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HYDROXYAPAPTITE LAYER FORMATION ON TITANIUM ALLOYS SURFACE USING MICRO-ARC OXIDATION

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ABSTRACT

In recent years, research on titanium and its alloys had increased significantly for hard tissue replacement and dental applications due to their excellent mechanical properties such as high strength to weight ratio, low density and biocompatibility. However, there are some surface originated problems associated with titanium (Ti): poor implant fixation, lack of osseoconductivity, wear and corrosion in physiological environment. As the interaction between the implant and host bone is a surface phenomenon, surface properties play a prominent role in determining both the biological response to implant and the material response to the biological condition. To improve osseointegration of titanium with bone, hydroxyapatite (HA) has been widely used due to its close similarity to bone mineral. Promising new studies have been reported regarding coating titanium implant with HA using various surface modification techniques to improve the long term stability of titanium implants. Micro-arc oxidation (MAO) has attracted a lot of interest owing to its ability to produce a thick microporous oxide layer on titanium implants. The significant part of MAO is that HA can be incorporated in the oxide layer when processed in electrolytes containing calcium and phosphorous ions. The oxide layer containing hydroxyapatite can be subsequently increased via hydrothermal treatment. The HA produced on titanium surfaces has attractive features such as high porosity and adherent layer which facilitate good clinical outcomes. This review presents the state of the art of MAO and possible further suggestion of MAO for the production of HA on titanium implants.

Keywords: titanium and its alloys, Hydroxyapatite, Micro-arc oxidation, surface modification.

1. INTRODUCTION

Titanium and its alloys are widely used as artificial hip joints, bone plates, screws and dental implants due to their superior mechanical properties and the passive oxide's superior chemical stability [1-4]. However, for the passive oxide and smooth surface, Ti and its alloy as a rather bioinert material and lack of biofunction and considered to have poor bone-bonding ability in vivo [5-7]. The problem of osseointegration (bone-bonding) i.e., the formation of a direct structural and functional connection between the implant and host bone is of critical importance, particularly for orthopaedic implants. In addition, their low surface hardness, high coefficient of friction and poor wear resistance are among the limiting factors which restrict their applications in biomedical sector.

To enhance the surface of titanium implant from wear, corrosion and improve its bio-functionality, surface modification is necessary because biofunction cannot be added during manufacturing processes such as melting, forging and heat treatment [8]. Surface modification is a process of changing the material's surface composition, structure and chemistry without altering the bulk properties. Recently, one used strategy to activate Ti surface is to deposit bioactive material on its surface. Hydroxyapatite has been widely used as a suitable bioactive material due to its excellent osteoconductivity, bioactivity and ability to form a direct bone contact at the implant-bone and guide bone formation along its surface [9-11]. However, the brittle nature of HAp ceramics restricts its application as bulk material under load bearing condition; therefore it is commonly employed as a coating material in clinical setting for Ti and its alloy. The bioactive and biocompatibility nature of HA ceramics guides bone formation and enhanced implant fixation [12, 13]. Compared to uncoated prosthetic devices, implants coated with HAp demonstrated longer time performance after implantation [14]. A range of surface modification technologies have been used to deposit bone like apatite (HAp) on Ti surface including sol-gel [15, 16], plasma spray [17, 18], electrophoretic deposition [19, 20] and micro-arc oxidation [21, 22].

Most commonly, HA ceramics are coated on Ti and its alloy using plasma spray coating technique which is considered as the most popular commercial method for depositing HAp ceramics. However, a major drawback remains in the poor interfacial bonding between the HAp coating and implant material which results in debonding [23, 24]. The particles from de-bonding can subsequently cause inflammatory reaction and loosening of the implants. Another surface modification technique that is becoming increasing widespread and being used to obtain highly adherent, rough and HA thin layer film on Ti surface is micro-arc oxidation. This review provides an overview of HA coated on Ti and its alloy using MAO technique and possible further suggestion for the production of HA on Ti implants.

