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Dip Coating of Nano Hydroxyapatite on Titanium Alloy with Plasma Assisted γ-Alumina Buffer Layer: A Novel Coating Approach

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This paper reported a novel coating approach to deposit a thin, crack free and nano-structured hydroxyapatite (HA) film on Ti6Al4V alloy with Al_2O_3 buffer layer for biomedical implants. The Al_2O_3 buffer layer was deposited by plasma spraying while the HA top layer was applied by dip coating technique. The X-ray diffraction (XRD) and Raman reflections of alumina buffer layer showed α- to γ-Al_2O_3 phase transformation; and the fractographic analysis of the sample revealed the formation of columnar grains in well melted splats. The bonding strength between Al_2O_3 coating and Ti6Al4V substrate was estimated to be about 40 MPa. The presence of dip coated HA layer was confirmed using XRD, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis. The SEM images exhibited that HA top layer enveloped homogenously the troughs and crests of the underneath rough (R_a = 2.91 μm) Al_2O_3 surface. It is believed that the novel coating approach adopted might render the implant suitable for rapid cement-less fixation as well as biocompatible for longer periods.

KEY WORDS: Ti6Al4V alloy; Biomaterials; Buffer layer; Ceramic coatings

1. Introduction

To restore the functions of diseased and broken calcified tissues, like our bones and teeth, orthopedic and dental implants are commercially employed. The successful fixation of these implants in our body depends upon the formation of a stable and strong interface between the implant and the bone[1]. Hydroxyapatite (HA) is chemically similar to the mineral part of human bone[2,3], and is known for its bioactivity (ability to form a physiochemical bond with the surrounding bone)[4–6]. However, it is mechanically weak and brittle[5] to be used in load bearing applications such as orthopedic endoprostheses. On the other hand, the titanium alloy (Ti6Al4V) is a light weight, corrosion resistant and high fracture toughness material but is not bioactive[4]; susceptible to the formation of a fibrous layer between the bone and the implant that may lead to implant loosening and ultimately its failure[1]. The application of HA coating on Ti alloy implants offers a possibility to combine the strength and ductility of a metal and the bioactivity of a ceramic like HA.

The methods employed for the coating of HA include plasma spraying, dip coating, electrophoretic deposition, sputtering and electrochemical deposition which are reviewed elsewhere[7]. Amongst all, the plasma spraying is the most widely used process for such coatings and has advantages like fast deposition rate and sufficiently low cost[8,9] but it has certain drawbacks. In this method the particles are first melted and then solidified on the substrate surface. The similarity in coefficients of thermal expansion (CTE) of the depositing material and the substrate is important to obtain coatings with good adhesive strength. Since HA and Ti have quite different CTEs of about 11×10^{-6}–15×10^{-6} K^{-1} and 8×10^{-6}–10×10^{-6} K^{-1}, respectively[10,11], a strong bonding between them is not expected. Moreover, the HA coatings produced by plasma spraying have undesirable phases (such as CaO and tetracalcium phosphate (TTCP)) in varied proportions depending upon the temperature and velocity of the impinging particles[12].

In the present study, an interlayer of alumina was inserted between the HA top layer and Ti6Al4V substrate. The alumina and Ti6Al4V alloy have similar CTEs, 8.7×10^{-6} K^{-1} and 8.5×10^{-6} K^{-1}, respectively[5,13]. Hence, a strong interfacial bond is envisaged. The adhesion between the alumina coating and Ti has been reported to be improved when they were heat

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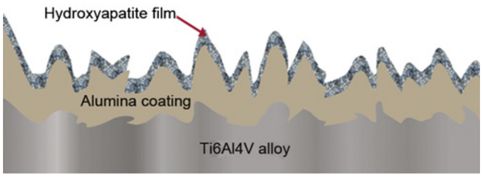

Fig. 1 Schematic diagram of the coating approach adopted in the current study.

treated at 800 °C after plasma spraying[14]. Similarly, the improvement in adhesion between the alumina coating and Cu substrate has also been reported by incorporating a Ti buffer layer[15]. Also, the adhesion between plasma sprayed HA and alumina substrate was improved by heat treatment at 900 °C[16].

Alumina is known to be a bioinert ceramic[5] and, therefore, it is prone to the formation of a fibrous layer on its surface in the physiological environment. But it has been reported that this fibrous layer is very thin around dense alumina implants[4]. The culturing of human osteoblast (HOB) cells on the porous alumina membranes bonded to Ti6Al4V alloy has shown favorable response by normal osteoblastic cell growth; the cells quickly spread and flatten on the alumina surface[17]. The alumina coating may also act as a barrier to the diffusion of harmful Al and V ions into the body. The release of Al and V ions from Ti6Al4V alloy is associated with long-term health problems such as Alzheimer disease, osteomalacia and neuropathy[18,19]. Moreover, the vanadium is also toxic both in the elemental state and as oxides (V_2O_5)[20−22].

