signs of deterioration. There are some corrosion pits on the Ti6Al4V surface, as shown in Figure 7.8 (b). The inhomogeneous corrosion of Ti6Al4V in a micro scale is due to micro-galvanic cells forming within the multi-phase structure of the metal. Similar corrosive behaviour on the Ti6Al4V surface is reported in Chapter 3. The surface of Ta/−100 V film shows no major degradation, indicating the sample provide good corrosion protection. Figure 7.8 (e) shows the formation of corrosion pits on the surface of Ta/−200 V film where the film protrudes and builds up in a round shape. These 60 µm rings originated from under the Ta film. The local inhomogeneity/defect that caused osmotic pressure under the film and the ingress of electrolyte under the film caused these blisters. These blisters would normally indicate cathodic domains while the corrosion pits indicate anodic sites or sites of metal dissolution. As Figure 7.8 (f) shows, the surface of Ta/−200 V film at high magnification shows the formation of blisters, but this phenomenon does not appear in the Ta/−100 V film (Figure 7.8 (d)).
Figure 7.8 SEM images of the samples after electrochemical measurements (a) and (b) Ti6Al4V substrate; (c) and (d) Ta/−100 V film; (e) and (f) Ta/−200 V film.

Figure 7.9 shows the high resolution XPS spectra of bare Ti6Al4V substrate and Ta/−100 V film after corrosion testing. The XPS spectra of Ta/−200 V film are similar to the Ta/−100 V film, where the Ti 2p spectrum shows an energy doublet located at 458.2 eV and 463.9 eV for Ti 2p\(3/2\) and Ti 2p\(1/2\), respectively. These peaks agree with those values for TiO\(_2\) in the literature \[31,32\]. The O 1s peak could be resolved into two peaks, the binding energy of 529.3 eV corresponds to the TiO\(_2\) [33] and the higher binding energy of 531.1 eV could be associated with carbonyl, =C=O peak [34]. A small amount of calcium phosphate (Ca\(_3\)(PO\(_4\))\(_2\)) was also detected on the Ti6Al4V surface. The Ca 2p spectrum shows a binding energy recorded at 350.8 eV [33]. The Ca and P are the results of a...
reaction between the Ti6Al4V substrate and the SBF solution. The Ta 4f spectrum is divided into four energy doublets. The representative peaks of tantalum pentoxide, tantalum sub-oxides and metallic tantalum are similar to the XPS result reported in Chapter 4. The O 1s spectrum of the Ta/−100 V film resolves into two peaks. The binding energy located at 530.0 eV is assigned to Ta-O bonds in tantalum oxide \([35,36]\) and the higher binding energy at 531.9 eV is attributed to either oxygen in the form of hydroxide or other adsorbed oxygen species \([36]\). There is no formation of calcium phosphate on the surface of Ta film. The XPS results verify the formation of an oxide layer and calcium phosphate on the Ti6Al4V substrate, and the curve fitting of the Ta 4f spectrum indicates that the contribution of oxygen in the tantalum pentoxide \((\text{Ta}_2\text{O}_5)\) is high.

The corrosive behaviour depends on the structure of the interface such as the microstructure, thickness of the coating and surface homogeneity \([37]\). The XPS analysis confirms the formation and stability of an oxide layer on the Ta surface after immersion in SBF for 7 days. The formation of a passive oxide layer on the Ta/−100 V film is the primary reason for improved corrosion resistance. Surface degradation of the Ta film formed at a high substrate bias of −200 V provides initiation sites for the corrosion process and cancels the protection offered by the Ta film comparing to the Ta/−100 V film. This accelerated degradation is apparently attributable to the pin-hole/blister prone film morphology in the Ta/−200 V film as shown in Figure 7.8, but the underlying mechanism is unclear yet and the low film thickness and thereby easier penetration by the solution liquid through defects may also play a role. The native oxide on the Ti6Al4V is more protective than the defective Ta/−200 V film. The contributing mechanism is the precipitation of calcium phosphate from SBF on the Ti6Al4V that increased the impedance over time. Ti6Al4V provides good nucleation sites for the formation of calcium phosphate. One other possibility is that a cathodic reaction generates hydroxide which then causes the precipitation of calcium phosphate \([38]\). The growth of apatite depends on adsorption of the ion at the surface or transport of the ions between the apatite and the SBF solution. The Ta/−100 V film presents a stable passive oxide layer which generates less Ta hydroxide after 7 days of immersion in the SBF and therefore no calcium phosphate was formed.
Figure 7.9 X-ray spectroscopy spectra after corrosion testing for the Ti6Al4V substrate (left) and Ta/−100 V film (right).

### 7.3.3 Cytocompatibility Analysis

Cell morphologies after 1 day, 4 days, and 7 days of culturing are shown in Figure 7.10. The cells spread evenly over and attached onto the control Ti6Al4V and the two types of
Ta coated disks. As Figure 7.11 shows, cracks appeared on the Ta/−200 V disk on day 4 of culturing; these cracks are attributed to low cohesion by the film onto the Ti6Al4V substrate and the stresses generated during cell culturing and corrosion.

