

Novel Techniques of Hydroxyapatite Coating on Titanium Utilizing Hydrothermal Hot-pressing

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Solidification of hydroxyapatite (HA) and its coating on titanium (Ti) rod was achieved simultaneously by utilizing a hydrothermal hot-pressing (HHP) 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 HA coating. The powder mixture and Ti rod was placed in an autoclave for HHP treatment. Some Ti rods were treated with alkali solution before HHP treatment.

Pull-out tests were conducted to obtain an estimate of the interfacial property or the HA/Ti interface. The shear fracture strength obtained from the pull-out tests was approximately 3.0MPa. In post-test observations after fracture tests, HA ceramics remained on Ti rod. It could be demonstrated that the fracture occurred into the HA ceramics, not into the HA/Ti interface. Especially, the alkali solution treatment could improve the fracture properties of the interface between HA ceramics coating and Ti rod.

Key words: Alkali solution treatment, Pull out test

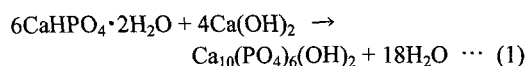
1. INTRODUCTION

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 hydroxyapatite (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 $\text{Ca/P}=1.67$ 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 coating HA ceramics to Ti by using the HHP method.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

A commercially available pure Ti rod (99.5%; Nilaco, Japan), 1.5mm in diameter, was used in this experiment. The Ti rod was cut into a length of approximately 18mm. The rods were cleaned in deionized water and acetone by using an ultrasonic cleaner. Ti surfaces were finished using 1500# emery paper. After the surface finish with emery paper, the titanium rods were washed again by deionized water, and then dried in air. Recently, it has been reported that if the Ti and its alloys surface is treated with sodium hydroxide (NaOH) solution it obtains the ability of joining HA directly by a biomimetic method.²¹ In order to investigate the effects of alkali solution treatment, the Ti rods were treated with alkali solution (5M NaOH). The conditions of a NaOH solution hydrothermal treatment were conducted at 150°C for 2h. After the hydrothermal treatments, the Ti rods were washed by deionized water, and then dried in air. 2 kinds of Ti rods were prepared, whether with the alkali solution treatment or without the treatment.

DCPD used as a starting powder was prepared by mixing 1.0M calcium nitrate solution (99.0%; $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KANTO CHEMICAL CO., INC., Japan) and 1.0M diammonium hydrogen phosphate solution (98.5%; $(\text{NH}_4)_2\text{HPO}_4$; KANTO CHEMICAL CO., INC., Japan). 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. 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. The synthetic DCPD and calcium hydroxide (95.0%; $\text{Ca}(\text{OH})_2$; KANTO CHEMICAL CO., INC., Japan) were mixed in a mortar for 30min with a Ca/P ratio of 1.67.

2.2 Autoclave for HHP treatment

The autoclave made of stainless steel (SUS304) has a pistons-cylinder structure with an inside diameter of 20mm, as shown in Fig.1. 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 of polytetrafluoroethylene (PTFE) is placed between a cast rod and push rod. The PTFE was used to prevent leakage of the hydrothermal solutions.

A pressure of 40MPa was applied to the sample through the push rods from the top and bottom at a room temperature. After the initial loading the autoclave was heated up to 150°C at heating rate of 10°C/min, and then the temperature was kept constant for 3hours. The

autoclave was heated with a sheath-type heater. The axial pressure was kept at 40MPa during the HHP treatment. After the HHP treatment, the autoclave was naturally cooled to a room temperature, and the sample

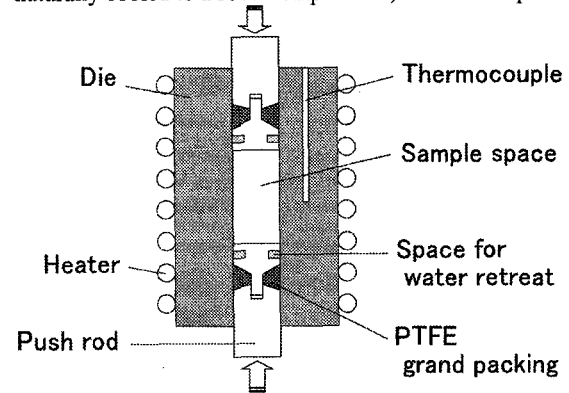


Fig.1 Schematic illustration of the autoclave for Hydrothermal Hot-pressing method

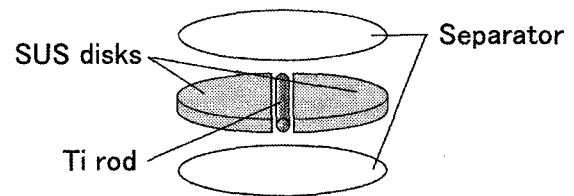


Fig.2 Schematic illustration of the configuration around the Ti rod.

