Corrosion behavior and microstructure of laser cladded bioactive coating on titanium alloy

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Abstract
Experimental results on bioactive modified treatment at titanium alloy was presented. A better metallurgical bonding of the single tracks with the substrate was obtained by the use of laser beam via an integral mirror. The samples were studied by Scanning Electron Microscope (SEM), Inductively Coupled Plasma (ICP), microhardness instrumentation and corrosion resistance testing. The facts show a significant influence of microhardness on the optimized experimental condition. Furthermore, it reveals that a significant influence of property, especially for corrosion resistance while the rare earth oxide ceria is mixed in the precursor powders. The dynamic factor is a possible influence of escape of granules. The laser-cladded bioceramic coating of ceria additive in pre-placed powders has more favourable corrosion resistance compared with the coating without rare earth oxide.

1. Introduction
Materials used in hard tissue are commonly exposed to very aggressive environments, such as excellent biocompatibility, high mechanical strength and toughness, extreme wearing and corrosion resistance, among others [1]. Titanium and its alloys are widely used in biomedical devices owing to their exceptionally properties such as high specific strength, excellent corrosion and excellent biocompatibility. However, due to their poor tribological properties, the application of titanium and its alloys under severe wear and friction conditions is severely restricted [2-4]. But rather in the sense that surface engineering has emerged as an intense research area in the field of materials science [5].

Therefore, many methods have developed to deposit bioceramic materials on metallic implants, such as plasma spraying, ion-beam sputtering, electrophoretic deposition, and so on. But most of coatings made by these methods suffer from weak adhesion. Functionally graded materials (FGMs) are advanced engineering materials designed for a specific performance or function in which a spatial gradation in structure and/or composition lend itself to tailored properties. This occurs by providing in-depth graded com-positions, microstructures and properties [6]. Laser cladding is one of the industrial preferred surface engineering techniques in which a laser is used as a heating source to overlay the precursor material with the substrate to form a sound interfacial bond, namely apply a chemically different material as a layer onto a given substrate [7,9]. Recently researchers have studied
the influence of composition in fabrication of bioceramic structures using laser cladding. However, a systematic analysis of the effect of process parameters and corrosion behavior are not dealt with.

In this present work, we have analyzed the microstructure of coating as a function of the laser processing parameters. The improving corrosion behavior of the composite coating in human body fluid has also evaluated considering their biomedical applications.

2. Experimental work

The calcium phosphate bioceramic coating was fabricated on titanium alloy (Ti-6Al-4V) substrate by TJ-HL-T5000 CO2 laser system equipped with integral mirror and processing lathe in argon shielding atmosphere. The preplaced powder was a mixture of calcium carbonate, calcium hydrogen phosphate, titanium powders and a little ceria. The weight per cent of calcium hydrogen phosphate and calcium carbonate is 81.1wt.% and 18.9wt.%, respectively. And 0.6 wt.%ceria was added in order to study the effect of rare earth oxide. To decrease thermal stress between coating and substrate during laser cladding, FGMs are advanced engineering materials designed for three-layer: (1) 80%Ti+20%M; (2) 40%Ti+60%M; (3) 100% M. Here, the “M” corresponds to the mixed powders mentioned above except titanium powders. Specimens with dimensions 50 mm×30 mm×5 mm. Synchronous powder feeding was not suitable for mixed cladding materials with density variation. Therefore, the gradient powders were mixed evenly, then pre-placed on the substrate and laser-cladded in sequence. The preplaced coating thickness is about 0.5mm.

The processing parameters of laser cladding were optimized at the experimental condition. In the condition of laser output power 2.5kW and laser beam size 15mm×1mm, laser scanning speed of 80, 100, 120, 140, 160mm/min, respectively.

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: 8.035g NaCl, 0.355g NaHCO3, 0.225g KCl, 0.231g K2HPO4·3H2O, 0.311g MgCl2·6H2O, 0.292g CaCl2, 0.072g Na2SO4, 6.118g (HOCH2)3CNH2 (Tris). Tris and HCl serve as buffers to keep the PH value at 7.4. The preparation procedure was referenced by the works of T. Kokubo [10]. The laser-cladded specimen and the untreated substrate were immersed in SBF 7 days and 14 days.