![SEM morphology of the rBMSCs after 1 day, 4 days and 7 days of culturing.](image)

Figure 7.10 SEM morphology of the rBMSCs after 1 day, 4 days and 7 days of culturing.
The number of cells of the control Ti6Al4V surface and the Ta films are shown in Figure 7.12 (a). There were no statistically significant differences in the proliferation of cells between the groups on day 1, but this changed dramatically after 4 days of culturing. The cells grown on the Ta films and the control Ti6Al4V surface on day 4 show insignificant difference. The number of cells in each group started to decrease when the culture period extended to day 7, with the average number of cells on Ta films being slightly less than the control Ti6Al4V surface; this suggests the cells reached a certain stage of maturity within 7 days. The number of cells cultured on both Ta films is less than those on the control Ti6Al4V surface on day 7 of culturing. Figure 7.12 (b) shows the quantitative ALP expressions of rBMSCs on the samples. On day 7, the ALP activity of the control Ti6Al4V surface and the Ta films had the same value at 1.0 µM/µg. The cell viability of all the surfaces increased after culturing for 14 days. This increase in ALP activity is especially obvious for the control Ti6Al4V, which is consistent with how easily a layer of calcium phosphate formed on the bare Ti6Al4V surface compared to the Ta coated surfaces (depicted in section 7.3.2). This formation of calcium phosphate promotes cell adhesion on the surface [26]. This explains the higher ALP activity level observed on the bare Ti6Al4V
surface as compared to Ta coated surfaces. The spreading of rBMSCs on Ta films and the increased number of cells on day 4 (Figure 7.12 (a)) denotes that cytocompatibility of Ta films is at least equivalent to that of Ti6Al4V. The good cytocompatibility of the Ta films is comparable to those Ta films generated by other methods of surface engineering as reported by other researchers [39–41].

Figure 7.12 (a) Proliferation of the rBMSCs cultured on the sample surfaces (b) Alkaline phosphatase (ALP) levels of the rBMSCs at different incubation time. Quantitative data represented as mean ± SD. * indicates significant difference between groups.

7.4 Summary
Ta films deposited on Ti6Al4V substrate using filtered cathodic vacuum arc deposition with two different substrate biases show clear differences in mechanical and corrosion properties. The corrosion performance of the Ta/−200 V film is inferior to the Ta/−100 V film because of the cohesive fracture and growth defects of the film. XPS analysis demonstrated titanium oxide and calcium phosphate were formed on the bare Ti6Al4V substrate after corrosion testing, and a tantalum oxide layer was formed on the Ta film. The surface layer on Ta films was very stable consisting of tantalum oxide/hydroxide with a lower tendency to nucleate calcium phosphate. This explains a lower ALP activity level on Ta films after a culture period of 14 days compared to the control Ti6Al4V. Ta films have no apparent superiority in proliferation and spreading of rBMSCs over the control Ti6Al4V, which suggests that Ta surface coating is a promising biocompatible material for implant applications.
References


[34] A. Schroeder, G. Francz, A. Bruinink, R. Hauert, J. Mayer, E. Wintermantel, Titanium containing amorphous hydrogenated carbon films (a-C:H/Ti): surface analysis and evaluation of cellular reactions using bone marrow cell cultures in


Chapter 8. Conclusions and Recommendations

8.1 Conclusions

Tantalum films were successfully deposited on Ti6Al4V alloy and Ti13Nb13Zr alloy substrates using magnetron sputtering and filtered cathodic vacuum arc deposition. The influences of deposition parameters such as the substrate voltage bias, substrate temperature, gas pressure, and buffer layer configuration, were studied to produce uniform and coherent films that possess potential in anti-wear and anti-corrosion biomedical implant applications.

In magnetron sputtering, Ta films with α-β dual-phase structure were fabricated. A quantitative phase in Rietveld refinement revealed that the Ti buffer layer increased the amount of α phase. The Ta films increased the hardness of the Ti6Al4V substrate and gave a high H/E ratio of 0.067. The compressive residual stress of Ta film with Ti buffer layer was 25% lower than pure Ta film; this lower residual stress improves adhesion between the coating and the substrate. The corrosion current density of bare Ti6Al4V substrate decreased by one order of magnitude and reached $2.4 \times 10^{-9} \text{ A.cm}^{-2}$ at a slower scan rate of 0.3 mV/s. The corrosion current density of the Ta coated surfaces are similar (at the middle of $10^{-9} \text{ A.cm}^{-2}$) at scan rates of 2 and 0.3 mV/s, a result that indicates the formation of a stable surface on the Ta films with insignificant capacitive behaviour.

