[Article ID] 1003 - 6326(2000)04 - 0477 - 04

Laser surface coating of RE bioceramic layer on TC4 ①

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[Abstract] A layer of premixed $CaHPO_4 \cdot 2H_2O$-$CaCO_3$-Y_2O_3 powders stuck on pretreated surface of Ti-6Al-4V alloy substrate was successfully transformed into a composite of rare earth bioceramic coating by laser synthesizing and cladding only once. The microstructure and properties of the coating material were introduced. The titanium alloy with bioceramic coating on one side were implanted into the femur bone and thigh muscles of adult Mongrel dogs for testing its biocompatibility. The results of implantation experiments show that the microstructure of the coating material is static, the bonding properties between coating and substrate are better. The bioceramic coating had not toxicity-side effectiveness on the body and there is a better compatibility of osteoconducton. No effect of the coating material on the bio-activity of osteoblast and osteoclast was found.

[Key words] laser cladding; bioceramic coating; biocompatibility; rare earth
[CLC number] TB333 **[Document code]** A

1 INTRODUCTION

For a long time, stainless steels, Co-based alloys, titanium and Ti-based alloys have been used as repairing and implanting materials for hard human tissues because of their excellent mechanical and machining properties. However, metal materials have no consanguinity with human body, have poor biocompatibility. Furthermore, they lack bioactivity and their bonding strength with tissues and new bones is not high enough and they would release ions into human tissues. So the metal materials is restricted to be implanted in bearing sections for a long time. Since 1980s, the bioglasses and bioceramics, which are good bioactive and biocompatible, have been paid more and more attention. These materials are osteo-conductable, can reduce healing time and increase the bonding strength of implants with bones and connective tissues. Thus they have been gradually applied in orthopaedics. But these sintered bioceramics are very brittle, low strength and difficult to manufacture, so they are usually used in the cases of low load or no load. Additionally, it is very difficult to make those artificial bones and joints that are thin and broad or novel shaped. With the development of modern surface technology, bioactive ceramics are cladded on the surface of metals in order to take the advantages of these two materials[1,2]. Such cladding techniques include liquid deposition[3], vapor deposition[4], solid hot-press[5], laser cladding[6], and hot spray, which have been applied in clinic[7], and so forth. Generally, the bond property rising from laser cladding is thought to be the best of all thick coatings. But amorphous phases and impurities are readily to appear in coating layer or cannot obtain a bioactive ceramic coating because the temperature is very high[8,9]. So it is beneficial to adding some powder to improve the structure and property of bioceramic coating cladded by laser.

In nature, appetite in phosphate mine usually contains rare earth elements and deposited phosphate is often abounding of yttrium and lack of cerium. The calcium phosphate shell of ocean zooplankton, shell deposited in continental shelf, coral in Tropic Ocean and animal bone are all consisting of rare earth elements. In fossil of biological phosphate, the concentrate of RE is high. As for a bone, more RE exist in its surface layer. The content of RE in animal's bone ash is between 0.000 2% ~ 0.8% with most yttrium[10]. Therefore, this paper reports the experiment results of synthesis and cladding bioceramic coating with Y_2O_3 on TC4.

2 EXPERIMENTAL

The substrate is TC4 that was premolten by laser, and a certain amount of mixed powder of $CaHPO_4 \cdot 2H_2O$, $CaCO_3$ and Y_2O_3 was stuck on its surface. The bioceramic coating was synthesized and cladded by W-CO_2 laser with lower heat flow density and higher scanning rate. The microstructure of coating layer was investigated with X-ray diffraction (XRD) and scanning electron microscopy (SEM), whose models are D/max-1200 and KYKY-1000 respectively.

Samples were cut and polished into gauge of 4

① **[Foundation item]** Project (59571045) supported by the National Natural Science Foundation of China
[Received date] 1999 - 03 - 02; **[Accepted date]** 1999 - 06 - 30

mm × 4 mm × 5 mm from the composite of Ti-based alloy substrate with bioceramic coating on one side cladded by laser, and they were autoclaved at 126 ℃ for 30 min before implanting. Three adult healthy Mongrel dogs were selected for implantation object in this experiment. Two specimens were implanted into femoral middle of each dog with coating top being faced with the bone, and the other two into thigh muscle. The operation was performed under general anesthetizing (3 mg pentobarbital sodium per 1 kg avoirdupois) and sterilizing condition. Consequently, the dogs were sacrificed by overdose abdominal injection of pentobarbital sodium at 15, 60 and 180 d postoperatively. Subsequently, the implants with surrounding tissues were collected and fixed in 10% buffered formalin solution immediately. A week later, the fixed samples were gradually dehydrated in series alcohol solutions and embedded with methyl methacrylate (MMA). Then sections (20 μm thick) were cut and stained with basic fuchsin and methylene blue for histological observation. The biological toxicity experiment was carried out in Chongqing Medical University. Culturing tests in vitro of osteal cells, fibrous cells and red cells of International Red Cross (IRC) pure-blooded mice were performed bacteria freely. During these tests, thigh muscle, femur and marrow of mice were collected and four samples were placed into them, and seven days later the sections were observed with microscopy to find the morphological changes of the cells.

