

GD-OES Analysis of the Interface between Titanium and Hydroxyapatite Ceramics Produced by Hydrothermal Hot-pressing Method

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Solidification of hydroxyapatite (HA) and its bonding with titanium (Ti) was achieved simultaneously by using a hydrothermal hot-pressing method at the low temperature as low as 150°C. A mixture of calcium hydrogen phosphate dehydrate(DCPD) and calcium hydroxide was used as a starting powder material for solidifying HA. 3-point bending tests were conducted to obtain an estimate of the fracture toughness for the HA/Ti interface as well as for the HA ceramics only. The fracture toughness tests showed that the induced crack from the pre-crack tip deviated from the HA/Ti interface and propagated into the HA. The fracture toughness determined on the HA/Ti specimen was closed to that of the HA ceramics only ($K_{IC}=0.30 \text{ MPam}^{1/2}$).

Depth profile of the chemical composition determined by glow discharge optical emission spectroscopy (GD-OES) method indicated that the bonding of HA and Ti was achieved though the formation of a reaction layer at the HA/Ti interface. The thickness of the reaction layer was estimated to be approximately 1 μm . It seemed that this reaction layer provided the bonding HA/Ti for absorbing the misfit between HA and Ti.

Key words: Hydrothermal hot-pressing, Bonding, Diffusion

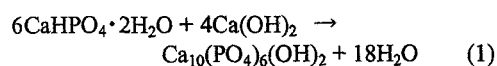
1. INTRODUCTION

Titanium (Ti) and its alloy are widely used as orthopedic and dental implant materials because of their high mechanical strength, low modulus and good corrosion resistance.¹ Traditionally, Ti and its alloys have been reported as bioinert. When embedded in the human body, a fibrous tissue capsules the implant isolating from the surrounding bone forms.

Some bioactive ceramics such as HA, bioglass and glass ceramics can directly bond to living bone when used as bone replacement materials.² HA ceramics are biomaterials which have been extensively developed recently.^{3,4} In the traditional method for solidifying HA, HA powder was sintered at high temperatures over 1000°C.⁵ The mechanical properties of bulk HA only allow applications for small non-loaded structure.⁶ The possibility of depositing it into films has permitted to exploit its bioactive properties in structural prostheses such as teeth root, hip, knee and shoulder joint replacement. Therefore, HA is also used as a coating material for those prostheses surface in order to prepare bioactive layers on titanium and its alloys.⁷ The HA surface improves the fixation of implants by the growth of bone into the coating, forming a mechanical interlock. A plasma spraying technique has been frequently employed for the coating process of HA.^{8,9} However, this high temperature method results in some of significant problems like a poor coating-substrate adherence¹⁰, lack of uniformity of the coating in terms of morphology and crystallinity^{11, 12}, that affect the long-term

performance and lifetime of the implants. Other techniques are also available such as: sintering, chemical vapor deposition, sol-gel deposition, ion implanting, laser deposition and electrochemical process like electrophoretic deposition, electrocrystallization and anode oxidation. Despite of all the investigations carried out, the produced coatings can suffer from at least one of the following problems: Lack of coating adherence to the substrate, poor structure integrity and non-stoichiometric composition of the coatings.¹³

HA is the most thermodynamically stable phase among the calcium phosphate compounds. Other calcium phosphate compounds are readily transformed into HA in the presence of some solutions at relatively low temperatures (below 100°C). The hydrothermal reaction of calcium hydrogen phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$; DCPD) to HA is relatively easy when it occurs in a solution.¹⁴⁻¹⁶ Moreover, the transformation into HA is accelerated by the supply of Ca^{2+} and PO_4^{3-} at the stoichiometric ratio of Ca/P=1.67 in HA. For example, the chemical reaction of DCPD and calcium hydroxide ($\text{Ca}(\text{OH})_2$) occurs in a liquid phase as follows:



This chemical reaction progresses at low temperatures (typically less than 80°C).¹⁷ The only products of the above reaction are HA and water.

Hydrothermal hot-pressing (HHP) method is a

possible processing route for producing a ceramic body at relatively low temperatures^{18, 19}. The compression of samples under hydrothermal conditions accelerates densification of inorganic materials. It is known that the water of crystallization in DCPD is slowly lost below 100°C. If the released water can be utilized as a reaction solvent during the HHP treatment, it is to be expected that the joining HA to metal can be achieved simultaneously under the hydrothermal condition, in addition to the synthesis and solidification of HA.²⁰

This paper describes a new technique of bonding HA ceramics and Ti by using the HHP method and the interface properties between HA ceramics and Ti.

