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# Influence of process parameters on plasma electrolytic surface treatment of tantalum for biomedical applications

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ABSTRACT

This work aims to quantify the effect of anodization voltage and electrolyte composition used during DC plasma electrolytic oxidation (PEO), operated as a 2-step process, on the surface properties of the resulting oxide coatings on tantalum. The first step consisted of galvanostatic anodization (150 mA $cm^{-2}$) of the tantalum workpiece up to several limiting voltages (200, 300, 400 and 500 V). After attaining the limiting voltage, the process was switched to voltage control, which resulted in a gradual decrease of the anodic current density. The anodic treatment was realized in a 0.5 M $Ca(H_2PO_2)_2$ solution, which was then modified by the addition of 1.15 M $Ca(HCOO)_2$ as well as 1.15 M and 1.5 M $Mg(CH_3COO)_2$. The increasing voltage of anodization led to the formation of thicker coatings, with larger pores and enriched with electrolytes species to a higher extent. The solutions containing $HCOO^-$ and $CH_3COO^-$ ions caused the formation of coatings which were slightly hydrophobic (high contact angle). In the case of the samples anodized up to 500 V, scattered crystalline deposits were observed. Bioactive phases, such as hydroxyapatite, were detected in the treated oxide coatings by XRD and XPS.



## 1. Introduction

Musculoskeletal system diseases are amongst the most widespread afflictions of the human race, which are especially common in elderly people. National Joint Registry reported [1] that between 2003 and 2014 there were over 1.8 million joint replacement procedures in the UK alone. Over 90% of those procedures were primary hip and knee operations, which require the use of implants made of suitable materials. There is a tendency to replace metallic biomaterials in favor of polymers and ceramics (or composites of the two) [2]. However, load bearing properties of metals and alloys are still unparalleled in comparison. Biocompatibility is considered the main factor for the successful implant, nevertheless, it relates to multiple material features, which have to be taken into account [3].

Through years of experiment and clinical work, the most successful metallic biomaterials turned out to be austenitic stainless steels, Co-Cr alloys and Ti alloys, which are satisfactorily strong and bioinert. An additional factor that determines the success of an implant is the "stress-shielding" effect. β-type Ti alloys were aimed to reduce the stress-shielding by decreasing Young's modulus (to bring it as close to that of a human bone – *ca.* 20 GPa) upon addition of β-stabilizing alloying elements, such as Nb, Zr and Ta to the titanium [4].

Concerns referring to the detrimental effect of the metallic biomaterial's corrosion have been raised early. Burke [5], in his paper on corrosion of metals in bone surgery, pointed out the problems associated with long exposure of metallic implants to host organism. Even quite stable metals may form possibly harmful complexes and cause local necrosis or affect the pH. In the work published by Black [6], a review describing stainless steel-based, cobalt-based

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and titanium-based alloys, in regard to their corrosion and its effect on the organism was also reported. These materials rely on the formation of "passive" oxide layer, which greatly decreases the rate of corrosion. The author argued, that although the corrosion rate of Co-Cr alloys and Ti alloys is substantially lower (11–22 mg/year) than that of the steels (susceptible to pitting corrosion *in vivo*), the human organism is not tolerable to even low concentrations of metals. Dissolution of metal ions from various "passive" biomedical alloys can occur by a mechanism proposed by Hanawa [7], whereby an implant surface may be physically abraded during normal use after which repassivation takes place. A metal ion can be considered more toxic when it does not form salts or hydroxides, which would impede its reactivity towards biomolecules. Corrosion of biomaterials is strongly dependent on the state of their surface and various steps of its preparation, such as mechanical or heat treatments [8].

Although most of the field of biomaterials for hard tissue reconstruction is dominated by Ti alloys, platinum group metals and other metals, such as tantalum, have also been tested. One of the first reports appreciating tantalum as a candidate biomaterial was published by Burke [5], and it showed a great promise after initial clinical studies (Ta sutures and plates). In his comprehensive review, Black [9] showed a long history of successful applications of Ta in animal and clinical tests. The author argued that the reason for the reluctance to introduce tantalum to the market in larger scale was caused by the advent of the use of Ti and Co-Cr alloys. A later study by Stielher et al. [10] confirmed that the differentiation of human mesenchymal stromal cells was accelerated on the surface of ultra-smooth Ta compared to Ti surface of the similar structure, which explained the high success rate of this material. Similar results were reported by Myllymaa et al. [11], where additionally the effect of surface patterning was taken into account.

Main limitations of Ta are its high density and cost as well as a mismatch of the Young modulus (185 GPa) with that of the bone. These issues were combated by coating Ta on top of cheaper and lighter materials [12,13] or by forming Ta foams [14]. Bobyn et al. [15] improved upon the above-mentioned approaches. First, a thermosetting polymer foam underwent pyrolysis to produce a low-density carbon skeleton, onto which Ta was coated by chemical vapor deposition (CVD)/infiltration. The resulting material was light-weight and consisted of repeating dodecahedrons structure, which guaranteed high porosity (75–80%). Bone ingrowth tests from porous tantalum upon retrieval after *ca.* 2 years after implantation have been performed by Hanzlik et al. [16]. In the research, only 2 out of 124 cases of acetabular loosening were noted, which brings promise regarding this material.

