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Mechanical Properties of Nanotextured Titanium Orthopedic Screws for Clinical Applications

In this work, we modified the topography of commercial titanium orthopedic screws using electrochemical anodization in a 0.4 wt% hydrofluoric acid solution to produce titanium dioxide nanotube layers. The morphology of the nanotube layers were characterized using scanning electron microscopy. The mechanical properties of the nanotube layers were investigated by screwing and unscrewing an anodized screw into several different types of human bone while the torsional force applied to the screwdriver was measured using a torque screwdriver. The range of torsional force applied to the screwdriver was between 5 and 80 cN · m. Independent assessment of the mechanical properties of the same surfaces was performed on simple anodized titanium foils using a tribointender. Results showed that the fabricated nanotube layers can resist mechanical stresses close to those found in clinical situations. [DOI: 10.1115/1.4023705]

1 Introduction

Synthetic materials in human medical therapy have been used for a long time. In recent years, research in the field of biomaterials has exploded, and new areas such as in the field of tissue engineering, with greater emphasis given to biological phenomena, have resulted. The concept of bioactivity of an implanted material, has spurred research in the field of tissue engineering with the aim of replacing tissues or even organs. In this context, medical applications of nanotechnology are promising because nanotechnology allows the surface of the biomaterial to be tailored (feature scale, etc.) to optimize the interfacial interaction between the biomaterial and its biological environment. Such interfaces are of interest in the domain of orthopedic surgery as they could have antibacterial functions or could be used as drug delivery systems [1–5]. Because of this, the development of orthopedics is moving towards better integration of biology in implants and surgical techniques, but the mechanical properties of implanted materials are still important for orthopedic applications. During clinical implantation, implants are subjected to large mechanical stresses. In order to obtain the best performance during clinical use, mechanical properties of implants need to be investigated and understood. To date, the growth of cell cultures has been used to study implants [6–14], but few studies have investigated the mechanical properties of nanotextured implants [15]. Titanium orthopedics have many advantages over traditional stainless steel implants, such as: better osteo-integration, a modulus of elasticity closer to that of bone, higher strength, and lower cost [12]. Different surface modification strategies for orthopedic implants have been investigated [16]. Reports on the synthesis of TiO₂ nanotubes have indicated nanoscale surface topography

affects cellular responses [17,18]. In order to assess if TiO₂ nanotube coatings can be used in clinical applications, the mechanical properties of the nanotube layers were investigated in environments similar to clinical use. In this study, the topography of a commercial titanium orthopedic screw was modified through electrochemical anodization in a 0.4 wt% hydrofluoric acid solution. The mechanical strength of the nanotube surface was tested by screwing and unscrewing an anodized screw into different type of human bone. Scanning electron microscopy was used to characterize the nanotube layers morphology.

2 Material and Method

2.1 Sample Preparation. To fabricate anodic TiO₂ nanotube layers on orthopedic screws, we used commercial screws (5 mm diameter, locking compression plate system) titanium screw (Synthes, West Chester, PA). The screws were degreased by successive sonication treatments in trichloroethylene, acetone, and methanol, followed by rinsing with deionized water and drying using nitrogen gas. The screws were then immersed in a HF : HNO₃ : HCl : H₂O (1:10:20:69) solution to remove the protective layer of oxide and subsequently rinsed with deionized water and blown dry with nitrogen gas. Finally, the screws were dried in an oven at 100 °C and cooled in a desiccator. Anodization was carried out at room temperature (20 °C) in a 0.4 wt% HF aqueous solution with the anodizing voltage maintained at 20 V. The fabrication method used to anodize the titanium foils has been described elsewhere [19].

2.2 Surface Characterization. The surface topography characterization of the screws was performed using a Zeiss Supra 55 VP scanning electron microscope (SEM) with secondary emission and in lens detectors. The accelerating voltage and the working distance were 3 kV and 5 mm, respectively. For the

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Manuscript received June 25, 2012; final manuscript received January 17, 2013; published online June 24, 2013. Assoc. Editor: Jyhwen Wang.

characterization of the scratches we used a JEOL JSM 880 with accelerating voltage of 15 kV.

2.3 Testing of the Screw. A femoral head was acquired from a surgical procedure for a total hip replacement. During this procedure, the surgeon removed the femoral head and a part of the femoral neck. The anatomical pieces were kept at 4 °C in a plastic box for transportation. The tests were performed 6 h after the removal. Anatomically, the sample contains different types of bone: a strong cortical bone around the neck, a cancellous bone inside the neck, a subchondral bone all around the head surface, and a sclerotic subchondral part because the joint was treated for osteoarthritis. In this work, testing was performed on these four types of bone. The bone was first drilled with 3.2 diameter drill as described in the operative technique. The drilled hole was not tapped because the screw was self-tapping. The screw was then inserted into the cavity and turned until half of the screw was inside the bone. The torsional force required for implantation was recorded for each condition with a torque screwdriver: (Torque-leader Model QSM/N SD); see Fig. 1. The screw was removed and cleaned in ethanol and blown with nitrogen gas and dried in the oven at 100 °C. After drying, the screw was degreased by sonication in ethyl acetate for 15 min.

