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Microstructure and in vitro bioactivity of laser-cladded bioceramic coating on titanium alloy in a simulated body fluid

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ABSTRACT

In order to obtain bioactivity on the surface of titanium alloy, the bioceramic coating on Ti–6Al–4V was designed and fabricated by laser cladding. The microstructure and bioactivity of laser-cladded bioceramic coating were investigated in vitro via soaking in a simulated body fluid (SBF). The results indicated that the laser-cladded bioceramic coating was metallurgically bonded to the substrate and contained such bioactive phases as hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP). A bone-like apatite layer was spontaneously formed on the surface of laser-cladded coating merely soaked in SBF for 7 days. And the appearance of flake-like and cotton-like morphology, which is the characteristic morphology of apatite, offered an advantageous condition for osseo-connection. The formation ability of apatite was remarkably accelerated on the surface of laser-cladded bioceramic coating compared with the untreated titanium alloy substrate.

1. Introduction

The bioactive materials, such as hydroxyapatite (HA) and certain glass–ceramic, have been used as important bone substitutes in clinic because they could spontaneously bond to living bone. However, the inherent mechanical properties of brittleness, low tensile strength, and poor impact resistance limit their scope in many load-bearing applications [1–4]. Titanium and its alloys have been widely used in skeletal repair and dental implants area due to well mechanical properties and biocompatibility. However they are bioinert materials and occasionally fail due to the wearing resistance and corrosion fatigue by which titanium implants suffered in body fluid [5–7]. Therefore, many strategies were developed to combine the advantages of two kinds of materials. Various techniques have been employed for depositing bioactive materials on metallic implant, including plasma spraying [8], sol–gel process [9], electrophoretic deposition [10], ion beam sputtering [11], and so on. But most of the coatings made by these methods suffer from weak coating adherence to the substrate, thickness non-uniformity, and non-stoichiometric composition of the coating [12,13]. Plasma spraying technology, for example, is the major method commercially available for coating implant devices because of reproducibility and economic efficiency. However, coating produced by this method presents poor coating/substrate adherence and is lack of uniformity in terms of both morphology and crystallinity [14–16].

In the past several decades, laser processes as surface treatment techniques are becoming more attractive in biomaterials engineering. HA thin films have been prepared by pulsed laser deposition technology since 1992 [17]. It was reported that calcium phosphate layers were prepared or synthesized on titanium alloy substrate by laser cladding using pulsed Nd:YAG laser or CO_2 laser [12,18–20]. Nowadays, laser cladding has been become an attractive processing technique to modify the surface of titanium alloy to enhance the bioactivity and biocompatibility. The remarkable advantage is that a sound interfacial bond zone can be formed between coating and substrate by metallurgical bond, which can improve the mechanical and physicochemical properties of the treated surfaces [21,22]. Different types of lasers have been used to obtain bioceramic coating. Researchers have mainly focused on the influence of deposition parameters, such as the nature of the reactive atmosphere, the pressure of this atmosphere, the target–substrate distance and the temperature of deposition, and microstructure and wettability characteristics, etc. [23]. Some results have been obtained and led to more interest in depositing bioceramic coating on metallic implants by laser cladding, but there is presently little literature on bioactivity research. However, the research of bioactivity is imperative in order to focus on the future important clinical development. In 1991, Kokubo et al. [2,24,25] proposed that the for-

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Table 1
Composition design of gradient coating.

Layer number	Pre-placed powders	
	M (wt.%)	Ti (wt.%)
The 1st gradient coating	20	80
The 2nd gradient coating	60	40
The 3rd gradient coating	100	0

mation of bonelike apatite is an essential prerequisite for bioactive materials to make direct bond to living bone when implanted in the living body. Therefore, the bone-bonding ability of a material can be evaluated by examining apatite formation on its surface when soaked in a simulated body fluid (SBF).

In the present study, the bioceramic coating was obtained on Ti–6Al–4V substrate by laser cladding using CO_2 laser. The microstructure and the phase analyses of laser-cladded bioceramic coating were studied. Moreover, the in vitro bioactivity of the laser-cladded coating soaked in SBF was investigated.

2. Experimental

The titanium alloy (Ti–6Al–4V) was adopted as the substrate. Calcium carbonate ($CaCO_3$), calcium hydrogen phosphate ($CaHPO_4 \cdot 2H_2O$), titanium powders (Ti) and a little ceria (CeO_2) were mixed as the precursor powders. Ca/P atom ratio of hydroxyapatite is 1.67. Due to the burning loss of phosphorus during laser irradiation, the Ca/P atom ratio of 1.4 in precursor powders was designed. Namely the weight per cents of $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$ were 81.1 wt.% and 18.9 wt.%, respectively. And a little ceria (<1.0 wt.%) was added because rare earth oxide may play an important role in inducing the formation of bioactive phases [26,27]. To decrease thermal stress between coating and substrate during laser cladding, gradient design of three-layer was adopted. The composition design of gradient coating is shown in Table 1. Here, the "M" corresponds to the mixed powders mentioned above except titanium powders. The gradient powders were pre-placed and laser-cladded in sequence. Laser cladding was carried out by TJ-HL-T5000 CO_2 laser system equipped with integral mirror and processing lathe. The processing parameters in this study were laser output power 2.5 kW, laser scanning speed 140 mm/min and laser beam size 15 mm × 1 mm. Argon gas was blown into the molten pool to provide shielding during laser cladding process.

