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# Laser cladding with HA and functionally graded $TiO_2$-HA precursors on Ti–6Al–4V alloy for enhancing bioactivity and cyto-compatibility

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## ABSTRACT

In the present study, the morphology and composition of Titanium alloy (Ti–6Al–4 V) surfaces were modified by laser cladding (LC) process to enhance the biocompatibility and bioactivity of orthopaedic implants. Ti–6Al–4 V substrates were processed using a pulsed Nd:YAG laser with various precursors: 100% HA and functionally graded $TiO_2$-HA material (FGM). A set of laser parameters having 21.6 $J/mm^2$ laser energy density or irradiance was applied for cladding, to execute a comparative study. The morphology, phases and wettability with different biological tests including bioactivity, protein adsorption, cell adhesion and cyto-compatibility were performed on cladded samples. The FGM cladding showed higher apatite precipitation than 100% HA cladding. Both LC samples had significantly higher amount of protein adsorption lead to higher cell adhesion and cyto-compatibility compared to non-cladded Ti-6Al-4 V alloy. In between the LC samples, FGM cladding had more protein adsorption and cell adhesion than 100% HA cladding. With six days of incubation, the proliferation rate of FGM cladding (215.6 ± 17.2%) was significantly higher than 100%HA cladding (134.6 ± 9.5%) and non-cladded Ti–6Al–4 V control (100%). All these outcomes reveal that the LC process improves the biocompatibility and bioactivity of Ti–6Al–4 V.

## 1. Introduction

Demand for artificial implants for orthopaedic and dental applications has been increasing in recent days. Thus different studies have been carried out to develop and improve the quality of implant regarding its functionality, durability and biological response. Biomaterials, which are either modified naturally or chemically synthesized, have been successfully used in different implants for repair or replacement of natural tissues. Calcium phosphate (Ca—P) based hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), is the most widely used biomaterial which has similar mineral constituents found in teeth and bones [1]. HA has the potential to combine with host tissue and stimulate strong bonding at the interface of tissue and material. It can help to grow the tissues and ignore the unexpected outcomes from immune system [2,3]. However, HA alone cannot be used as a bulk material for load-bearing implants due to its lower fracture toughness and lower fatigue strength. Thus, HA coating on bio-inert metal such as Ti-6Al-4 V alloy was developed to achieve the superior mechanical performance of the metal as well as excellent bioactivity of HA simultaneously.

To modify the surface of a metal alloy by Ca—P based surface chemistry, several techniques have been applied to enhance bioactivity and biocompatibility of the implant. These techniques include electrophoretic deposition [4], ion-beam sputtering [5], magnetron sputtering [6,7], plasma spraying [8], and sol-gel coating [9]. Also, pulsed laser deposition is used to irradiate Ca—P from the target material and deposit on metal alloy [10,11]. Surface coatings with the nanoscale thickness of silanes self-assembled monolayers (SAMs) have also been used to improve the biocompatibility of the materials with controlled wettability and surface chemistry [12,13]. However, most of the above mentioned methods neither provide strong adherence of the coating to substrate nor textured surface for attachment and growth of new bone cell at the tissue implant interface. Hence, laser cladding (LC) process was developed to fabricate Ca—P coatings due to its ability to form a strong metallurgical bonding between the coated material and Ti-6Al-4 V substrate. Also, LC has the potential to obtain suitable surface chemistry and surface textures to enhance the biocompatibility as well as bioactivity of metallic surfaces at tissue–implant interface [14].