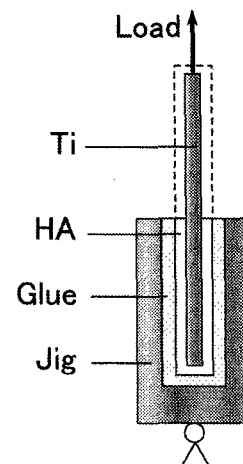


Fig.3 Schematic illustration of the pull out test in a cross section view.

removed from the autoclave.

A Ti rod and the powder mixture of DCPD and $\text{Ca}(\text{OH})_2$ were placed into the middle of the autoclave simultaneously. The configuration is shown in Fig.2. The mixed powder of DCPD and $\text{Ca}(\text{OH})_2$ were located between separators. The separators were made of PTFE membranes. A Ti rod was located between 2 pieces of stainless steel (SUS304) disks as shown in Fig.2. SUS disks which could not be bonded to HA ceramics by

HHP method were made semicircle shape in order to keep appropriate space for a Ti rod and the HA starting powder. Thickness of the SUS disks was 2mm. Upper and lower sides spaces of separators were filled with pressure media which was aluminum oxide powder (3.0 μ m; BUEHLER LTD., USA). The separators were used to reduce the mixing of aluminum oxide powder and HA starting powder.

2.3 Coating Strength evaluation

Pull out tests were conducted in order to evaluate bonding strength of the HA ceramics coating. The detail of pull out tests is drawn in Fig.3. The HA coated samples were fixed to the test jigs by epoxy resin (Araldite; CHIBA-GEIGY). And then the part of HA coating without attaching to the jig was removed with a knife and a grinder. The specimens were loaded at a cross-head speed of 0.5mm/min until the Ti rods were pulled out entirely. Fracture behaviors were observed and the stress-displacement curves were measured.

3. RESULTS AND DISCUSSION

As demonstrated in Fig.4, the HA ceramics could be coated to the all surface of Ti rods at the low temperature of 150 $^{\circ}$ C using the above-mentioned HHP treatment.

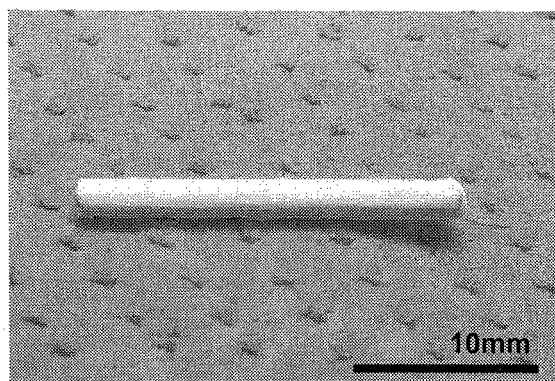


Fig.4 Photographs of the sample of HA coating on Ti rod.

Fig.5 shows photographs of the specimens after pull out tests. The left parts of the specimens were fixed onto the test jigs. The photograph of Fig.5(a) and (b) are the specimens without the alkali solution treatment and with treatment respectively. As shown in Fig.5(b), it can be seen that HA coating remains on the Ti rod in contrast with Fig.5(a). It can be noted that the fracture occurs not at the HA/Ti interface, but in 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.

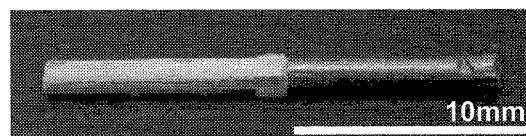
The load-displacement curves in pull out tests are shown in Fig.6(a) and (b) without the alkali solution treatment and with the treatment respectively. It is seen in Fig.6(a) that the load decreases approximately linearly after the peak as the displacement is increased. This observation in conjunction with Fig.5(a) suggest that the interface between the HA and Ti rod is held just by interfacial friction and no significant chemical bond is expected for the interface without the alkali solution

treatment.

