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Surface chemistry and cytotoxicity of reactively sputtered tantalum oxide films on NiTi plates

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ABSTRACT

NiTi, an equiatomic alloy containing nickel and titanium, exhibits unique properties such as shape memory effect and superelasticity. NiTi also forms a spontaneous protective titanium dioxide (TiO_2) layer that allows its use in biomedical applications. Despite the widely perceived biocompatibility there remain some concerns about the sustainability of the alloy's biocompatibility due to the defects in the TiO_2 protective layer and the presence of high amount of sub-surface Ni, which can give allergic reactions. Many surface treatments have been investigated to try to improve both the corrosion resistance and biocompatibility of this layer. For such purposes, we have sputter deposited tantalum (Ta) oxide thin films onto the surface of the NiTi alloy. Despite being one of the promising metals for biomedical applications, Ta, and its various oxides and their interactions with cells have received relatively less attention. The oxidation chemistry, crystal structure, morphology and biocompatibility of these films have been investigated. In general, reactive sputtering especially in the presence of a low oxygen mixture yields a thicker film with better control of the film quality. The sputtering power influenced the surface oxidation states of Ta. Both microscopic and quantitative cytotoxicity measurements show that Ta films on NiTi are biocompatible with little to no variation in cytotoxic response when the surface oxidation state of Ta changes.

1. Introduction

Nitinol (NiTi) is an equiatomic alloy of nickel (Ni) and titanium (Ti) and exhibits unique thermo-mechanical properties such as shape memory effect and superelasticity [1]. These unique properties have allowed the use of NiTi in both hard and soft tissue biomedical applications that include orthodontic wire guides, braces, self-expandable vascular stents, urinary stents and catheters [2,3]. There had been a concern over the use of NiTi in biomedical devices due to the high concentration of Ni (approximately 56% by weight). However, the presence of a high amount of Ni in the bulk NiTi has found to be less of a concern due to the presence at the surface of a strong passivating oxide of Ti, which made the alloy biocompatible. This TiO_2 protective layer grows spontaneously on the surface when exposed to air and prevents the release of undesirable Ni^{2+} ions [4–10]. There remain some concerns still regarding the stability of the naturally grown TiO_2 layer. For example a possible breakdown of this layer within the body fluids may cause the release of toxic Ni^{2+} ions [11–13]. Atomistic simulations of the oxidation of NiTi showed that the process intrinsically involves a pull-out of Ti at the surface to form the oxide while leaving a Ni-rich sub-surface region [14]. This Ni-rich sub-surface region is much of a concern from a biocompatibility point of view especially if there are discontinuities in the surface coverage by, or defects in, the protective TiO_2 layer. Various different methods such as anodic oxidation, thermal oxidation, electropolishing and sputter deposition have been attempted to improve the stability and quality of this TiO_2 layer [15–23]. Coating with a stable, adherent film such as Ta is one such method of improving the biocompatibility of NiTi by reducing the risk of potential Ni release. Ta is known to be both biocompatible and unaffected by body fluids [8,24,25]. Ta films may be grown by electrochemical methods such as electrodeposition and physical deposition methods such as sputtering. Both methods have their advantages but sputtering offers an ease of deposition and better control of the thickness of the film.

The deposition of Ta has received some attention in literature [21–23,26–30]. Reactive sputter deposition of tantalum oxide films has been carried out on a plethora of substrates such as silicon, silicon dioxide, glass and platinum coated silicon [29–34] to investigate the structure, composition, optical and electrical properties of Ta oxide films. Reactive sputter deposition (RSD) of Ta-oxide films on NiTi has received relatively less attention. The aim of this study is to investigate the effect of varying deposition parameters such as deposition time and power on the film surface chemistry, crystallinity, roughness, morphology and biocompatibility.

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2. Methods

Sputter deposition of tantalum oxide was performed by RF-magnetron sputtering in an ATC Orion Deposition System (AJA International Inc., USA) with a base pressure better than 1.33×10^{-4} Pa. NiTi composition was Ti–55 wt.% Ni representing a slightly Ti-rich composition. All samples were cut into $20 \times 10 \times 1$ mm plates from an as received cold rolled NiTi sheet from American Elements, USA. The substrates were polished to a 4000 grit finish. All substrates were sputter cleaned for 5 min before deposition.

For reactive sputtering, oxygen was introduced into the chamber along with argon at a total pressure of 0.4 Pa with argon to oxygen ratio of 90 to 10 (90/10) with a distance of 15 cm between the target and substrate. These parameters were chosen to avoid oxidation of the Ta target [35]. The NiTi substrates were heated to 80 °C during deposition. Both the deposition power (75, 100 and 150 W) and deposition time (20, 50 and 90 min) were varied. The thickness of the films was measured by an in line quartz crystal microbalance. Increasing deposition powers increases the deposition rate and consequently, for a given amount of time, increases the film thickness. The deposited films were annealed in a furnace at 500 °C for 1 h each to crystallise the film.