LC is a thermo-chemical process where a non-treated surface being melted with the coating material by application of high power laser beam onto a small area. So, the initial properties of metal surface is modified which leads to inter-metallic bonding between coating and substrate with little dilution [15]. The deposited material can be

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transferred to substrate either by powder injection or preplaced powder method. Compared to powder injection method, preplacing powder method is easier to handle with less powder wastage. Also, due to the non-compact behaviour of the preplaced powder layer, the laser energy is absorbed more efficiently [16]. Different lasers are used to clad CaP coating on different metals, particularly in stainless steel and Ti alloy. Zhang et al. [17] paved the step HA or $CaHPO_4.2H_2O$-$CaCO_3$ powders on stainless steel and cladded using $CO_2$ laser to obtain bioceramic composite layer coating on the substrate. It was found that lower laser power with higher scanning sped is the favorable condition for laser cladding of bioceramic coating. Lusqinos et al. [18,19] produced CaP coatings on Ti-6Al-4 V using Nd:YAG laser cladding technique by powder injection method. They found $CaTiO_3$ and titanium phosphate at the interface of coating/substrate and reported it as the evidence of strong bonding between CaP and Ti alloy. Wang et al. [20] developed composite layer consisting 42.6% HA and 57.4% β-$Ca_2P_2O_7$ on 316 L stainless steel in situ by laser cladding with preplaced powder (80% $CaHPO_4.2H_2O$ and 20% $CaCO_3$). They found granular HA with overlapped club-shaped or needle like β-$Ca_2P_2O_7$. Lusquinos et al. [21] investigated the effect of different parameters such as laser beam power, powder mass flow and substrate speed on cladding dimensions as well as the surface roughness during laser cladding of HA on Ti-6Al-4V. Different phases such as HA, β-TCP, α-TCP and $Ca_2P_2O_7$ were found by Deng et al. [22] on the cladding surface during preplaced cladding of 80% $CaHPO_4.2H_2O$ and 20% $CaCO_3$ mixture on Ti alloy with a laser power density of 12.73–15.27 $MW/m^2$ and 10.5 m/s scanning speed. Wang et al. [23] obtained HA, α-$Ca_2P_2O_7$, CaO and $CaTiO_3$ phases in the coating during laser cladding of HA on Ti substrate with 600 W laser power and 3.5 mm/s scanning speed.

Though LC is superior to other surface modification treatment, there indeed are some defects, such as cracks and pores in the laser cladded layer. Due to a large mismatch in elastic moduli, thermal coefficient of expansion and hardness between Ca—P based bioceramic and Ti alloy, a sharp interface is generated between coating and base material. i.e. no gradual change in microstructure between coating and substrate. This leads to reduction of bond strength and crack formation [24]. To control the cracks and improve the bonding strength, many researchers mixed a certain percentage of pure Ti powders with Ca—P based bioceramic due to similar thermal expansion coefficient of Ti with that of the substrate [25]. Furthermore, to enhance metallurgical bonding at the interface and bioactivity on the surface of coating, a functionally graded coating was designed and fabricated with laser cladding [26]. In order to reduce the thermal stress between coating and substrate during laser cladding, Zheng et al. [27] adopted gradient design of three layers: (1) 80% Ti + 20% M; (2) 40%Ti + 60% M; (3) 100% M. "M" represents the mixed powder of $CaHPO_4.2H_2O$ and $CaCO_3$. HA and β-TCP with CaO, $CaTiO_3$, $TiO_2$ and α-TCP are appeared on the top surface of coating and this coated surface shows better osteoblast response than untreated surface. Zhu et al. [28] prepared a functionally graded bioceramic coating on Ti alloy by using laser cladding three times for three layers: (1) 70% Ti + 30% M; (2) 40%Ti + 60% M; (3) 10%Ti + 90% M. "M" represents the mixed powder of 81%$CaHPO_4.2H_2O$, 19% $CaCO_3$ and 0.6% $Y_2O_3$. Zheng et al. [29] carried out gradient coating of three layers: 20% of the calcium phosphate with 80% Ti at inner layer, 50% calcium phosphate and 50% Ti at middle layer and 100% calcium phosphate at outer layer. It was revealed that strong metallurgical bonding occurs between coating and substrate. Improvement of apatite formation was observed on the laser coated surface compared to untreated titanium alloy.