On the other hand, the load-displacement curve of the specimen treated with the alkali solution, as shown in Fig.6(b), shows the different tendency where the load temporarily increases after the peak. The results of Fig.6(b) and fracture surface observation imply that there is a chemical bond between the HA and Ti rod. As described previously, the crack propagation took place in the HA, not along the interface. The deviation and kinking of the crack path from the interface may induce an additional frictional resistance to the crack propagation in the pull-out test. This may explain the second peak in the load-displacement curve shows in Fig.6(b).

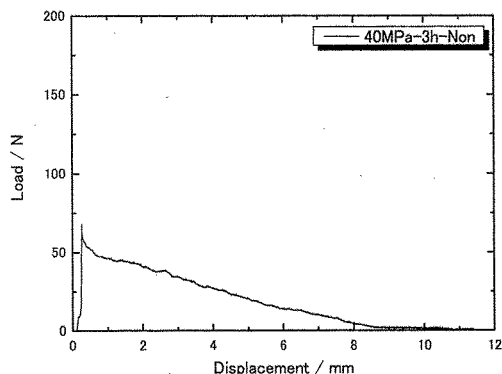


(a) Without the alkali solution treatment.

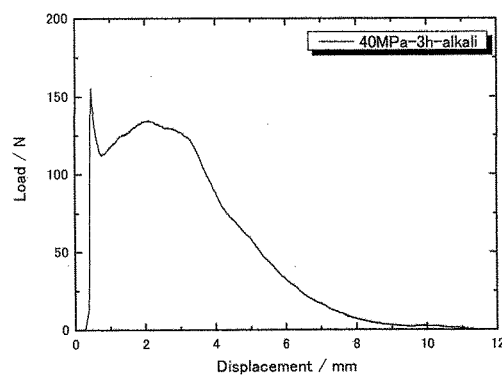


(b) With the alkali solution treatment.

Fig.5 photographs of the samples after pull out tests.



(a) Without the alkali solution treatment.



(b) With the alkali solution treatment.

Fig.6 The stress-displacement curves of pull out tests.

In order to evaluate the effects of the alkali solution treatment quantitatively, the shear strength and fracture energy were calculated from the results of pull out tests, and are plotted in Fig.7. The shear strength, τ is computed based on the following equation:

$$\tau = \frac{P_{\max}}{\pi dL} \quad \dots (2)$$

where d is the diameter of Ti rods (1.5mm), L is the fixed length of Ti rods, P is load, P_{\max} is the maximum value of P . τ is estimated to be 1.5MPa for the specimen without the alkali solution treatment and 3.0MPa for the treated specimen, respectively. The averaged shear strength over the embedment length L maybe taken as a fracture property of initiation. The alkali solution treatment improved the initiation resistance two times more than the non-treated condition. The fracture energy G is calculated using the following equation:

$$G = \frac{A}{\pi dL} \quad \left(A = \int_0^L P dx \right) \quad \dots (3)$$

where x is the displacement of cross-head. G is estimated 4.0Nmm^{-1} for the specimen without the alkali solution treatment and 11.9Nmm^{-1} for the treated specimen, respectively. It was shown three times improvement. It is seen that the alkali solution treatment on Ti rods allows us to improve the interfacial fracture property.

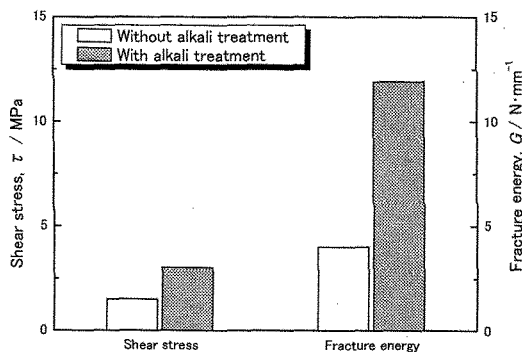


Fig.7 Shear fracture stress and fracture energy calculated from pull out tests.

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 coating HA on Ti in order to produce a bioactive layer in biomaterials.

4. CONCLUSIONS

In this paper, it was demonstrated that HA ceramics

could be coated to Ti rods using a hydrothermal hot-pressing method at the low temperature as well as 150°C . Especially for the sample treated with alkali solution, the pull out tests conducted on the HA coating sample revealed that fracture occurred not along the interface but in the HA ceramics. The fracture property of the HA/Ti interface was also suggested to be close to or higher than that of the HA ceramics. Investigation of the bonding mechanism and in vivo tests of the HA coating samples are in progress.

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