



Corrosion behaviour and adhesion properties of sputtered tantalum coating on Ti6Al4V substrate

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ABSTRACT

Tantalum coating on Ti6Al4V substrate was prepared by sputtering and the mechanical and corrosion performance of the tantalum coating was investigated. In addition to the normal structure of a sole tantalum film on the substrate, a buffer layer of titanium was first deposited on the substrate in a hope to improve the film adhesion. XRD examination shows that the Ta coatings exhibit a α/β dual-phase structure. Both the sole Ta coating and the Ta coating with a Ti buffer layer increased the apparent hardness of the surface of the Ti6Al4V substrate significantly. The compressive residual stress of the Ta/Ti of the order of 0.9 GPa is noticeably reduced comparing to 1.2 GPa of the sole Ta coating, resulting in an improved adhesion between the coating-substrate interface. The hydrophobicity of the Ti6Al4V surface after Ta coating also increased, which is believed to help in protein absorption and enhance lubrication. The corrosion current density of the Ta coated Ti6Al4V decreased from 2.0×10^{-8} to $3.4 \times 10^{-9} \text{ A} \cdot \text{cm}^{-2}$ (at high scan rates) comparing to the uncoated Ti6Al4V substrate. The mechanisms of the improved corrosion current density by the Ta coating and the enhancement of mechanical bonding of the Ta coating by a Ti buffer layer are further discussed.

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1. Introduction

The earliest biomedical use of tantalum (Ta) was in the manufacture of stents for endovascular surgery [1] and orthopaedic applications. The desirable properties (high hardness, moderate hardness to elastic modulus ratio, excellent corrosion resistance and biocompatibility) of Ta can sustain load bearing, facilitate natural bone growth [2,3] and help with occasional multinucleated macrophage [4]. It was proven that cell activity/interactions between human mesenchymal stem cells (MSCs) on Ta surfaces increases compared to other surfaces, such as titanium (Ti) and chromium [5]. The formation of a passive oxide on the surface of the metal makes Ta a good candidate for a nanometer-thick coating with high chemical stability [6].

There are a number of factors that affect on the structure of tantalum films deposited by magnetron sputtering, such as type of substrate, positioning of the substrate toward the target, substrate bias and gas pressure [7]. Formation of β -Ta (meta-stable tetragonal) is commonly observed on silicon substrates with the native oxide intact [8]. It has been reported by Lee et al. [9] that strong (002) fiber-textured β -Ta was formed at sputter gas pressure of 1.3 Pa and lower, while more random beta oriented Ta was found at gas pressure of 2.6 Pa or higher. With

a negative bias voltage of -100 V , a mixture of predominantly β -Ta and minority of α -Ta (body-centered cubic) is formed [10]. The use of aluminium substrate and niobium underlayer leads to α -Ta, because of the close lattice match between the underlayer material and α -Ta [10, 11]. Alami et al. [7] claimed that α -Ta formed on untreated silicon substrates with an inclination angle of the substrate and a higher target voltage of 1000 V by using a high power impulse magnetron sputtering. As the inclination angle increased, the number of neutral deposition atoms reaching the substrate reduced. As a result, an increased ion bombardment in relation to deposition rate is achieved, while the negative substrate bias maintained a flux of ions to the substrate. Stress generated during film growth affects the phase formation as well. Phase transition from β -Ta to thermodynamically stable α -Ta occurred upon annealing in the temperature range of 600–800 °C, as a result of stress release by the post-deposition annealing [12].

Ti6Al4V is widely used in metal implants owing to the very high specific strength and excellent corrosion and oxidation resistance [13, 14]. However, Ti alloys have poor wear resistance and generate wear debris in sliding motion applications. The latter can cause biological contamination to the surrounding tissue and, subsequently, bone resorption, loosening and failure [15–17]. As the demand for orthopaedic implants for younger patients is growing, 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 previously explored as a means