1.1 Micro-Arc oxidation

Micro-arc oxidation (MAO) or plasma electrolytic oxidation (PEO) [25] is an enhanced electrochemical treatment technology using a conventional anodizing and plasma arc discharge within an electrolyte solution under high voltage to produce highly adherent TiO_2 ceramic coatings on light materials (Ti, Al, Mg, Nb, Ta and their alloys) [26-28]. It is a relatively convenient and effective technique to introduce Ca and P into porous TiO_2 coatings on titanium and its alloys. Typical MAO equipment consists of an electrolyte bath, working electrode and a stainless steel which serves as counter electrode. The morphology and structure of the layer are determined by the electrolyte ingredients, electrolyte concentration, substrate material and processing parameters, such as deposition time and voltage [29, 30]. MAO treatment is usually carried out at higher voltage than the dielectric breakdown potential of the growing oxide layer, usually up to 350 V [31, 32] or even higher up to 450 V [33, 34] or 500 V [35-37] as against the conventional anodizing which operates within the range of 20-80 V [30]. A schematic setup and an example of actual experimental conditions during MAO process is shown in Figure-1.

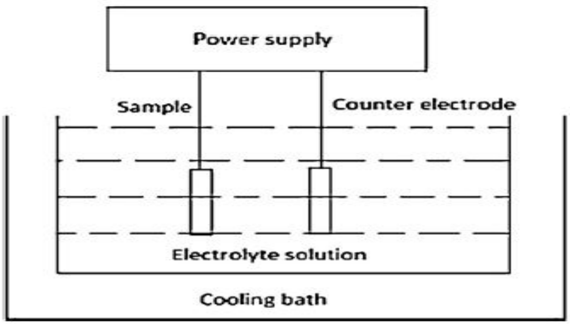

Figure-1. Schematic diagram of PEO experiment [38].

During MAO treatment, the samples are used as anode plates and immersed in electrolyte of interest and mechanically stirred by a mixer.

When the samples of light metal or their alloys are immersed in electrolytes, the metal surface generates a layer of insulating oxide film after energization. As the applied voltage exceeds a critical value, a micro arc discharge with high temperature and pressure develop in the discharge channels resulting in porous and a highly dense thick layer. The ingredients in aqueous electrolyte can be incorporated into the oxide layers by the discharges and the coating containing Ca and P can be deposited onto the surface of metallic materials. The deposited Ca and P usually exist in TiO_2 layer and in this case hydrothermal treatment is usually used to make MAO coating recrystallize. Typical morphology of an oxide layer produced by MAO at different voltages is depicted in Figure-2. MAO can be performed in both direct, pulse biased current and alternating current. Because MAO coating is formed on the metal surface via a series of localized electrical discharge events, many micropores are left in the coating. Thus, the bone cells can be led to grow into these pores and compatibility can be improved.

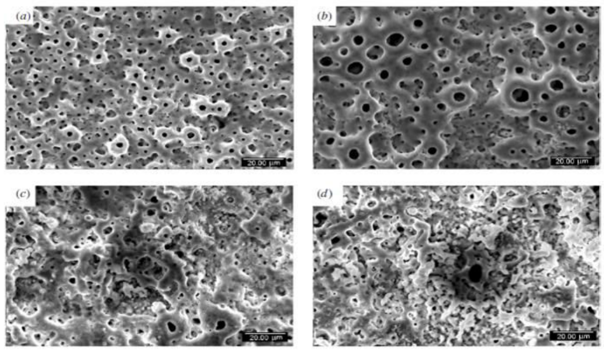

Figure-2. SEM surface morphologies of Ti surfaces treated with MAO with different voltages: (*a*) 300 V, (*b*) 400 V, (*c*) 450 V and (*d*) 500 V. [33]. MAO coatings are of interest in biomedical applications of titanium since they impede release of metal ions by forming thick, hard and well adherent coatings and assists tissue developments through their microporous and rough surface formation as compared to conventional surface modification techniques.

Various electrolytes compositions have been reported for the formation of HA layer on Ti and its alloy. The ingredients of electrolytes and its temperature during MAO treatment play a crucial role in determining the properties of MAO coatings. Different electrolytes result in different phase composition, structure and elemental distribution of MAO treatment. Generally, the electrolytes used for MAO coating are acid and alkaline based electrolytes [39, 40]. Table-1 summarizes different types of electrolytes along with temperature used for HA layer formation on Ti.

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Table-1. Electrolytes used for formation of HA layer on Ti.

