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Review of the biocompatibility of micro-arc oxidation coated titanium alloys

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ABSTRACT

Titanium and its alloys are expected to be ideal materials for biomedical applications. Various approaches have been used for biological properties improvement. Among various surface modification techniques, micro-arc oxidation (MAO), which can produce porous, adhesive and bioactive coatings for implantation, has aroused considerable attention. This paper gives a brief overview of biological assessment of bioactive coatings. It focuses mainly on the strategies of improving biological properties of MAO coated titanium and its alloys. The influence of the electrolyte, process parameters, pretreatment and post-treatment on the coating characteristics (surface micrograph, adhesion strength and biological compatibility etc.) is detailed in this article. MAO assisted by other methods to achieve superior biocompatibility is also discussed. Finally, the trend of development in the future is forecasted.

1. Introduction

The materials used for medical applications especially for dental and orthopedic implants should possess excellent biocompatibility, corrosion resistance in body environment, and superior mechanical properties, wear resistance, and nontoxicity [1–4]. Titanium and its alloys are expected to be ideal materials for medical application because of their excellent characteristic such as high strength, low density (high specific strength), high immunity to corrosion and enhanced biocompatibility [5,6]. However, unlike bioactive ceramics, bio-glass, hydroxyapatite (HA) and glass ceramic, titanium implants cannot bond directly to the bone due to their poor osseointegration and osteoinductive properties [7,8]. Surface morphology, composition, hydrophilicity and roughness are key factors of implant–tissue interaction and osseointegration [9]. The bioactive calcium phosphate (Ca–P) containing coatings on titanium are similar to biomimetic implant materials used for bone tissue. Thereby, focus can be made on the development of Ca–P-based surface coatings on titanium-based materials for load-bearing implant applications. Typical coating methodologies like sandblasting [10,11], plasma spraying [12–14], alkaline treatment [15], acid etching [16], laser surface treatment [17–19], anodic oxidation [20] and MAO [21,22] are extensively studied at laboratory scale. Compared with other surface modification techniques, MAO is one of the most applicable methods to deposit a porous bioceramic layer on Ti and its alloys. The MAO coated surface can contain calcium and phosphorus ions according to the selected electrolyte. These precipitations containing Ca–P ions in the titanium oxide layer can further crystallized into HA through a hydrothermal treatment [23]. The HA facilitates the adhesion of cells and growth of new bones. So MAO should be a good surface modification process to improve the biological properties of titanium. Characteristics of MAO coatings are influenced by the nature of substrate, electrical parameters, electrolyte components, micro-are oxidation time and temperature. So far, the effects of process parameters on MAO coatings have been widely conducted.

2. The method of micro-arc oxidation

The MAO, also referred as plasma electrolyte oxidation (PEO), or anodic spark deposition (ASD), is a high voltage plasma-assisted anodic oxidation process which is widely used for the surface modification on valve metals [24,25]. The valve metals are metals which can form adherent, electrically insulating anodic oxide films after anodizing, such as aluminum, tantalum, niobium, titanium and zirconium [26].

2.1. Process of micro-arc oxidation

The MAO can be described as a combination of electrochemical oxidation, plasma chemical reaction and thermal diffusion in an electrolyte [27]. During the MAO process, the component is immersed in an aqueous electrolyte bath which contains modified species in form of dissolved salts (e.g. silicates, phosphate and calcium salts) [28]. The valve metals (e.g. Al, Ti and Mg) serve as anodes and stainless steel plates

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are used as cathodes in the electrolytic bath. A water-cooled stainless steel vessel serves as the container. The MAO treatment is typically carried out for 5–180 min at a current density ranging from 500 to 2000 $A \cdot m^{-2}$ and voltage of up to 1000 V [29]. Fig. 1 illustrates the schematic representation of MAO setup [30].

The discharge appearance changes and the plasma emission intensities vary with the plasma coating process. The detailed mechanism of MAO process has not yet been revealed; however, most investigators agree that during each alternating current (AC) period several principal stages occur [31,32]:

Stage I The voltage exhibits a rapid and linear increase with time to the breakdown voltage. Some tiny oxygen bubbles and an oxide layer can be observed on the sample surface, corresponding to the traditional anodizing stage (Fig. 2(a)).

Stage II When the applied voltage exceeds a certain critical value, dielectric breakdown takes place, resulting in the formation of spark discharges. In this stage, the current flow concentrates only at regions of breakdown, leading to localized thickening of the oxide coating. The new formed coating can restore the resistance to current flow while other regions where the resistance is smaller are prone to breakdown. In this stage, simultaneous with a shrill sound, numbers of small white sparks are randomly distributed and quickly moving over the entire anode surface (Fig. 2(b)).

Stage III The continuous formation and breakdown of the oxide film causes the cell potential to fluctuate. Gasification of both the valve metals and the electrolyte enables direct formation of ceramic oxide coating. Breakdown of the coating occurs at a vulnerable spot of the growing oxide film. With the increase of processing time, the discharge sparks grow bigger and their color varies from white to orange or red. In this region, the micro-arcs transform into powerful arcs (Fig. 2(c)).

