



# The structure, bond strength and apatite-inducing ability of micro-arc oxidized tantalum and their response to annealing



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## ABSTRACT

In this study, the tantalum oxide coatings were formed on pure tantalum (Ta) by micro-arc oxidation (MAO) in electrolytic solutions of calcium acetate and  $\beta$ -glycerophosphate disodium, and the effect of the applied voltage on the microstructure and bond strength of the MAO coatings was systematically investigated. The effect of annealing treatment on the microstructure, bond strength and apatite-inducing ability of the MAO coatings formed at 350 and 450 V was also studied. The study revealed that during the preparation of tantalum oxide coatings on Ta substrate by MAO, the applied voltage considerably affected the phase components, morphologies and bond strength of the coatings, but had little effect on surface chemical species. After annealing treatment, newly formed  $\text{CaTa}_4\text{O}_{11}$  phase mainly contributed to the much more stronger apatite-inducing ability of the annealed tantalum oxide coatings than those that were not annealed. The better apatite-inducing ability of the MAO coatings formed at 450 V compared to those formed at 350 V was attributed to the less amorphous phase and more crystalline phase as well as more Ca and P contained in the MAO coatings with increasing the applied voltage.

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## 1. Introduction

Tantalum (Ta) metal is known to be a biocompatible material with high malleability and ductility [1–4] and have displayed excellent corrosion–erosion resistance in comparison to titanium and stainless steel implants [5]. Dating back to the mid-1900s multiple medical devices have been fabricated that utilize the Ta, including: pacemaker electrodes, foil and mesh for nerve repair, radiopaque markers, and cranioplasty plates [3]. Ta-based implants have displayed an exceptional biocompatibility and safety record in orthopedic, cranio-facial, and dentistry literature [6]. However, Ta is typically not bioactive and thus is unable to directly bond to surrounding bone [7]. Much attention has been paid on bioactive metal because of its tight fixation in bony defect as well as high biological affinity with soft tissues. Bioactive Ta metal is, therefore, worth to be developed in order to be more extensively used [8]. The anodized  $\text{Ta}_2\text{O}_5$  nanotube films on pure Ta can improve its anticorrosion, biocompatibility, and osteoinduction [9]. It has been reported that the essential requirement for artificial materials to bond to living bone is the formation of a bone-like apatite layer on their surfaces in the body [10,11], and the formation of the apatite layer on the surfaces of bioactive ceramics can be

reproduced in an acellular simulated body fluid (SBF), which has an ion concentration close to that of body fluid [12]. Compact Ta metal previously treated by NaOH treatment or by the alkali- and heat-treatment can form apatite on its surface within one week after soaking in SBF attributed to the catalytic effect of the Ta–OH groups while untreated Ta needs four weeks to induce apatite [6,8,13–15]. The porous Ta metal after the micro-arc oxidation and NaOH treatment can form more apatite on its surface than the one untreated after soaking in SBF for the same time [16]. However, the  $\text{Ta}_2\text{O}_5$  nanotube films [9] and the sodium tantalate layers [14,16] are relatively poor in adhesion strength to the underlying substrates and cannot maintain the effective life spans of the bioactivated Ta.

Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO), is a relatively convenient technique for forming oxide ceramic coatings on valve metals such as Al [17,18], Ti [19–21], Mg [22], Zr [23] and their alloys with complex geometry [24,25], and the MAO coatings are microporous and usually exhibit good adhesion to substrates. Our previous works have demonstrated that the MAO formed  $\text{TiO}_2$ - and  $\text{ZrO}_2$ -based coatings containing Ca and P exhibits enhanced bone-like apatite forming ability [19,23,26] and osteoblast function express, and can promote new bone formation [23,27]. A few papers have reported the micro-arc oxidation of Ta.  $\text{WO}_3$ - and/or  $\text{SiO}_2$ -containing  $\text{Ta}_2\text{O}_5$  layers were formed by PEO process [28–30]. In our previous study [31], we reported our efforts in the formation of  $\text{CaTa}_2\text{O}_6/\text{Ta}_2\text{O}_5/\text{TaO}$  layer

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containing Ca and P on Ta by MAO for different time, with emphases of the outward–inward growth behavior of the coatings.

It is known that phase structure, morphology and chemical composition are the key factors to affect bone-like apatite-inducing ability of the coatings [32–34]. Amorphous  $\text{TiO}_2$  nanotubes can transform to anatase or rutile after annealing treatment [35] and this transformation is beneficial to apatite growth [36]. Apatite-inducing ability of amorphous  $\text{ZrO}_2$  is lower than that of monoclinic or tetragonal one, because tetragonal or monoclinic  $\text{ZrO}_2$  may provide atomic arrangements in their crystal structures suitable for the epitaxy of crystals [34]. It has also been reported that the Ta–OH [8], Ti–OH [37] and Zr–OH [38] groups on the coating surfaces can enhance the bioactivity. So, it is essential to make clear that how the factors affect the bioactivity of the formed coatings.

So far, little information in previous literature can be obtained about the effect of annealing treatment on the apatite-inducing ability of micro-arc oxidized Ta containing Ca and P. In this study, Ca- and P-containing tantalum oxide coatings were formed on commercially available Ta substrates by MAO at various applied voltages. The effects of the applied voltage and the annealing treatment on the microstructure and bond strength of the coatings were systematically studied. The apatite-inducing ability of tantalum oxide coatings and their response to annealing treatment were investigated. The reasons for the enhanced apatite-inducing ability of the micro-arc oxidized Ta after annealing treatment were also discussed.