We evaluated the strength of dry TiO₂ nanotubes on an anodized Ti foil using a Hysitron Triboindenter system with a diamond tip with a top radius of 1 μm and scanning electron microscopy. Our measurements involved “scratching” the nanotube surface using a uniform lateral translation (constant speed) under a variable applied vertical load. Typically the vertical load varied in time (and, hence, space due to deformation) over the duration of a single scratch, varying linearly from the maximum load value to zero and then back to the maximum load. While the sample was translated, the lateral force required for translation was measured. These variable-load measurements allowed us to investigate the transition of damage behavior between different regimes, while simultaneously measuring the frictional behavior. This was

done by examining the scratch after the triboindenting procedures with scanning electron microscopy, which is sensitive to changes in surface morphology associated with the scratch. Typically, the end points of the scratch are easily identified because they correspond to positions where the applied vertical load is a maximum. Then for any position along the scratch, the applied vertical load and measured lateral (horizontal force) can be determined by measuring the distance between the identified end points and comparing to the known applied force versus position curve. For example, for the symmetric maximum-to-zero-to-maximum load curves we used, at the midpoint between the two observed end points no vertical load was applied and typically no lateral force was measured and no damage observed. Thus, using plan-view SEM images, damage associated with indenting can be identified and correlated with scratch position. This variable-load scratch method is more fully described in Ref. [20]. Scratch measurements were made using unannealed and annealed samples with maximum vertical loads ranging from 20 μN to 1000 μN. The anneal was for 1 h at 500 °C in oxygen, following a recipe to maximize the anatase content of the nanotubes [19]. For improved statistics, three measurements were made for each maximum vertical-load value. SEM imaging was used to characterize the effect of the triboindenter on the surface topography.

3 Results and Discussion

3.1 TiO₂ Nanotube Growth Process. The anodization growth was governed by a competition between anodic oxide formation and chemical dissolution [21] of the oxide as soluble fluoride complexes according, respectively, to reactions (1) and (2):

Figure 2 shows a characteristic current versus time curve for Ti anodization in our operating conditions. It can be seen that there is an initial exponential decay of the current to a local minimum around 17 mA about 14 s after the anodization was started. After this, the current increased to a local maximum of 30 mA around 205 s. At 20 min of growth the current was 28 mA. The weak decrease of the current between 205 and 1200 s shows that the dissolution rate of oxide is slightly higher than the oxide growth velocity. The lower inset of Fig. 2 shows an SEM image of the

Fig. 1 Anodized screw, couple-meter screw driver (a) and femoral head. The front region of the screw ((b), dotted arrow) is inserted into the bone and the rear region ((c), full arrow) is used as a control; (d) image of the bone after drilling.

Fig. 2 Typical anodization current versus time curve for the Ti screw anodization. Anodization was carried out at room temperature (20 °C) in a 0.4 wt% HF aqueous solution with the anodizing voltage maintained at 20 V. Inset in upper right-hand corner shows the current characteristics from 0 s to 120 s. Inset in lower part shows the SEM top-view image of as anodized screw after 20 min of growth.

Fig. 3 SEM images of the anodized screws (control part, left, and inserted part, right) for: (a) cancellous; (b) cortical; (c) subchondral; and (d) sclerotic bones. All images are same magnification with scale bars shown.

as-grown titanium dioxide nanotube. We observed nanotube arrays with tubes approximately 100 nm to 105 nm in diameter.

3.2 Nanotube Layers Resistance. The screw was divided in two regions as shown in Fig. 1. The front region was screwed into the bone and the rear region was left untouched and used as a control. Figure 3 shows SEM images of the anodized screws (control and inserted parts). Figures 3(a)–3(d) show the top-down view of the control and inserted regions of the screws inserted into cancellous, cortical, subchondral, and sclerotic bone, respectively. The torsional forces applied were: 10 cN · m to 13 cN · m for cancellous, 50 cN · m to 67 cN · m for cortical, 20 cN · m to 25 cN · m for subchondral, and 35 cN · m to 80 cN · m for the sclerotic bone. From the SEM images we see that the TiO₂ nanotube layers remain intact and undergo minimal mechanical damage after screwing and unscrewing the screw into the bone samples. These results are very promising.