The metallographic samples were prepared by standard mechanical polishing procedure and were chemically etched. The morphologies and the elemental distribution in different soak fluid of specimens were analyzed by scanning electron microscope (SEM, JEOL JSM-6700F, Japan) and Energy Dispersive X-ray analysis (EDX). The ion concentration soaked in SBF was tested by Inductively Coupled Plasma (ICP, Optima4300DV, Japan). Microhardness and corrosion resistance testing were also been evaluated. With a load of 300g and a loadtime of 10s, the distribution of microhardness was test by HX-1000TM Vickers microhardness tester.

3. Results and Discussion

The primary aim of this work is to study the effect of laser power and scan speed on microstructure, phase constituents and microhardness of laser cladded bioceramic coating on titanium alloy. The changes of laser scanning speed mean that the energy changes absorbed by the material surface, then directly affected the melting depth and width of molten pool. According to Tab. 1, the relation among scanning speed, melting depth and width of the laser cladded coating reveals that the melting depth and width of molten pool increased while the laser scanning speed reduced. The scanning speed should be selected higher than 100 mm/min because of the thickness of substrate. According to microstructure observation, microhardness and analytical calculations about heat transmission and mass transfer during laser cladding, the optimal processing parameters of laser cladding were as follows: laser output power 2.5kW, laser scanning speed 140mm/min, and laser beam size 15mm×1mm.
Table 1. Relation among scanning speed, melting depth and width.

| scanning speed (mm/min) | 80   | 100  | 120  | 140  | 160  |
|------------------------|------|------|------|------|------|
| melting depth          | >5mm | >5mm | 4.64 | 3.38 | 2.88 |
| melting width          | 16.62| 16.14| 15.42| 15.12| 14.86|

The microstructure of laser-cladded composite coating was investigated. The results indicated that the coating was metallurgically bonded to the titanium alloy substrate by the action of laser. The content of titanium was gradually decreased and the calcium and phosphorus were gradually increased. The laser-cladded composite coating contained such bioactive phases as hydroxyapatite (HA), $\beta$-tricalcium phosphate ($\beta$-TCP) and calcium titanate (CaTiO$_3$), etc. The surface morphology of the laser cladded coating is shown in Fig.1. The appearance of irregularity microstructure on coating and more contact area may be in favor of the osseous tissue to grow along.

![Fig.1 The surface morphology of the laser cladded coating](image1)

![Fig.2 Distribution of ion concentration soaking SBF](image2)
Corrosion resistance testing in different soaked liquids indicated that the composite coating at the experimental condition was of bioactivity by SEM, EDX and ICP. The relationship between ion concentrations soaked in SBF at different periods is shown in Fig.2. As shown in the figure, ion concentration of phosphorus rises by the extension of soaking time. And the tends to be stabilization after a week later. The ion concentration of calcium in the beginning, and then appears a slight decline, and finally continue to rise. The ion concentration of calcium and phosphorus rise at preliminary stage, because the ions separate out from the surface of coating. As the extension of immersion time, this value of calcium and phosphorus easily to the equilibration in SBF. Apatite deposit is appeared on laser cladded coating. The ions of calcium and phosphorus should be consumed. While the addition of apatite deposit, ion concentration of calcium and phosphorus continued to increase and reached stabilization by the dissolution.

![Fig.3 Morphology on surface soaked in SBF for 7 days](image3.jpg)  ![Fig.4 Morphology on surface soaked in SBF for 14 days](image4.jpg)

After soaking in SBF 7 (Fig.3) and 14 days (Fig.4), the flocculent precipitates were increased on the surface of coating and the apatite phases were gradually nucleated and grew. The morphology of precipitates was mainly composed of flake-like and the globular, flocculent and acicular morphology were also appeared. Moreover, the appearance of a small quantity of crystal whisker (diameter about 400nm, slenderness ratio about 40–100) in local zone sufficiently benefited intensify toughness. The diffraction peak of apatite extremely intensified and the CaO distinctly decreased when the coating soaked in SBF. It indicated that the coating had the ability of depositing apatite quickly. However, the untreated substrate surface was merely formed trace of soaking and some precipitation of salts.

4. Conclusion
The optimal processing parameters of laser cladding adopted according to microstructure, microhardness and analytical calculations about heat transmission and mass transfer. The results showed retention of large amount of calcium phosphate due to high cooling rates associated with laser processing. The corrosion resistance found to increase with laser cladded coating on titanium alloy substrate. The laser-cladded bioceramic coating of ceria additive in pre-placed powders has more favorable corrosion resistance compared with the coating without rare earth oxide. Under present experimental conditions, the laser cladding found to have strong influence on microstructure, phase constituents and corrosion resistance of composite coating.

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