Grades	Electrolyte	Electrolyte temperature (°C)	Ref.
Ti6Al4V,Ti 6Al 7Nb	$(CH_3COO)_2Ca.H_2O$, Na_3PO_4	30	[35]
CP-titanium	$CaCl_2$, $NH_4H_2PO_4$	48	[41]
Ti6Al7Nb	$Ca(H_2PO_2)_2$, H_3PO_4	NA	[42]
CP-titanium	$(CH_3COO)_2Ca$,$C_3H_5(OH_2)PO_4Ca$	25	[43]
CP-titanium	H_2SO_4, H_3PO_4,Na_2SO_4	NA	[44]
Ti6Al4V	$(CH_3COO)_2Ca$,$C_3H_5(OH_2)PO_4Ca$	30	[45]
CP-titanium	$C_3H_7Na_2O_6P$, $(CH_3COO)_2.Ca\ x.H_2O$	70	[46]
CP-titanium	$C_3H_7Na_2O_6P$, $CH_3COO)_2Ca.H_2O$	NA	[47]
CP-titanium	$CH_3COO)_2Ca.H_2O$, $NaH_2PO_4.H_2O$	25	[32]
CP-titanium	$CH_3COO)_2Ca$, $C_3H_7Na_2O_6P$	30	[48]
Ti6Al4V	$CH_3COO)_2Ca.H_2O$, $Na_3PO_4.10H_2O$	30	[49]
CP-titanium	$CaHPO_4$, $Na_6P_6O_{18}$, Na_3PO_4	20	[50]
CP-titanium	$Na_2Ti_{16}O_{13}$, $Na_2Ti_4O_9$	NA	[51]
Grade 4	$CH_3COO)_2Ca$,$C_3H_5(OH_2)PO_4Na$	50	[52]

1.2 HA layer production on Titanium by MAO

Using MAO, it is possible to produce HA layers [53]. In these studies Ca/P ratio in the coating was controlled by varying the concentration of electrolytes in the electrolyte bath. A highly crystalline HA coating layer (10-25 µm) with fine coarse structure was formed on the surface of Ti. Lin *et al*. [54] showed that control of Ca/P ratio is possible but unexpectedly, no peaks corresponding to the Ca and P containing phases was detected in XRD analysis. The formation of HA is restricted by the surrounding TiO_2 matrix in form of amorphous. The work was extended by carrying out hydrothermal treatment to recrystallize the HA within the TiO_2 matrix in the MAO coating. Hydrothermal treatment of MAO coating containing calcium and phosphorus films results in the formation of a thin layer of HA over TiO_2 layer [55-57]. After hydrothermal treatment, the degree of crystallinity increases and becomes larger and more glaring [33, 45, 47]. This is attributed to the outward migration of Ca^{2+} and PO_4^{3-} ion from TiO_2 thick oxide layer into HA crystals. The hydrothermal treatment is done on already existing MAO coating by immersion of coated sample in an autoclave or in pressure control reactors containing alkaline or neutral aqueous solution. The hydrothermal treatment is usually performed at a relatively low temperature range 100-250 ^{0}C for 2-24 hrs [10, 55, 56, 58-60] and PH 7-13 [61]. Figure 3 shows the SEM micrographs of oxide films treated hydrothermally at 190 ^{0}C for 10 hrs in three different PH water solutions by Liu *et al*. [55]. The morphology of oxide films revealed that hydroxyapatite can be precipitated as columnar crystals as shown by XRD (Figure-4) and the rough and porous structure of MAO coating can still be retained after hydrothermal treatment (Figure-3).

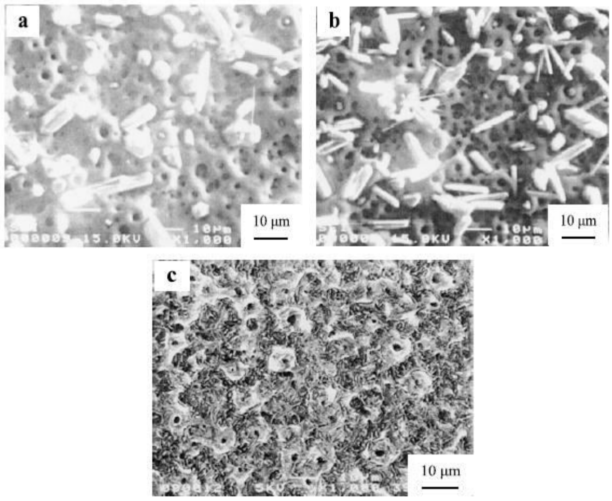

Figure-3. SEM micrographs of oxide films treated hydrothermally at190°C for 10 h. (a) Water solution pH 7.0; (b) water solution pH 9.0; and (c) water solution pH 11.0. [55].

The XRD pattern of oxide film showed that the films have high crystallinity and consist of a significant amount of anatase TiO_2, little amount of TiO_2 and amorphous phase. After hydrothermally treated at 190 ^{0}C for 10 h, HA crystals were precipitated on the film surface as depicted in Figure-4.