2. EXPERIMENTAL PROCEDURES

2.1 Sample preparation

Firstly DCPD used as a starting powder was prepared by mixing 1.0M calcium nitrate solution ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; KANTO CHEMICAL CO., INC., 99.0%) and 1.0M diammonium hydrogen phosphate solution ($(\text{NH}_4)_2\text{HPO}_4$; KANTO CHEMICAL CO., INC., 98.5%). The mixing was carried out at a room temperature (approximately 20°C). In order to control the value of pH, acetic acid and ammonia solution were added fitly. The precipitate from the mixture was filtered and washed with deionized water and acetone. The washed filter cake was oven-dried at 50°C for 24h, and then the dried cake was ground to a powder.

A commercially available pure Ti rod, 20mm in diameter, was used as a bioinert material. The Ti rod was cut into disks with a thickness of 10mm. And the disks were cleaned in deionized water and acetone by using ultrasonic cleaner. Ti surfaces were treated by two different methods: the Ti surfaces were finished using 1500# emery paper. After emery paper finish, the titanium disks were washed by deionized water, and then dried in air. Synthetic DCPD and calcium hydroxide ($\text{Ca}(\text{OH})_2$; KANTO CHEMICAL CO., INC., 95.0%) were mixed in a mortar for 30min with a Ca/P ratio of 1.67. The powder mixture and Ti disks were placed into the middle of the autoclave simultaneously, as shown in Fig.1.

The autoclave which was made of stainless steel (SUS304) has a pistons-cylinder structure with an inside diameter of 20mm in this research. The pistons possess escape space for hydrothermal solution squeezed from the sample, and this space regulates the appropriate hydrothermal conditions in the sample. A grand packing made of polytetrafluoroethylene (PTFE) is fixed between a cast rod and a push rod, and it is deformed by pressure from the top and bottom to prevent leakage of the hydrothermal solutions.

A pressure of 40MPa was applied to the sample through the loading rods from the top and bottom at room temperature. The pressure was kept 40MPa automatically in all stage. After the loading the autoclave was heated up 150°C at heating rate of 10°C/min, and then the temperature was kept constant for 2hours. The autoclave was heated with a sheath-type heater. The initial axial pressure was kept at 40MPa at initial state of the HHP treatment. After the treatment, the autoclave was cooled to room temperature naturally, and the sample removed from the autoclave.

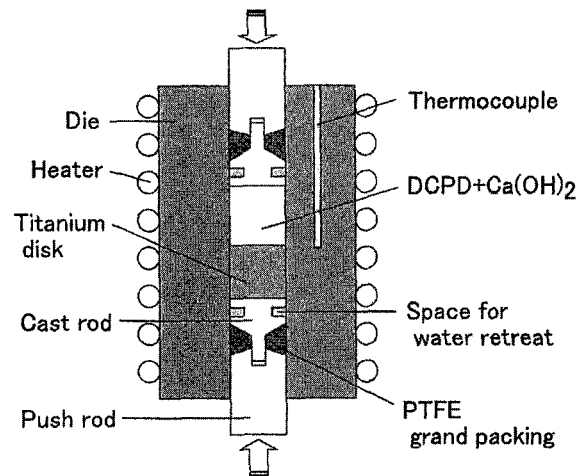


Fig.1 The schematic illustration of the autoclave for Hydrothermal Hot-Pressing(HHP).

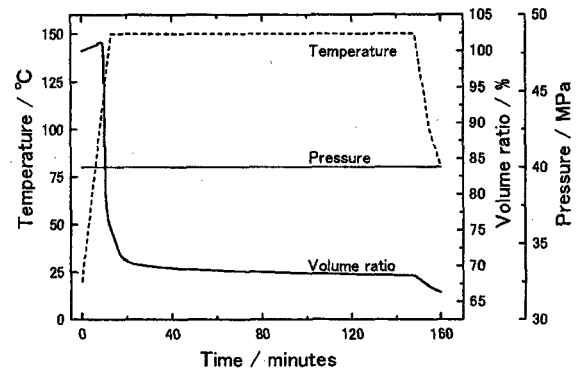


Fig.2 The indication of the temperature, shrinking behavior and pressure during HHP treatment.

The shrinkage behavior of the sample during the HHP treatment was monitored by measuring the relative movement between the two pistons using a displacement gage. The displacement data were used to determine the volume ratio V of the sample, defined as follows:

$$V = \frac{h_i - \Delta h}{h_i} \times 100 \quad (2)$$

where h_i is initial sample height, and Δh is the relative displacement during the heating process.

The typical example of temperature and pressure record is shown in Fig.2, along with volume ratio data. It is seen that the shrinkage started at approximately 90°C. This temperature is close to the dehydration temperature of DCPD. Thus, it is thought that the shrinkage is initiated by the dehydration of DCPD. The shrinkage rate became larger with the increasing temperature, and then the shrinkage rate became smaller. The shrinkage continued during the HHP treatment. The pressure was held at 40MPa constant for the whole period of HHP treatment.