In vitro experiments were conducted in corrected SBF (c-SBF) with ion concentrations nearly equal to those that have almost similar compositions of inorganic ions to human blood plasma. The reagents and amount for preparation of each liter c-SBF were listed as follows: 8.035 g NaCl, 0.355 g $NaHCO_3$, 0.225 g KCl, 0.231 g $K_2HPO_4 \cdot 3H_2O$, 0.311 g $MgCl_2 \cdot 6H_2O$, 0.292 g $CaCl_2$, 0.072 g Na_2SO_4, and 6.118 g $(HOCH_2)_3CNH_2$ (Tris). Tris and HCl serve as buffers to keep the PH value at 7.4. The preparation procedure was referenced by the works of Kokubo and Takadama [28]. The laser-cladded specimen and the untreated substrate were immersed in SBF for 7, 14 and 28 days, respectively.

The morphologies and the elemental distribution of specimens were analyzed by scanning electron microscope (SEM, JEOL JSM-6700F, Japan) and electron probe microanalysis (EPMA, EPMA-1600, Japan). The phase composition of the bioceramic coating was investigated by X-ray diffraction (XRD, RIGAKU D/max-2400, Japan) using Cu target Kα radiation with a step size of 0.02°.

3. Results and discussion

3.1. Microstructure of laser-cladded bioceramic coating

The SEM micrograph of the surface morphology of laser-cladded bioceramic coating is shown in Fig. 1. It could be seen that the coating on the substrate was composed by spherical flocculent microstructure, and among them some tabular crystal was formed with interlaced arrangement. The coarse and accidented morphologies of surface were highly advantageous to the growth of new bone.

As could be seen from the cross-section morphology of composite (Fig. 2), the microstructure of coating is compact. And the morphology of the zone between coating and substrate is shown in Fig. 3. According to the microstructure and the elemental distribution of the interface zone between coating and substrate by SEM and EPMA, the bioceramic coating was metallurgically bonded to the titanium alloy substrate. As is known to all, laser cladding is a process including rapid heating and solidification. Consequently distinct solidification structures were presented between the coating and substrate.

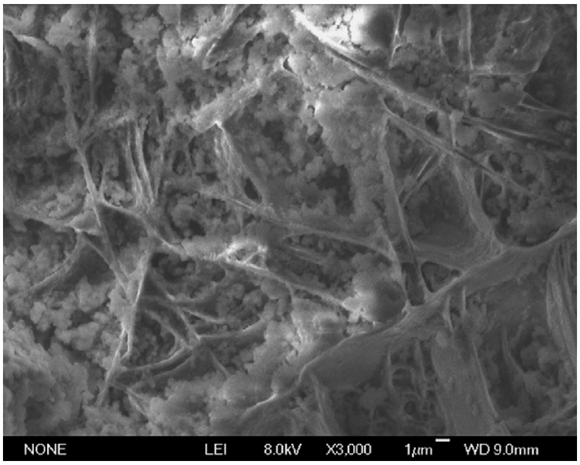

Fig. 1. The surface morphology of coating.

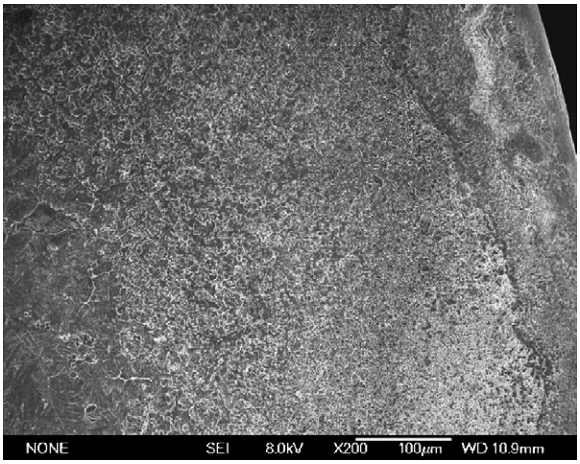

Fig. 2. The cross-section morphology of composite.