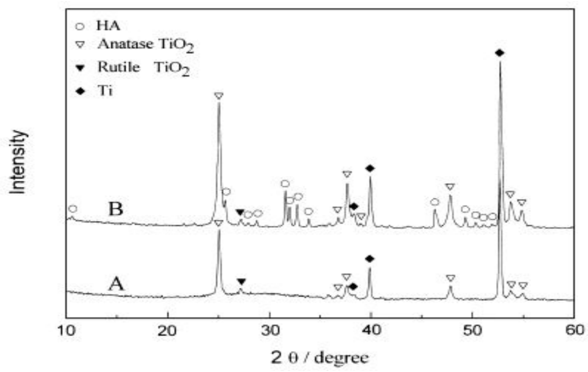

Figure-4. X-ray diffraction patterns of oxide film surface formed in electrolyte of 0.06M Ca-GP and 0.25M CA at 50 A/m^2 and 350 V.(A) Before hydrothermal treatment; (B) after hydrothermal treatment.

However, hydrothermal treatment lowers the bonding strength and roughness of MAO coating because of introduction of additional phases [47]. It is a known fact that surface morphology plays a vital role in the overall success of an implant [62]. Either rough or crater like surface morphology of an implant is needed in any particular clinical setting. Micro-arc oxidation deposition technique allows us to prepare highly dense, uniform and continuous coatings [36, 42, 49]. The technique allows us to prepare porous structure (1-20 μm) with higher coating thickness (16.1-63.4 μm) between CaP and Ti substrate as depicted in Figure-5 [63].

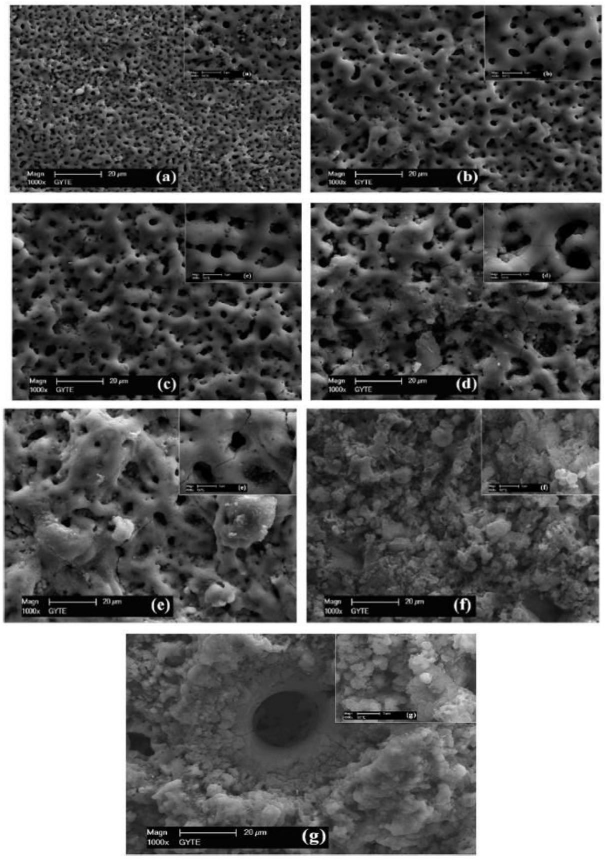

Figure-5. Surface morphologies of MAO coatings: (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 40 min, (f) 60 min and (g) 120 min.

The average thickness and the average pore sizes of the MAO coating increases with treatment time. The MAO porous surface can be of beneficial contribution to cell attachment and infiltration of new bones [63].

CONCLUSIONS

This paper aimed to provide a broad overview of the HA produced on titanium and its alloys using micro-arc oxidation technique. It is clear that micro-arc oxidation is a relatively novel technique that can be used to deposit highly adherent, dense, microporous thick layer surface on titanium substrate. The existence of Ca and P containing phases in the thick layer produced by MAO provides further capacity for the induction of HA layer via hydrothermal treatment. The degree and concentration of Ca and P are significantly higher after hydrothermal treatment as compared to MAO treated Ti surface. The MAO coating process is simple and convenient, but according to recent study, the growth of HA crystals inside open pores cause surface roughness and cohesive strength of hydrothermally treated to be less than the original MAO coated sample. As a result, mechanical interlocking between the coating and implants will be limited due to low surface roughness. Therefore, a high quality coating is still worth investigating which has a higher roughness, good mechanical interlocking and a longer wear life. More improvements should be done for the MAO technique which is of great importance in different biomedical sectors.

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