Figure 4 shows the SEM images of the annealed sample after indentation. The annealed sample was more resistant to permanent damage than the unannealed sample, with little to no damage occurring when the vertical load was 20 μ N. For example, examining the SEM images of the 20-0-20 μ N scratches we see little permanent damage at all. In fact, it is difficult to see evidence of the scratch, although we know where the scratch was made based on the positions of adjacent scratches. Superficial damage occurred when the vertical load was between 20 and 50 μ N. From Fig. 4, it can be seen that superficial damage occurred when the load was slightly greater than 20 μ N. Areas of clear superficial damage are labeled in the appropriate higher magnification images of the individual scratches. The annealed sample began delaminating at the same vertical load as the unannealed sample. We found that delamination occurred at the end of the 200-0-200 μ N scratches. These areas are labeled in the appropriate lower and higher magnification images of the individual scratches. The

Fig. 4 Plan-view SEM images showing surface damage from variable normal-load lateral scratches. Upper left: shows array of all scratches with the maximum normal force labeled. Lower: shows all the individual scratches magnified, first to show the full scratch, and next to show damage threshold. Regions of superficial damage and delamination are shown where appropriate. Inset in lower-left image: shows area where removed TiO_2 layer is inverted. Upper right: graphs of applied normal versus measured lateral force for maximum normal forces of 100 and 200 μN . Italic labels show, A: undamaged area; B: superficially damaged area; C: delaminated area; and D: debris.

delaminated areas in the annealed sample were smaller than those of the unannealed sample, indicating that annealing increased the nanotube layer's resistance to delamination. The delamination of the nanotubes from the substrate was found to occur at the interface between the oxide and Ti foil. Figure 4 shows the barrier regions of the oxide, the bottom caps of the nanotubes, have been separated from the Ti substrate (shown in the insert for the row 1 column 1 (R1C1) 0–1000 μN scratch).

Based on these triboindenter results, we categorized the indentation into one of three mechanical regimes. For the unannealed sample, when the vertical-load was less than 20 μN , we found that little or no damage occurred. When the vertical-load was greater than 20 μN , the nanotubes underwent permanent deformations. When vertical-loads were 200 μN and greater, delamination occurred (see Table 1). The regimes we observed are consistent with Crawford et al. [22] who found three different deformation regimes for TiO_2 nanotubes. Regime I was characterized by a linear increase in the Young's modulus due to the densification of pores. In regime II, the indenter begins to wear the densified surface. And in regime III the film delaminates. Crawford et al. found

that delamination only occurred if the film was less than 600–650 nm. The nanotubes evaluated in this study were 450 nm tall, so our observation of delamination is consistent with Crawford et al. [22].

Because we were able to measure the lateral force required to translate the substrate, we were able to find the coefficient of friction between the triboindenter tip and nanotube surface. For the best results, we looked at scratches with a medium maximum vertical-load and regions where the vertical-load was varying from zero to the maximum load. This reduced the chance that delamination played a role in the low-load regions. For both the annealed and unannealed samples we found that the coefficient of friction (COF) was approximately 1 and was constant across all three regimes. A COF of about 1 is typical of dry glass on glass (0.9) and steel on steel (0.8), so our observed value for dry contact is not that surprising. It is expected that the COF associated with the fresh bone system, involved in our studies, will be substantially less because of the wetness associated with this system (for example, the COF of steel on steel is 0.8 dry and 0.2 wet). A final observation involves the nature of the TiO_2 debris scratched off the nanotube layer by the triboindenter. Even after a gentle N_2 blow, the SEM images indicate the TiO_2 moved by triboindentation remains on the side of the scratch even in the case of delamination. This indicates that the nanotube layer is surprisingly ductile.

Table 1 Vertical load ranges for the three deformation regimes for the annealed and unannealed sample

	Vertical load regimes, unannealed sample	Vertical load regimes, annealed sample
Elastic regime (superficial damage)	< 20 μN	< 50 μN
Inelastic regime (permanent damage)	20–200 μN	50–200 μN
Delamination	> 200 μN	> 200 μN

4 Conclusions

It is important to realize that improved surfaces based on lab measurements have not always demonstrated superiority in clinical use. With this in mind, the results of this preliminary work are encouraging because the mechanical characteristics of this surface

treatment appear to be sufficiently robust to withstand realistic clinical operating conditions that our *in vitro* experiments were designed to simulate. These results show that the nanotube layers remain intact after the implantation process. This may allow for the exciting possibility of nanotubes being loaded with molecules. Examples of such molecules include antibiotics and proteins to encourage healing. Further work is still required to take these ideas and create a proof of concept that can be translated to clinical applications.

Acknowledgment

The triboindenting part of the frictional study was performed with Hengyu Wang and Professor Min Zou of the Dept. of Mechanical Engineering, University of Arkansas and the SEM investigation was performed with Dr. Preston Larson of the Samuel Roberts Noble Electron Microscopy Laboratory, University of Oklahoma. This work was supported by the National Science Foundation funded center for Semiconductor Physics in Nanostructures (C-SPIN), the Oklahoma/Arkansas Materials Research and Engineering Center (MRSEC) (DMR-0520550) and by Université d'Auvergne.

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