2.2 Evaluation method

3-point bending tests were conducted to obtain an estimate of the fracture toughness for the HA/Ti interface. Core-based specimens were used for the fracture toughness tests and a pre-crack was introduced along the HA/Ti interface of the bonded specimens, following the ISRM suggested method²¹. The stress intensity factor K was used to evaluate of the bonding strength of the HA/Ti. The critical stress intensity factor is used in order to evaluate the fracture toughness for the HA/Ti interface. K is expressed as follows:

$$K = 0.25 \left(\frac{S}{D} \right) Y'_c \frac{F}{D^{1.5}} \quad (3)$$

where D is the diameter of the specimen 20mm, S is supporting span = $3.33D$, F is load, Y'_c is dimensionless stress intensity factor. The value of Y'_c is a function of the relative length, a/D . Y'_c was used to calculate the stress intensity factor²¹.

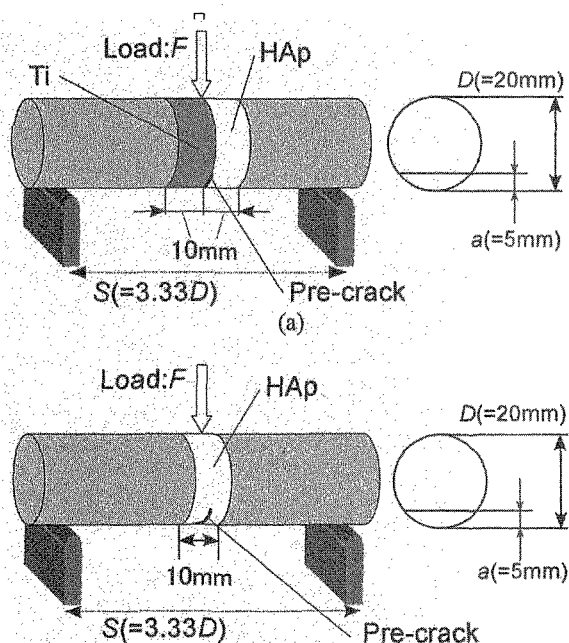


Fig.3 Schematic illustrations of 3-point bending test.

The configuration of the core-based specimen is shown in Fig.3(a) schematically. The steel-rods were attached to HA/Ti body using epoxy resin in order to prepare standard core specimens required for the ISRM suggested method. It should be mention here that the formula given in equation(3) is derived under the assumption of isotropic and uniformed materials. The jointed specimen used in this study for 3-point bending test composed 2 or 3 kinds of materials and is in a homogeneous beam. While exact anisotropic solution is needed for quantitative evaluation of the critical stress intensity factor, the isotropic solution in equation(3) is used to obtain and estimate of the fracture toughness for the HA and HA/Ti in this study. The specimens configurations shown in Fig.3 were used in order to examine the fracture behavior for the HA/Ti bonding body. The pre-crack was induced at the HA/Ti interface. The width of pre-crack

was less than 50 μ m. In case of 3-point bending tests specimens of HA ceramics only, a pre-crack was introduced in the center of HA ceramics as shown in Fig.3(b). The pre-crack was located the center position between two supporting points. The specimens were loaded until a fast fracture took place at a cross-head speed of 1mm/min.

2.3 Interface properties

In order to investigate the construction near the interface between HA ceramics and Ti disk, the bonding bodies were applied to analyses of glow discharge optical emission spectroscopy (GD-OES: JOBIN-YVON HORIBA, JY-500RF). It is known that GD-OES analysis have features include are relatively simple experimental setup without the ultra-high vacuum technology, virtually no sample preparation, high speed of the analysis and the ability to analyze quantitative depth profiles of minor elements, with applications to diffusion phenomena in thin films or bulk materials²².

3. RESULTS AND DISCUSSION

As demonstrated in Fig.4, the HA ceramics could be bonded to the Ti disks at the low temperature of 150 $^{\circ}$ C using the above-mentioned HHP treatment. X-ray diffraction analysis had showed that the DCPD and Ca(OH)₂ powder materials were completely transformed into HA by the HHP treatment already²⁰.

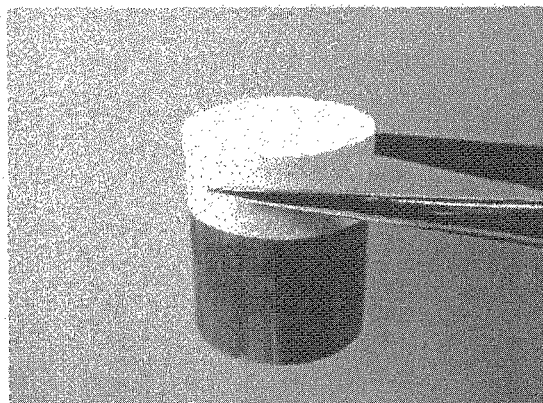


Fig.4 Photograph of the jointed body of HA ceramics and Ti.