Stage IV The intense sparking and gas release trigger the formation of large size pores and thermal cracking of the film. Along with the disappearance of sparks and gas bubbles, the voltage decreases rapidly, implying the end of the MAO process (Fig. 2(d)). The architecture of the MAO coating is a two-layered morphology: a barrier inner layer and a porous outer layer with numerous fine and course cavities [33]. The thickness of the coating varies from 1 to 100 μm [34].

3. Biological assessment of the bioactive coatings

The importance of materials to the medical device industry cannot be over emphasized. Along with higher demand for medical grade materials, the medical device industry has enhanced its awareness and concern for the safety of materials used. The implementation of chemical and material characterization testing is an essential part of establishing biological safety [35].

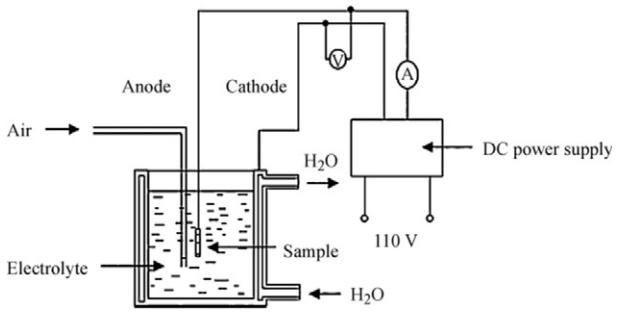

Fig. 1. Schematic representation of micro-arc oxidation setup [30].

3.1. In vitro assay of the coatings

In vitro assay plays an important role in biological assessment of new biomaterials. It gives a simulation of the behavior of implants in biological environments.

3.1.1. Apatite induction in biological fluids

A considerable number of biological assessments have been performed in simulated body fluid (SBF) [36–38] and Hank's solution [39]. The deposition of apatite coatings upon socking in biological fluids depends on many aspects, including roughness, morphology (porosity, size of lamellas) and crystallinity [40]. The enhancement of the kinetics of apatite nucleation on coating surface in biological fluids is significantly related to the interactions. Many studies have given that the nanocrystalline structure has more nucleation sites for apatite formation due to the high energy of surface boundary.

Simulated body fluid has been used extensively for bioactivity prediction and biomineralization. The ion concentrations of SBF and human blood plasma according to the ISO standard are shown in Table 1. Previous studies have assumed that the in vitro apatite forming ability measured by SBF is a prediction of the in vivo bioactivity. By studying and comparing a large number of literatures, Zadpoor [41] has given the relationships between in vitro and in vivo test and concluded that, in most cases, the SBF soaking test could predict the biological property of the biomaterials in vivo. A summary of studies of apatite-forming ability measured in vitro using SBF solution is shown in Table 2.

3.1.2. Hemocompatibility

Hemocompatibility is a key property of biomaterials that comes in contact with blood. The hemolysis ratio, lactate dehydrogenase (LDH), clotting time, and platelet adhesion of different coatings are used to evaluate blood compatibility. Huang et al. [46] made a systematic evaluation of hemocompatibility, including in vitro clotting time, thrombin time, prethrombin time and platelet adhesion.

3.1.3. Cytocompatibility

Cellular responses to an implanted biomaterial are related to several surface properties, akin to protein adsorption. Cell-surface interaction highly depends on the class of material. It is also associated with surface topography, crystallinity, chemical element, roughness, porosity, surface macro and microstructure [47]. Biological trials use different cell lines, mostly, mesenchymal stem cell [48,49], MG63 osteoblast cells [50,51], mouse osteoblast cell line [52], NIH-3T3 murinefibroblast cell [38], and human CCD-18Co fibroblasts cell lines [53]. Cell viability is quantitatively analyzed via dimethylthiazol-diphenyl tetrazolium bromide (MTT) assay [19,54,55], which has been widely used for appraising cytotoxicity and proliferation. Cell proliferation is commonly observed by using a fluorescent microscope [56]. Surface energy and roughness are important factors for cell/materials interaction. The rougher surface has the lower contact angle and higher surface energy values. Materials with high surface energy have more electron-acceptor sites to encourage osteoblastic differentiation. [55]. Crystallinity is known to be another important factor in the biological properties of HA coatings. More cells are adsorbed and proliferate on a well crystallized HA coating than on an amorphous HA coating with comparable particle size. The main purpose of heat treatment is to enhance the crystallinity of CaP coatings, and various studies have reported that heat treatment enhances the cellular activity on the surface of CaP coatings [57–59].

3.2. In vivo assays of the coatings

In vitro experiments may offer a valuable indication of biological responses to implants in humans. However, results obtained from in vitro studies cannot always be extrapolated to the in vivo performance to ultimately represent the dynamics of bone growth. Therefore,