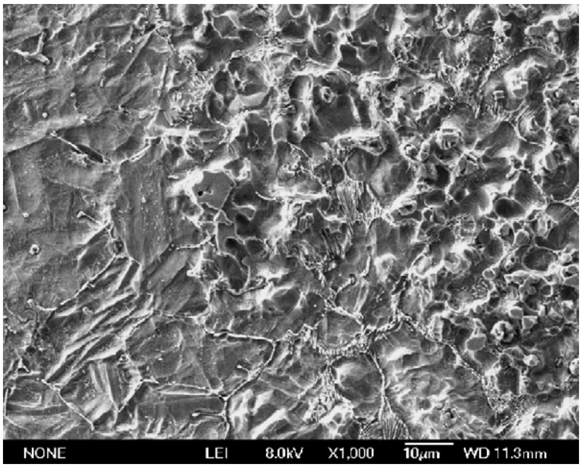

Fig. 3. The micrograph of the zone between substrate and coating.

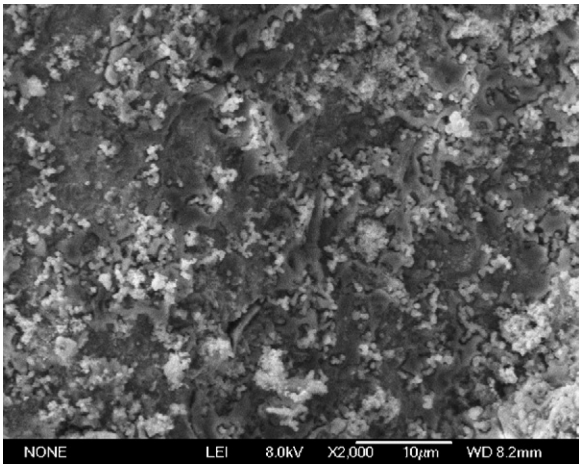

Fig. 4. Surface morphology of laser-cladded coating soaked in SBF for 7 days.

3.2. *Microstructure of laser-cladded bioceramic coating soaked in SBF*

The laser-cladded bioceramic coating and the untreated substrate showed different apatite-forming abilities after they were soaked in SBF at diverse immersion period. The SEM micrographs of the precipitates deposited on the surface of laser-cladded coating soaking in SBF for 7 days are shown in Fig. 4. It could be seen that some flocculent precipitates were spontaneously formed on the surface of laser-cladded coating merely soaked in SBF for 7 days. The similar precipitates were not observed on the specimen of untreated substrate. The results indicated that the laser-cladded bioceramic coating induced apatite nucleation.

As to the morphology of laser-cladded coating immersed in SBF for 14 days (Fig. 5), the new precipitates were formed. The appearance of flake-like (Fig. 5a) and cotton-like (Fig. 5b) pine needle-like (Fig. 5c) morphology, which is the characteristic morphology of apatite, offered an advantageous condition for osseous connection. The untreated substrate was not formed bone-like apatite at all even after 14 days. It could be concluded that the formation ability of apatite was remarkably accelerated on the laser-cladded bioceramic coating soaked in SBF, while untreated substrate unformed the apatite after a long immersion period.

3.3. *The phase analyses of laser-cladded bioceramic coating in vitro*

There is no doubt that the XRD patterns obviously reflected different characteristics for each specimen. The XRD patterns of the laser-cladded bioceramic coating un-soaked and soaked in SBF of 14 days are shown in Fig. 6.

The phases of un-soaked bioceramic coating treated by laser cladding are displayed in Fig. 6a. The results indicated that the mixed powders were completely melted and formed bioactive phases during laser cladding. The presence of hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP) implied that bioactive phases were formed on the top surface of specimens. However, the peaks of HA and β-TCP were weak and peaks of CaO and $CaTiO_3$ were more intensive. Fig. 6b shows the laser-cladded layer soaked in SBF for 14 days. After soaking in SBF, the XRD pattern shows that the HA phase observably increased. Moreover, one may notice that diffraction peaks corresponding to the CaO phase observed in the XRD pattern of Fig. 6a observably decreased after soaking in SBF. Therefore, the laser-cladded bioceramic coating soaked in SBF has an impact on the formation of bioactive phases and apatite-forming ability. Although a small quantity of other calcium phosphate phases were obtained, the laser-cladded layer seems to induce the formation of