Fig.5 shows a photograph of the fracture surface in the bonded HA/Ti body after 3-point bending test. It can be noted that the crack initiated from the pre-crack tip and propagated not along the HA/Ti interface, but into the HA. This observation suggests that the fracture toughness of the HA/Ti interface is close to or higher than that of the HA ceramics only. The critical stress intensity factor K_c was 0.30MPam^{1/2} for the HA ceramics, and 0.28MPam^{1/2} for the bonded HA/Ti. The toughness data are the average value obtained from at least five specimens. The K_c value for the bonded HA/Ti body gives a slightly lower value than that of the HA ceramics only. The difference in K_c data is potentially due to the residual stress induced by the thermal expansion mismatch between HA and Ti. The fracture appearance in Fig.5 may suggest that the interface toughness should be equal or higher than that of the HA ceramics only.

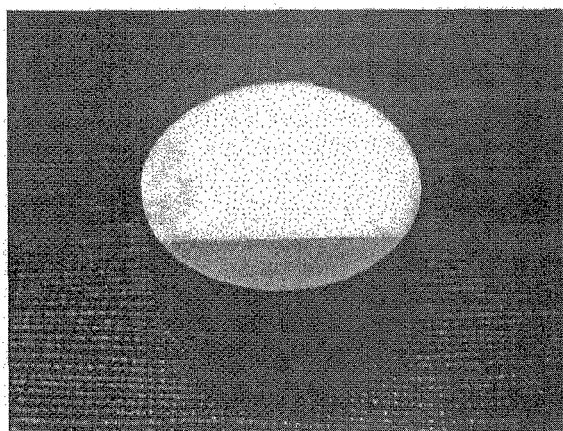


Fig.5 Photograph of fracture surface after 3-point bending test.

As shown in Fig.6, Depth profile of the chemical composition of Ti, Ca and O determined by GD-OES method indicated that the bonding of HA and Ti was achieved through the formation of a reaction layer at the HA/Ti interface. The thickness of the reaction layer was estimated to be approximately 1 μm . Moreover, it was shown the elements of Ti and Ca were exchanged alternatively in HA ceramics. It seemed that the reaction layer and diffusion provided the bonding HA/Ti for absorbing the misfit between HA and Ti.

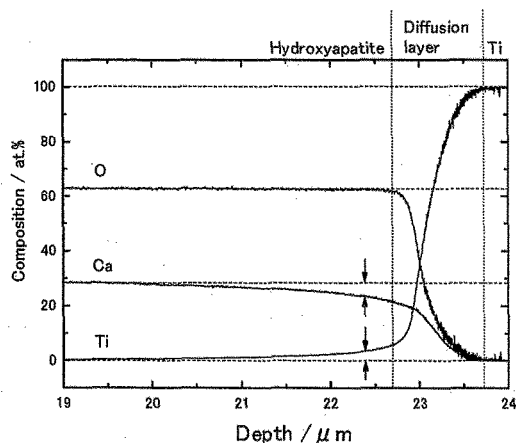


Fig.6 GD-OES analysis of the interface between the HA ceramics and Ti.

While further development is needed to improve the fracture property of the solidified HA, the HHP treatment may have the advantage over the plasma-spraying technique in the preparation of thermodynamically stable HA. The above results demonstrate the usefulness of the HHP method for bonding HA and Ti in order to produce a bioactive layer in biomaterials.

4. CONCLUSIONS

In this paper, it was demonstrated that HA could be bonded to Ti using a hydrothermal hot-pressing method at the low temperature of 150 °C. The fracture toughness tests conducted on the bonded HA/Ti body revealed that

the crack propagation from the pre-crack tip occurred not along the interface, but into the HA ceramics. The fracture toughness of the HA/Ti interface was also suggested to be close to or higher than that of the HA ceramics. This derived from the interface properties which HA and Ti changed the gradient within 1 μm and which Ti and Ca were exchanged alternatively in HA ceramics.

ACKNOWLEDGEMENTS

This study was supported in part by the Japan Ministry of Health, Labour and Welfare under Grants-in Aid for Research on Advanced Medical Technology. Author T.O. was supported by research fellowship of the Japan society for the promotion of science for young scientists. Thanks are due to Mr. T. Nakamura of Horiba Company, Tokyo, Japan, for provision of time on a JY-500RF GD-OES instrument.

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