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Table 1

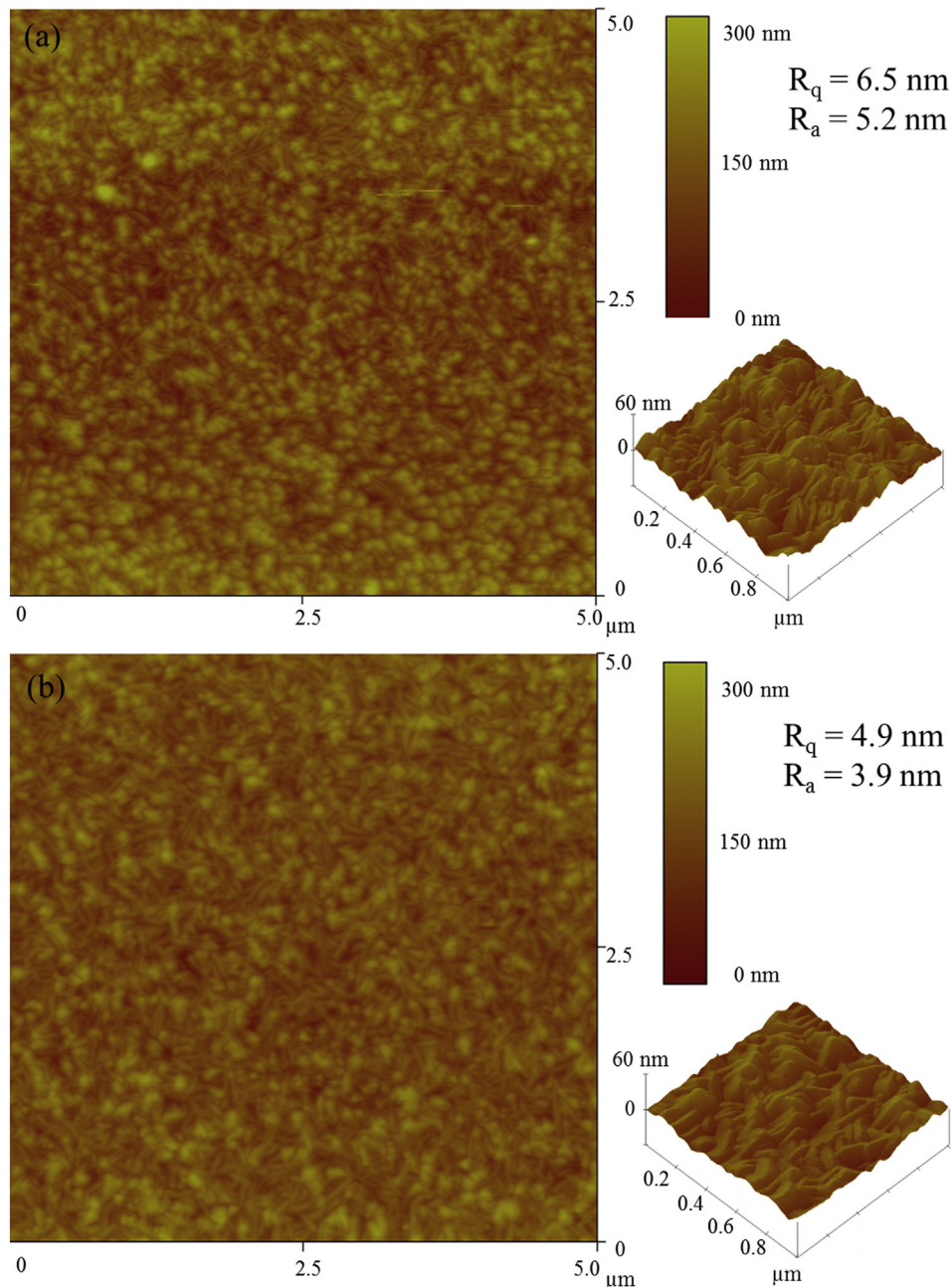
Mechanical properties of uncoated and coated surfaces at applied load of 10 mN.

Samples	Hardness (GPa)	Elastic modulus (GPa)	H/E
Uncoated Ti6Al4V	6.8 ± 0.6	198 ± 16	0.034
Ta coating	14 ± 1.2	210 ± 15	0.067
Ta/Ti	13 ± 0.8	261 ± 12	0.050

to enhance the bone-implant contact. However, cracking, delamination and the low fracture toughness of ceramic coatings are huge obstacles for their widespread application. Hence, further advancements in the load bearing metal implants with excellent mechanical and electrochemical performance are still required.

To combine the good properties of Ta and Ti6Al4V alloy, there are investigations on Ta coatings on Ti6Al4V substrates. It was found that the

corrosion resistance of Ta film coated on Ti6Al4V can be still inadequate. Silva et al. [1] reported that some perturbation of the Ta occurred which may be associated with a reduction in polarization resistance, demonstrating that the film might be less resistant to corrosive attack. Badawy et al. [18] found that the anodic oxide film formed on Ta behaves as a perfect dielectric, however, passive films on Ti do not perform as well. The corrosion behaviour of NiTi alloy with a thin layer of Ta coating was improved, giving a wider passive region and a higher breakdown potential [19]. Understanding the corrosion mechanism of Ta coating in physiological environments is important to diminish the risk of metal degradation in the human body. In this study, Ta coatings were prepared by magnetron sputtering. A Ti buffer layer was applied on the Ti6Al4V substrate to reduce the compressive stress and therefore improve the adhesion between the Ta coatings and the Ti6Al4V substrate.

**Fig. 1.** Atomic force microscope (AFM) images of (a) Ta coating and (b) Ta/Ti.

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