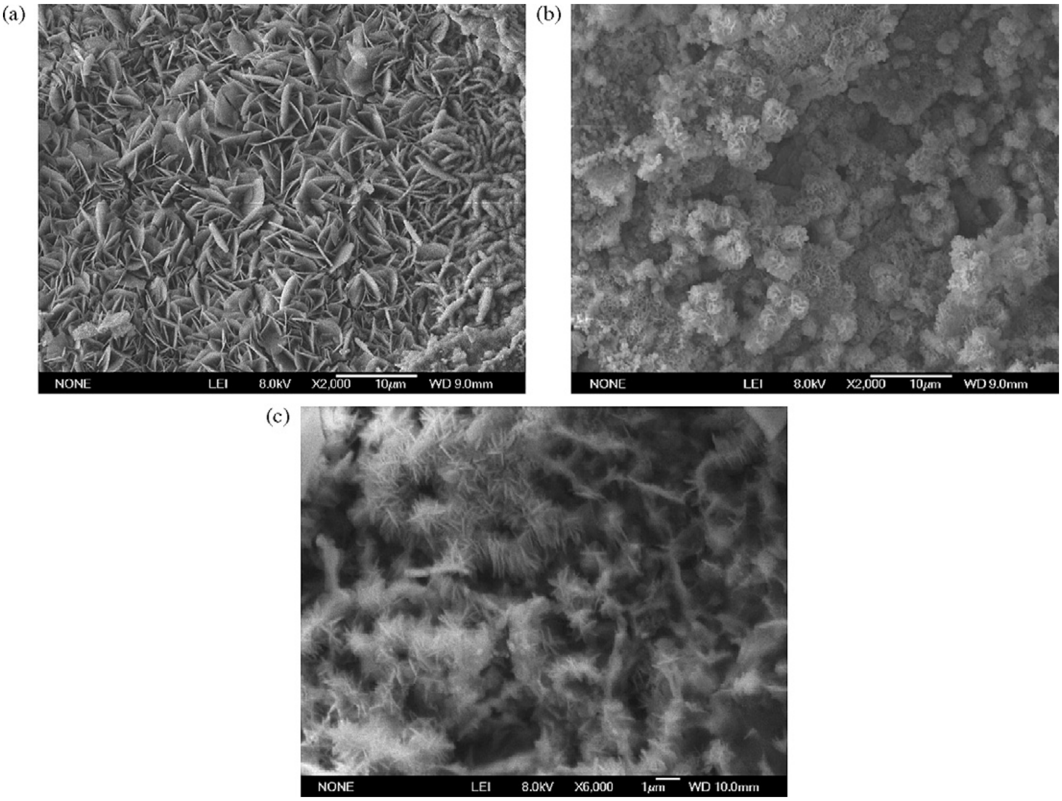

Fig. 5. Surface morphology of laser-cladded coating soaked in SBF for 14 days (a) flake-like; (b) cotton-like morphology; (c) pine needle-like.

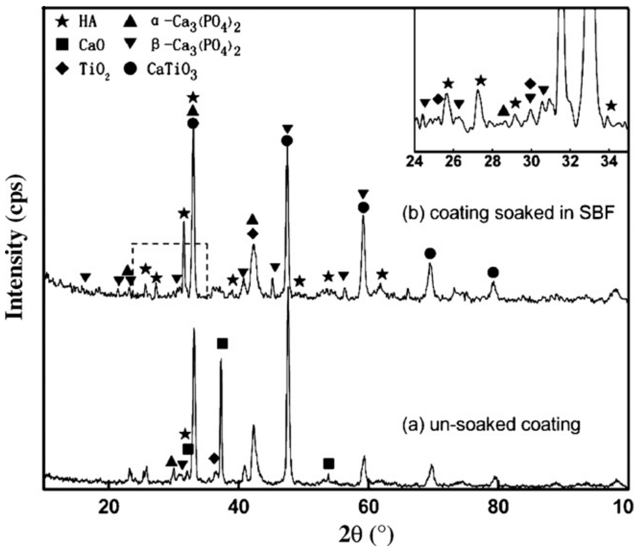

Fig. 6. XRD patterns of laser-cladded coating (a) un-soaked (b) soaked in SBF for 14 days.

apatite in SBF. The illustration at the top right corner of Fig. 6 is the enlarger of Fig. 6b at the range of 24–35°. The formation of such apatite phases on laser-cladded bioceramic coating after soaking in SBF indirectly indicated the laser-cladded coating offered an advantageous condition for osseo-connection because of the bioactivity.

4. Conclusions

In conclusion, the calcium phosphate bioceramic coating on titanium alloy (Ti–6Al–4V) was designed and fabricated by laser cladding. The bioceramic coating was metallurgically bonded to the substrate. The synthesis of bioactive phases such as HA on the top layer of coating offered an advantageous condition for osseous germination. Furthermore, the bone-like apatite was spontaneously formed on the surface of laser-cladded coating merely soaked in SBF for 7 days. And the appearance of flake-like and cotton-like characteristic morphology offered an advantageous condition for osseo-connection. The formation ability of apatite was remarkably accelerated on laser-cladded bioceramic coating in SBF, while untreated substrate unformed the apatite after a long soaking period. Therefore, the laser-cladded bioceramic coating was of favorable bioactivity in vitro after soaking in SBF.

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