Although a thin layer of TiO_2 is formed instantaneously at the Ti surface that may protect the metal in physiological conditions but higher oxide (such as alumina) thickness on Ti surface will make the implant more corrosion resistant since the oxide thickness is an important parameter that affects the corrosion resistance[23,24]. The rough surface of the implant provides greater area for the tissue−implant interaction and therefore it is liable for increased bone apposition as compared to smooth surface[25]. The enhancement in shear strength between the bone and the implant in the early stage (4 weeks) has also been reported on the rough surface in a canine model[26].

The morphology of HA coating could be micro- or nano-structured. The building blocks in the calcified tissues, like bone and teeth, have dimensions on the nano-scale[27,28]. Thus it is quite natural to expect better mineralization on the nano-structured surfaces as compared to their micro-structured counterparts. In fact, an enhanced adhesion of the osteoblast cells is reported on nano-structured ceramics[29,30] and coatings on titanium[31,32] as compared to their micro-structured analogs.

How thick HA coating must be? The thickness of HA coating has not been specified in FDA (food and drug administration) document[33]. However, the work of Wolke et al.[34] has shown that 1 μm thick HA coating deposited by sputtering is sufficient for inducing bioactivity. The employment of thicker coatings may not be beneficial in the long run. The coatings tended to dissolve *in vivo* and a substantial portion of HA coating (>50 μm) on Ti by plasma spraying was found missing after six months of implantation[35]. However, this dissolution of HA coating did not result in loosening of the implants[35]; supporting the hypotheses that once a good early fixation is established between the bone and the implant, the long-term stability of HA coating may become irrelevant.

The use of TiO_2 as a buffer layer between the metallic substrate and HA coating is extensively studied for expected improvement in the implant life[36−39] but an alumina buffer layer is rarely investigated.

In the light of above mentioned literature reports, a scheme of coatings has been designed and is shown in Fig. 1. In this scheme a thin HA top layer with an alumina buffer layer is proposed. The alumina will be deposited by atmospheric plasma spraying followed by synthesis of HA film by dip coating process. The HA top layer is expected to make the surface bioactive in the initial stages after implantation while the presence of alumina buffer layer is assumed to act as a barrier to diffusion of harmful Al and V ions into the body even after the dissolution of bioactive HA top layer. Since the surface morphology of plasma sprayed coatings is usually rough and irregular in nature[40,41], dip coating technique is a method of choice to deposit films on such surfaces. The novel approach (by combining the plasma spraying and the dip coating techniques) adopted in the current study for the alumina and HA deposition has not been reported.

2. Experimental

2.1. Deposition of alumina buffer layer on Ti6Al4V by atmospheric plasma spraying

The alumina powder was sprayed on Ti6Al4V coupons, diameter 25.4 mm and 4.5 mm thick, using atmospheric plasma spraying (Sulzer Metco 3 MB Gun). The coupons were fixed on a cylinder that was rotated at a speed of 128 r/min during the

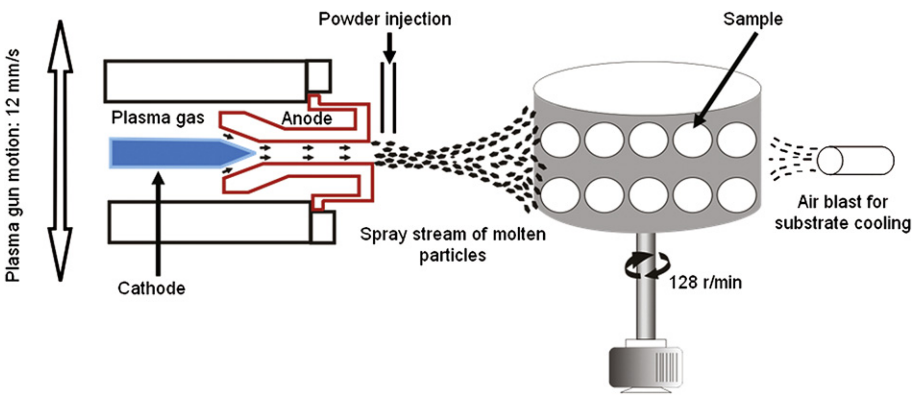

Fig. 2 Schematic diagram representing plasma spray coating process.