In filtered cathodic vacuum arc deposition, Ta film showed a purely β-tetragonal structure at zero substrate bias and an α-body centre cubic structure appears as the substrate bias increased to −100 V. The surface roughness of the Ta film at −100 V was twice the roughness of the Ta film at zero substrate bias. Ta films showed a hydrophobic surface with a water contact angle that reached 100º, presenting a lower surface free energy that reduced the attraction of the surface to the water particles and increased the compatibility with foetal bovine serum. Film cohesion of Ta film at −100 V is much stronger than the one without a substrate bias. X-ray photoelectron spectroscopy revealed the shift to a tantalum pentoxide surface dominance on the Ta film surface during corrosion, which is the contributing factor in enhancing and protecting against corrosive degradation by the Ta film at −100 V for the Ti6Al4V substrate.
As the nitrogen to argon gas ratio increased, a hexagonal Ta-N phase was detected. Both Ta and Ta-N films increased the corrosion resistance of Ti6Al4V substrate with the best protective characteristics achieved in Ta-N film deposited at 0.25 N2/Ar gas ratio. This enhanced corrosion resistance was attributed to the formation of tantalum oxide and oxynitride compound at the surface, as verified by X-ray photoelectron spectroscopy. Resistance to pitting corrosion decreased by increasing the nitrogen to argon gas ratio. The corrosion and coating to substrate adhesion of the Ta-N films deteriorated as the film thickness increased from about 300 nm to 1 µm.

Ta film has an amorphous structure which changes to a mixture of α and β phases as the Ti13Nb13Zr alloy substrate was heated to 300 °C during deposition. The Ta films reduced the coefficient of friction of the Ti13Nb13Zr alloy substrate by 27%, when sliding against an alumina ball counter-face. The wear rates of the Ta-coated disk surfaces are slightly lower than those of the bare Ti-13Nb-13Zr alloy, while the wear rate of alumina balls was one order of magnitude higher when it slid against the Ta-coated samples than when it was slid against the Ti-13Nb-13Zr alloy. The 1 µm thick Ta coating wear through quickly and produced wear debris which may increase the risk of aseptic loosening. The Ta film with (α+β) phase has a high charge transfer resistance and polarisation resistance, providing high corrosion protection to the Ti13Nb13Zr substrate.

The substrate bias plays an important role in the structure and performance of electrochemical corrosion. The Ta film deposited at −200 V has a highly coherent film but the resistance to corrosion deteriorates due to the associated growth defects which lead to the formation of blisters and pits. The film with a substrate bias of −100 V revealed a significant improvement in corrosion resistance upon exposure to simulated biological fluid due to the stable oxide layer. In vitro studies showed that Ta films have no adverse effect on mammalian cell adhesion and spreading proliferation.

Overall, the physical properties and corrosion performance of a range of tantalum films on both Ti6Al4V alloy and Ti13Nb13Zr alloy substrates were optimised by varying the conditions in physical vapour deposition. The results showed that tantalum films enhanced the mechanical properties, corrosion resistance and wear resistance of titanium alloy
substrates which are promising for orthopaedic implants. A cytocompatibility analysis confirmed the nontoxicity and cell growth on tantalum coated surfaces.

### 8.2 Recommendations

Multilayer Ta-N/Ta thin films can be coated on titanium alloy substrates, and will improve their durability and corrosion resistance. The formation of oxynitrides on the first layer of the Ta-N film and the formation of tantalum pentoxide on the second layer of Ta in simulated biological fluid could enhance the corrosion protection of titanium alloy substrate, and the fracture of multilayer thin films will be less severe than with monolayer thin films. Cytocompatibility of the Ta-N films should be examined to verify such coating is suitable as implant materials.

The deposition of tantalum oxytrinide thin films can be investigated by adjusting the oxygen-to nitrogen ratio in order to achieve a combination of desired mechanical, corrosion, and biological properties. The biocompatible tantalum oxynitrides TaO$_x$N$_y$ can benefit from the properties of tantalum oxides and tantalum nitrides. TaN is a chemically inert, corrosion resistant, and hard ceramic, while Ta$_2$O$_5$ possesses high dielectric constant which acts as a barrier to corrosion. The surface oxidation of tantalum oxytrinide films can be analysed by X-ray photoelectron spectroscopy and ion scattering spectroscopy.

The adsorption of proteins on tantalum films is important to evaluate the biocompatibility of orthopaedic implants. Quartz crystal microbalance with dissipation (QCM-D) is an alternative tool to measure the protein adsorption of tantalum or tantalum oxytrinide thin films. An understanding of the interaction of metallic implant surfaces with physiological environment containing blood or tissue is the first step in reducing the corrosive degradation of metallic implants used in a human body.

The effect of micro-dimpled surface textures of titanium alloy substrates can be carried out prior to tantalum film deposition. Laser surface texturing can improve the tribological performance with each micro-dimple serving as micro-dynamic bearing or micro-reservoir for lubricant. Dimple geometry and dimple features (diameters and densities) have different effects on the friction and wear reduction, so the investigation of wear particles generated from pin-on-disk testing in terms of particle size and dose is important for the
development of tantalum films in orthopaedic implants. Also, the biotoxicity of the lubrication (simulated biological fluid) after exposure to tribochemical reactions should be tested to verify the atrophy, pathological changes, or rejection of living tissue.