3 RESULTS AND DISCUSSION

3.1 Microstructure of RE-bioceramic coating on titanium by laser cladding

The laser re-melted process parameters were optimized as follows: heat flow density $q = 40 \sim 50$ W/mm^2, scanning speed $v = 300 \sim 350$ mm/min; the laser cladding process parameters were optimized as follows: $q = 10 \sim 20$ W/mm^2, $v = 600 \sim 650$ mm/min. Fig.1 shows the microstructure of a cross-section of coatings. It can be seen that the bond between coating and substrate is excellent, the coatings have melted and combined, the interface consists of fine and dense microstructure, and are difficult to distinguish, few cracks are found. Moreover, Ca-P-based bioceramic coating was synthesized and cladded simultaneously, there are not decomposition and uncrystallization of hydroxypatite (HA) and β-TCP etc. The microstructure of coating is directional fine and erose polygonal grains with a few isolated granules; coating and substrate are interlocked and metallurgical bonded. The reason may be that adding Y_2O_3 to the coating decreased the tendency of coating crack while laser processing, some high electronegative Ti and Al atoms are converted into $V_3Ti_6O_{17}$, Ti_2O_3, TiAlN, etc, which restrain the activity of Ti and Al in substrate surface as well as form a transition layer with a hard lager between ceramic and substrate. This layer can relax the heat stress and structure stress. The formation of HA and other bioceramics is ensured by lower laser heat flow density, higher scanning rate and increased gradient of concentration and chemical composition in molten pool by Y_2O_3[11]. XRD analysis revealed that phases in coating are mainly $Ca_5(PO_4)_3OH$, β-$Ca_3(PO_4)_2$, $Ca(PO_4)_2$ and γ-$Ca_2P_2O_4$.

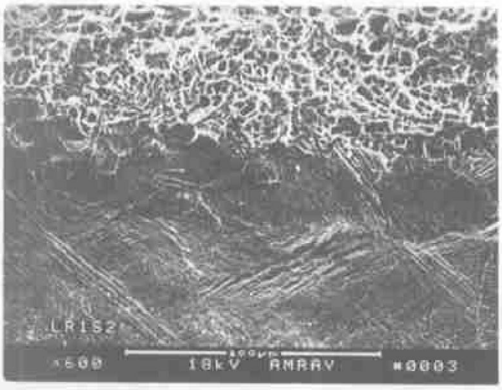

Fig.1 Morphology of coating layer

3.2 Mechanical properties of RE-bioceramic coating on titanium by laser cladding

The main mechanical properties of RE-bioceramic coating on titanium by laser cladding and biological hard tissue are displayed in Table 1. The bioceramic coating cladded by laser has high strength and hardness that is similar to human density bone, so the biomechanic matching can be improved. Furthermore, the microstructures of fracture surface of the coating are fine and even with pushing-out dimples (Fig.2). It is obvious that Y_2O_3 is beneficial to fining the microstructure and increasing the strength and toughness of the bioceramic tested.

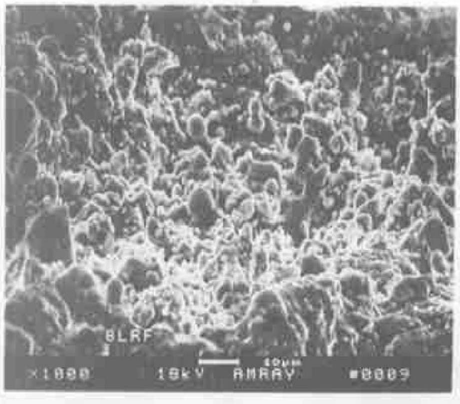

Fig.2 Fractograph of coating layer

3.3 Biological toxicity of RE-bioceramic coating on titanium cladded by laser

The results of biological toxicity of RE-bioceramic coating are listed in Table 2. It can be concluded

Table 1 Mechanical properties of coating and bone

Material	$HV_{0.2}$	σ_{bb}/ MPa	σ_c/ MPa	E/ GPa	σ_b/ MPa	δ/ %
Bone	~689	~230	~330	~49.0	~110	~0.10
Dentine	72	-	295	18.2	-	-
Tooth enamel	350	-	384	82.2	-	-
Sintered HA	539	101	492	104.0	-	-
Laser coating	718	1198	950	69.5	859	1.18