Instead of pure Ti powder, Titania ($TiO_2$) powder was mixed with Ca—P based bioceramic to enhance the adhesion between bioceramic and Ti substrate as its coefficient of thermal expansion is nearly equal to Ti substrate. Araghi and Hadianfard observed better adhesion strength as well as chemical stability with no cracks during electrophoretic deposition of HA-$TiO_2$ coating on Ti alloy as compared to HA coating [30]. Cannilo et al. carried out laser treatment of plasma sprayed $TiO_2$-HA graded coating at different laser power and defocused distance [31]. In addition, $TiO_2$ promotes calcium and phosphate precipitation and has the chemical affinity for both Ti substrates as well as Ca—P based bioceramic [32,33]. He et al. found better osteoblast response during dip coating of nano-$TiO_2$/HA than HA coating [32].

Despite the fact that, CaP-$TiO_2$ coatings have been carried out successfully on Ti alloy by various processes, however, there is limited reported literature regarding LC of CaP-$TiO_2$ on Ti alloy. In addition, less attention has been paid for observing different biological responses during LC of CaP-$TiO_2$ on Ti alloy. Hence, in the present study, a pulsed Nd:YAG laser was used during LC of Ca—P based bio-ceramic coating on Ti-6Al-4 V alloy with different precursors: 100 wt% HA and functionally graded HA-$TiO_2$ material (FGM) in order to obtain multiphase, microtextured coating with better metallurgical bonding at the interface. The coating characterization such as surface morphology, elemental composition, phases and wettability of produced coatings were studied in this study. In vitro bioactivity, protein adsorption as well as in vitro biocompatibility consisting cell adhesion and cyto-compatibility were also investigated.

## 2. Materials and methods

### 2.1. Materials

Titanium alloy (Ti-6Al-4 V) sheets were purchased from Narendra Steel, India. Table 1 represents the mechanical properties of Ti-6Al-4 V at room temperature whereas Table 2 shows the elemental composition of Ti-6Al-4 V, which was confirmed by energy dispersive spectroscopy (EDS). Polyvinyl alcohol (PVA, Cat. No. 05315) granule was purchased from Loba Chemie, India. Tri-hydroxymethyl aminomethane [$(CH_2OH)_3CNH_2$, Cat. No. 108382] and titania ($TiO_2$, Cat. No. 1.93803.0521) powders were obtained from Merck, India. Hydrochloric acid (HCl, Cat. No. AS003), sodium chloride (NaCl, Cat. No. MB023), sodium bicarbonate ($NaHCO_3$, Cat. No. TC230), potassium chloride (KCl, Cat. No. MB043), dipotassium hydrogen phosphate trihydrate ($K_2HPO_4 \cdot 3H_2O$, Cat. No. RM9194), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Cat. No. MB040), calcium chloride ($CaCl_2$, Cat. No. GRM710), disodium sulphate ($Na_2SO_4$, Cat. No. GRM419), and dimethyl sulphoxide (DMSO, Cat. No. TC185) were procured from Hi-Media, India. Double distilled water (Mili-Q, 18 mΩ, Millipore systems) was used throughout the work.

### 2.2. Substrate preparation

Ti-alloy plates with 40 × 30 × 3 $mm^3$ dimension were cut by wire-electro discharge machining (WEDM) process and used as the substrate. In order to remove the oxide layer from the surface, the cut substrates were polished with 80 μm grit silicon carbide emery papers and then rinsed with acetone. The substrate surface was immediately preplaced by the mixture of precursor and PVA in order to prevent oxidation after sandpaper grinding.

HA powder was used as the main coating material for LC. HA powder of nanoscale dimensions was synthesized from abundantly available raw fish scales wastes using the method described previously with slight modifications [34,35]. After calcinating at 800 °C, HA flakes were processed in high energy ball milling for 10 h to get powder in nanometer range. The synthesized nano-HA was characterized for

**Table 1**
Mechanical properties of Ti-6Al-4 V at room temperature.

| Yield strength (MPa) | Ultimate tensile strength (MPa) | Young's modulus (GPa) | % elongation | Hardness (HV) |
|---|---|---|---|---|
| 850 | 957 | 113 | 11 | 298–302 |

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