A Hitachi SU-70 field emission scanning electron microscope (FE-SEM) and an energy dispersive X-ray spectroscopy (EDX) probe both operated at 20 kV were used to investigate the morphology and elemental composition of the Ta-oxide film respectively. The surface chemistry and oxidation states of the films were investigated by a Kratos AXIS 165 X-ray photoelectron spectrometer (XPS) operated at beam voltage of 15 kV and beam current of 10 mA and benchmarked against an electrochemically grown 30 nm Ta-oxide film on metallic Ta obtained from National Physical Laboratory (NPL), UK. C 1s at 284.8 eV was used as charge reference in determining the binding energies. Construction and peak fitting of synthetic peaks in narrow region spectra used a Shirley type background and the synthetic peaks were of a mixed Gaussian–Lorentzian type. Relative sensitivity factors used are from CasaXPS library containing Scofield cross-sections. The spin orbit split applied was 0.75. Various oxidation states of Ta have been assigned based on the discussion given in McNamara et al. [36]. The crystalline nature of the deposited films was studied by both glancing angle and conventional gonio-scan in a Philips X'Pert PRO MPD X-ray diffractometer (XRD) with copper source. The interface between the film and substrate was analysed using a JEOL JEM-2100F field emission transmission electron microscope (FE-TEM) operated at 200 kV using a LaB_6 filament and an EDAX Genesis EDX detector was used to carry out energy dispersive X-ray spectroscopy (EDX) on the sample interface. A focused ion beam (FIB) lift off technique was used to prepare the sample for TEM analysis and this was done using a FEI-FIB 200 workstation. An Agilent 5500 atomic force microscope (AFM) was used to analyse the surface roughness of the film and was compared against the substrate roughness measured with similar AFM. For quantitative values of AFM surface roughness three randomly selected points were taken on each film within a $20 \times 20\ \mu m^2$ field of view.

The biocompatibility of these Ta-oxide films was investigated by cytotoxicity testing using an ASTM Standard ASTM F813-07 Standard Practice for Direct Contact Cell Culture Evaluation of Materials for Medical Devices [37]. The results were analysed by neutral red quantitative assay as well as microscopic examination. L-929 mouse fibroblast cell line was used in the analyses. The cells were grown to a near confluent monolayer in Eagle's minimal essential medium. Once confluent the cells were removed and a cell suspension was prepared. 2 ml of this cell suspension was then added to each tissue culture (TC) dish and incubated for 24 h to reach a confluent monolayer. All samples were autoclaved to sterilise them before they were placed on the cell monolayer. Stainless steel and NiTi were used as negative controls and phenol and latex were used as positive controls. All test samples were prepared in duplicates. After 24 h incubation the specimen were examined microscopically to determine if the specimen is cytotoxic. After microscopic examination the samples underwent analysis by neutral red quantitative assay. The neutral red medium was prepared 24 h before use. The neutral red medium was added in an amount of 1 ml to the cells and incubated for 2 h. The dye was extracted from the cells using a neutral red destaining solution and shaking the TC dishes on an orbital shaker. The absorbance of the extracted dye solution was measured at 520 nm by using a TriStar LB941 plate reader [38]. Cell surface analysis was performed using ImageJ software: to analyse the percentage of viable cells. The percentage of viable cells was calculated using the formula $A = \left(\frac{B}{C}\right) * 100$ where A is the percentage of viable cells, B is the surface area occupied by viable cells and C is the total surface area of cells exposed to specimen.

3. Results and discussion

Table 1 gives the deposition parameters such as sputtering power, rate, time and the estimated thickness of reactively sputtered Ta-oxide films on NiTi. Reactive sputtering in the presence of a low oxygen mixture thus yields a thicker film and offers better control of the film quality when compared to sputtering in high oxygen mixtures [36]. In this system the sputtering power controls the voltage applied to the circuit and therefore the current. From Table 1 it can be seen that the minimum thickness is achieved by sputtering at 75 W for 20 min and maximum film thickness can be achieved by sputtering at 150 W for 90 min. Fig. 1 shows a typical SEM micrograph showing the morphology of one of the films which was deposited for 90 min with a sputtering power of 100 W.

Fig. 2 shows AFM topography of the films deposited using various sputtering parameters. As can be seen from Fig. 2 (a, d and g) the surface of the Ta-oxide coatings initially appear to have a relatively smooth topography (Fig. 2a). However this initial smoothness deteriorates with an increase in the deposition time from 20 min to 50 min (Fig. 2b, e and h). By increasing the deposition time to 90 min (Fig. 2c, f and i) the film roughness decreases. Increasing the deposition time beyond 50 min thus allows for smoother film morphology. Fig. 3 shows a quantitative variation of the roughness of the films with increasing deposition time. The figure shows that, similar to the qualitative observations made earlier on, the surface roughness is initially low between 13 and 22 nm but as the deposition time increases the roughness increases between 22 and 41 nm. When the deposition time is increased further the surface roughness decreases to between 7 and 22 nm. When a film reaches a certain thickness the rough features of the underlying layers are not detected anymore as the incoming atom flux increasingly fills in the valleys to reduce film roughness. From Figs. 2 and 3, it is apparent that a 100 W sputtering power typically produces a better surface roughness profile.

Glancing angle XRD measurements of the as-deposited Ta-oxide film showed very weak Ta-oxide peaks. Also, the films are in general very

Table 1
List of deposition powers and rates used to deposit the Ta-oxide films RSD.

Sample I.D. and deposition time (minutes)	Deposition power (W)	Deposition rate (nm/s)	Deposition time (min)	Thickness (nm)
RSD_75W/20	75	0.04	20	48
RSD_75W/50			50	120
RSD_75W/90			90	216
RSD_100W/20	100	0.1	20	120
RSD_100W/50			50	300
RSD_100W/90			90	540
RSD_150W/20	150	0.18	20	216
RSD_150W/50			50	540
RSD_150W/90			90	972