## 2. Materials and methods

### 2.1. Sample preparation

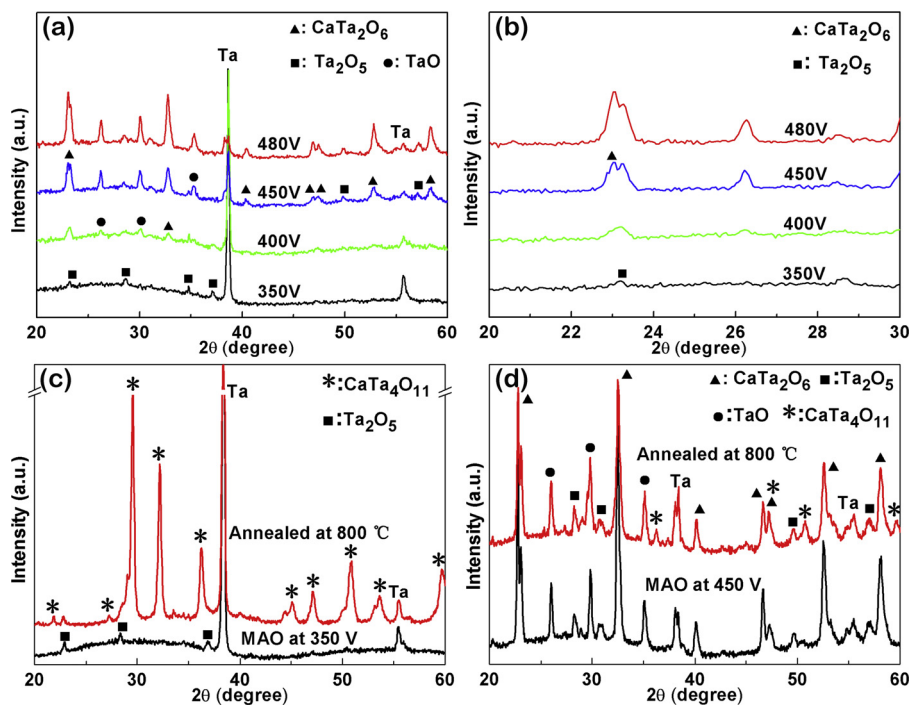
A bipolar pulse power supply was employed for micro-arc oxidation (MAO) of Ta plates. Commercially pure Ta discs with a size of  $\varnothing 10 \text{ mm} \times 2 \text{ mm}$  were used as substrates. The surfaces of the plates were polished with abrasive papers and ultrasonically cleaned with acetone, ethanol and distilled water prior to micro-arc oxidation

treatment. The Ta plates were used as anodes while a stainless steel cylinder container was used as a cathode, in which an aqueous electrolyte containing 0.2 M calcium acetate ( $(\text{CH}_3\text{COO})_2\text{Ca}\cdot\text{H}_2\text{O}$ , CA) and 0.02 M  $\beta$ -glycerophosphate disodium ( $\text{C}_3\text{H}_7\text{Na}_2\text{O}_6\text{P}\cdot 5\text{H}_2\text{O}$ ,  $\beta$ -GP) was placed. Ta plates were treated at various applied positive pulse voltages of 350, 400, 450 and 480 V, a negative pulse voltage of 70 V, a pulse frequency of 100 Hz and a duty ratio of 26% for 10 min. During the MAO, the electrolyte contained stainless steel cylinder was mounted in a water bath cooled by a cooling system, to keep the temperature of the electrolyte at  $20^\circ\text{C}$ . Then the samples were washed with distilled water and dried at room temperature.

A part of the micro-arc oxidized (MAOed) samples at 350 V and at 450 V for 10 min were encapsulated in quartz tubes with vacuum of  $7.5 \times 10^{-4} \text{ Pa}$  to receive annealing treatment at  $800^\circ\text{C}$  for 3 h.

### 2.2. Apatite-inducing ability evaluation of the MAOed samples before and after annealing treatment

The MAOed samples at 350 and 450 V before and after annealing treatment were immersed in SBF for a period of time to evaluate their apatite-inducing ability. The SBF solution was prepared according to Kokubo and Takadama [39] by dissolving reagent-grade chemicals (NaCl,  $\text{NaHCO}_3$ , KCl,  $\text{K}_2\text{HPO}_4\cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$ ) in distilled water, and buffered at pH 7.4 with tris-hydroxymethyl-aminomethane and HCl at  $36.5^\circ\text{C}$ . The ion concentrations (mM) of the solution are 142  $\text{Na}^+$ , 5  $\text{K}^+$ , 1.5  $\text{Mg}^{2+}$ , 2.5  $\text{Ca}^{2+}$ , 147.8  $\text{Cl}^-$ , 4.2  $\text{HCO}_3^-$ , 1  $\text{HPO}_4^{2-}$  and 0.5  $\text{SO}_4^{2-}$ , nearly equal to those of human blood plasma. Each sample was immersed in a plastic vial containing 50 mL of SBF and was kept under static conditions inside a biological thermostat at  $36.5^\circ\text{C}$ . The SBF was refreshed every two days so that a lack of ions would not inhibit the apatite formation as suggested by Kokubo and Takadama [39]. After immersing for selected days, the samples were removed from the SBF, washed with distilled water and then air dried.



**Fig. 1.** (a) XRD patterns of the MAO coatings formed at 350, 400, 450 and 480 V; (b) enlargement of the angular region from  $20^\circ < 2\theta < 30^\circ$  in (a) where the peaks of the  $\text{CaTa}_2\text{O}_6$  and  $\text{Ta}_2\text{O}_5$  phases are expected to be; (c) XRD patterns of the MAO coatings formed at 350 V before and after annealing treatment at  $800^\circ\text{C}$ ; (d) XRD patterns of the MAO coatings formed at 450 V before and after annealing treatment at  $800^\circ\text{C}$ .

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