Table 2 Bio-toxicity of coating

Experimental names	Experimental results
Skeletal muscle cells	The shape of muscle fiber is normal, the cell nucleus arrange orderly, the muscle fiber is clear and across line is apt to observe. The break of muscle fiber, vacant hole and deformation or any other toxic morphology phenomena are not found.
Fibreforming cells	The percentage of cells attaching to the wall is the same, the cells are flat, raised and starlike, cytoplasms are abundant and a little basophil. The nucleuses are large and round or elliptical, the caryotins are loose and lightly dyed, the nucleoli are distinct.

from Table 2 that the said material has not virose side effect on the skeletal muscle tissues, fibreforming cells and red cells. On the condition of laser beam heating, Y_2O_3 has catalysis on the synthesizing of HA and stabilizes the phase structure of Ca-P-based bioceramic as well as prevents them from decomposing[11], so the coating phases are almost all HA and β-TCP and other Ca-P-based bioceramics, which are the primary mineral composite hard tissues of animal. Therefore the biocompatibility of coating is excellent.

3.4 Biocompatibility of RE-bioceramic coating on titanium cladded by laser

After the materials being implanted into dogs, it was found by macro-investigation that there were no infections in the implantation sections and the dogs were healthy after operation. After the specimens been removed, it was found that there was no tissue absorption or hyperplasia either.

Fifteen days after operation, there were predominately fibreforming connective tissues on the surface of Ti-based alloy, but fewer such tissues and high population of cells on the surface of bioceramic coating. Sixty days later, new bones directly grew on the surface of the coating and osteoclasts appeared on the coating surface, which implied that osteoclasts may be involved in the degrading process of bioceramic coatings. But there wasn't osteogenesis on the surface of the alloy. In Fig.3, the morphology of 180 d after operation was revealed. The coating surface contact with bone directly. However, the coating began degrading, it partly disappeared and some degraded particles were found surround soft tissue. After osteo-conversion, there weren't sections on the alloy surface directly contacting with bone[12].

Similarly, by means of implanting the material into dog muscle, the results demonstrate that no matter 15, 60 or 180 d later, the coating is covered with fibreform connective tissue, and there is not inflammation, tissue hyperplasia, necrosis or other repellent reactions. This proves the excellent biocompatibility of the material (Fig.4).

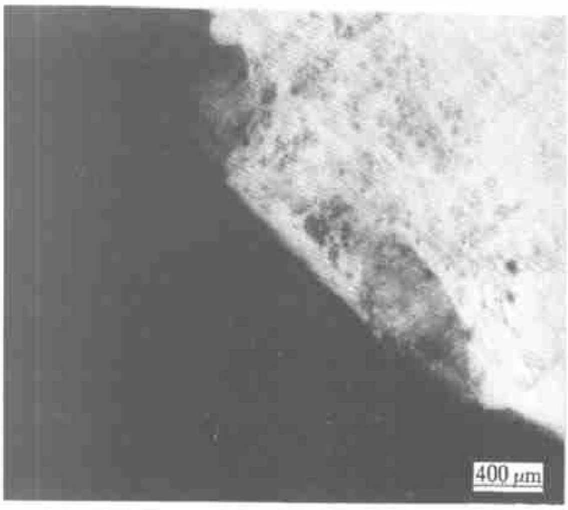

Fig.3 Morphology in bone after operation for 180 d

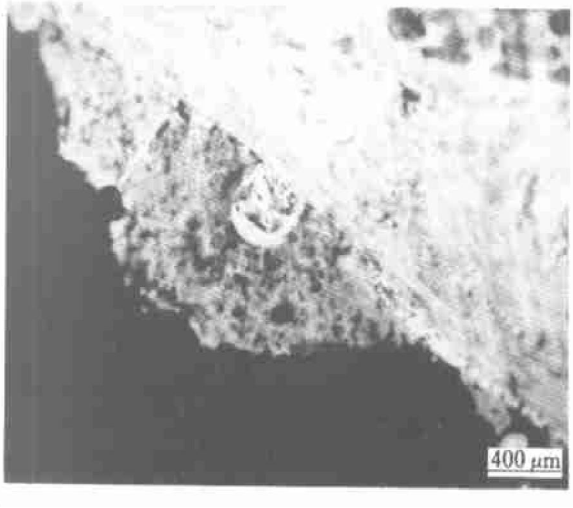

Fig.4 Morphology in muscle after operation for 180 d

4 CONCLUSIONS

1) By means of low heat flow density and high scanning speed laser beam, a Ca-P-based bioceramic coating containing HA and β-TCP can be synthesized and cladded simultaneously. The coating well bonds with the substrate. It is hard, strong and tough. So the match of implant with biological hard tissue is improved.

2) The studied material has no toxic side effect on muscle tissue, connective tissue and blood cell. The biocompatibility of the coating is good.

3) The coating is osteoconduct and doesn't affect the activity of osteoblast and osteoclast. But it would degrade by cells in vivo.

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(Edited by HUANG Jin-song)