Modern biomaterials are usually required not only to remain harmless with respect to host organism but to fulfill a specific role. Various surface treatments can bring about changes that will functionalize the surface in a particular way. For the orthopedic implants, it is usually desired that the material remains bioactive, *i.e.* it binds with the bone, a short time after implantation. This process is initiated by the formation of a natural mineral component of the human bone – hydroxyapatite $Ca_5(PO_4)_3(OH)$ (HA) – on the surface of a biomaterial. This provides a linkage between the metal and the bone. Surface functionality can be attained in a myriad of ways. For example, titanium and some of the other valve metals (*e.g.* Nb or Ta) can be rendered bioactive by alkali treatment in concentrated NaOH solution, followed by heat treatment as it was proposed by Kokubo et al. [17].

Ceramics present a group of biomaterials with excellent bioactive behavior and HA can be regarded as one of the notable members of this group. Mg, like Ca, is also a biologically significant element, the presence of which is necessary for many biological pathways such as calcification of bone. It also reduces the risk of osteoporosis. Mg forms divalent ions, which makes it possible to substitute calcium in hydroxyapatite crystal lattice by $Mg^{2+}$. There were attempts to accomplish that by Webster et al. [18], who determined that among the studied elements (Mg, Zn, Cd and Y) yttrium is the one that better promotes the osteoblast adhesion on the substituted HA surface, but magnesium is the second best. However, the presence of Mg ions within HA crystal lattice destabilize the structure, which affects the degree of crystallinity of the material. Aina et al. [19] resolved this problem by co-substituting HA with $Sr^{2+}$ alongside $Mg^{2+}$.

The main disadvantages of bioceramics are that they are brittle and even if coated on top metallic surfaces, they usually do not form covalent bonding with the substrate. However, the formation of well-adherent ceramic coatings on many metals (*e.g.* Ti, Mg, Zr, Nb and Ta) is possible *via* plasma electrochemical oxidation (PEO), also known as micro-arc oxidation (MAO). This technique relies on high-voltage anodization of metallic workpieces in suitable passivating electrolytes, which leads to the formation of anodic oxide coatings on the treated surfaces. Once the voltage of anodization is high enough, so that the oxide breakdown can occur, plasma formation commences, which leads to a series of plasma- and thermochemical reactions. The resulting coatings are relatively thick (up to several hundred μm), porous and can be considerably enriched with electrolyte components. These surface characteristics can be controlled by anodization voltage, anodic current density or electrolyte composition. A comprehensive review of the use of the technique for biomedical purposes was reported by Krzakała et al. [20]. Although, there is a general tendency to process metals *via* PEO by the use of dilute solutions containing Ca and P, Rokosz et al. [21] presented a method, whereby a workpiece was treated with a concentrated acid solution (*e.g.* 85% phosphoric acid) with addition of different loadings of a chosen salt (the researchers used $Cu(NO_3)_2$). The proposed treatment resulted in the formation of the oxide coatings, significantly enriched in phosphorus and copper. The latter was meant to provide the bacteriostatic effect to the material's surface.

So far, modifications of tantalum surface by PEO for the biomaterial use were relatively scarce in the literature. An extensive study of PEO-modified Ta scaffolds (synthesized from the annealed Ta-polyurethane foam) was reported by Gao et al. [22], which consisted of *in vitro* and *in vivo* examinations. The researchers used a $Na_3PO_4$ + KOH solution during AC PEO, which was followed by consecutive soaking in 0.5 M NaOH (24 h) and in simulated body fluid (1 week; composition: 142 mM $Na^+$, 5 mM $K^+$, 1.5 mM $Mg^{2+}$, 2.5 mM $Ca^{2+}$, 147.8 mM $Cl^-$, 4.2 mM $HCO_3^-$, 1 mM $HPO_4^{2-}$, 0.5 mM $SO_4^{2-}$). A different approach was undertaken by Wang et al. [23], whereby a commercially used porous tantalum (Trabecular Metal™, TM) was first AC PEO-ed in calcium acetate and sodium β-glycerophosphate, then it was subjected to hydrothermal treatment (140 °C). It was found that the coatings were comprised of the $CaTa_2O_6$ matrix with HA nanorods, which were found to greatly enhance the proliferation and survival of osteoblasts. The same group took a more thorough look at the effect of anodization voltage and annealing temperature on the composition and surface features of the obtained coatings, in their subsequent study [24]. The same electrolyte system was investigated in parallel by Zhao et al. [25] and their results matched with those obtained by Wang et al. [24].

In our previous work [26], we have investigated the formation of PEO coatings on Ta in silicate solutions, which greatly enhanced corrosion resistance of the metal and led to a significant incorporation of Si species. To authors' knowledge, no reports of incorporation of Mg along with Ca and P into Ta substrate has been published in the literature. Additionally, most of the present studies are concerned with AC PEO process in relatively dilute electrolytes. The present work is aimed at finding the effect of limiting anodization voltage as well as electrolytes composition applied in a 2-step DC PEO process on the surface characteristics of the resulting oxide coatings on pure tantalum.