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Preparation and Evaluation of Zn doped HAp Plasma Spray Biocombatible Coatings on Titanium

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Hydroxyapatite (HAp) is one of the most promising biomaterials because it is the main inorganic component of bones and other hard tissues. Recently, the preparation of Zn doped HAp has been carried out by many researchers mainly because Zn has been reported of having the stimulatory effect on the growth of bones (1-2). The development of Zn doped HAp plasma spray coating on titanium has been done successively by our group (3). After high temperature sintering, Zn was doped into the crystal structure of HAp for the mixture of 3wt% ZnO and HAp. However, the existence of ZnO was confirmed by X-ray diffraction for the mixture of 5wt% or 10wt% ZnO and HAp even after high temperature sintering. In this study, the condition of high temperature sintering for HAp with the addition of 5wt% ZnO was investigated. With the sintered Zn doped HAp, HAp plasma spray coating was applied on titanium substrate. The long-term credibility of Zn doped HAp plasma spray biocompatible coatings on titanium was evaluated by monitoring the changes in corrosion resistance with electrochemical impedance technique in physiological saline. The dissolution of Zn ion from Zn doped HAp was detected by ICP in physiological saline after a long-term immersion. The adhesion of Zn doped HAp plasma spray coatings to titanium substrate was evaluated by three-point bending test.

EXPERIMENT PROCEDURES

ZnO was used as Zn resource since it is considered to be more stable than metal Zn during the post plasma spray process. The powder of ZnO (5wt%) and HAp were mixed and sintered at 1150˚C for 5 hours. In order to be ready for plasma spraying, the sintered block of ZnO and HAp mixture was crashed into small particles by ball miller and screened into powder with a size about 75μm in diameter by sifter. 99.9% titanium was used as metallic substrate for Zn doped HAp plasma spray coatings in this study. Titanium rode samples and rectangular shape samples were used for long term credibility test and three-point bending test, respectively.

Zn doped HAp plasma spray coatings on titanium were prepared under air atmosphere condition. A Ti intermediate layer was applied on titanium substrate by plasma spray process for improving the adhesion of HAp coating to titanium substrate. Both Zn doped HAp top layer and Ti intermediate layer were prepared at a plasma spray current of 400A. Post heat treatments were conducted on all coating samples at 600˚C, Ar atmosphere for 1 hour.

Electrochemical impedance measurements have been carried out for evaluating the long-term credibility of Zn doped HAp plasma spray coatings. The changes in corrosion resistance was monitored by electrochemical impedance measurements in physiological saline at 40˚C for about three months. 3-electrode arrangement was used for electrochemical impedance measurements. Pt sheet and SSE (Ag/AgCl) were used as counter and reference electrode, respectively. A sinusoidal perturbation of 10mV was applied and the frequency was scanned from 10^{5}Hz to 10^{-2}Hz. The changes in corrosion potential were also recorded at the same time.

For evaluating the adhesion of Zn doped HAp plasma spray coatings on titanium substrate, three-point bending test was conducted. The ractangullar samples were set on a universal purpose mechanical tester with surface of Zn doped HAp coating layer downward..

The changes in composition of Zn added HAp powder after sintering and the changes in crystalinity of HAp coatings with post heat treatment were analyzed by X-ray diffraction. The surface morphology and cross section profile of plasma spray coating samples were observed by scanning electron microscope (SEM). The dissolution of ions such as Zn^{2+} and Ca^{2+} from Zn doped HAp coating was measured by ICP analysis.

RESULTS AND DISCUSSION

1. Preparation of Zn doped HAp poweder

In order to get all Zn^{2+} ions into HAp crystal structure, sintering conditions were changed from previous study. By increasing sintering time from 1h to 5 h, the ZnO peak disappeared on X-ray diffraction results. The EDX element analysis showed the existence of Zn in the sintered mixture powder. Therefore, it is concluded that a Zn doped HAp with the addition of 5wt% ZnO was successfully prepared.

2. Credibility of Zn doped HAp plasma coatings

Zn doped HAp plasma spray biocompatible coating on titanium has excellent corrosion resistance during long-term immersion in physiological saline. Also, the dissolution of Zn^{2+} ion from Zn doped HAp was detected by ICP analysis after the long-term immersion, meaning the possibility of having enhancing function on bone growth.

3. The adhesion of Zn doped HAp plasma coatings on Ti

From the results of three-point bending test, it was found that the adhesion of Zn doped HAp plasma spray coatings to titanium substrate was strong enough as a biocompatible coating.

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