

approximately 1 μm diameter, with an incident power of 2mW.

Table1. Ti surfaces treated conditions with NaOH solution

	Temp.(°C)	Time(h)	600°CHeat
A	50	24	No
B	50	24	Yes
C	150	1	No

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 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 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.

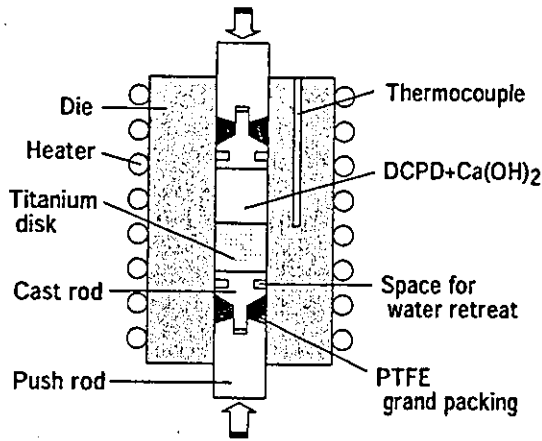


Fig.1 The schematic illustration of the autoclave for Hydrothermal Hot-Pressing(HHP).

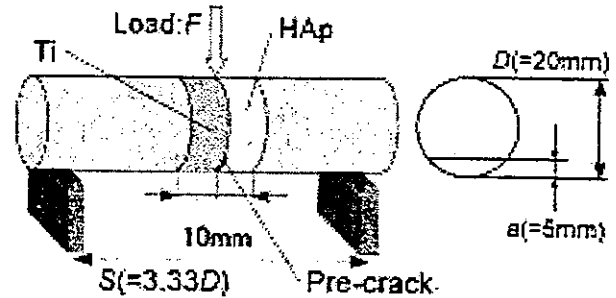


Fig.2 Schematic illustrations of 3-point bending test.

A pressure of 40MPa was initially applied to the sample through the loading rods from the top and bottom at room temperature. After the initial loading the autoclave was heated to 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. 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.

3-point bending tests were conducted to obtain an estimate of the fracture toughness for the HAp/Ti interface as well as for the HAp ceramics only. Core-based specimens were used for the fracture toughness tests and a pre-crack was introduced along the HAp/Ti interface of the bonded specimens. The stress intensity factor K was used to evaluate the bonding strength of the HAp/Ti. K is expressed as follows [8]:

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

where D is the diameter of the specimen (=20mm), S (= 3.33D) is supporting span, F is load, Y'_c is dimensionless stress intensity factor. The value of Y'_c can be found in Ref.[8] as a function of the relative length, a/D . The configuration of the core-based specimen is shown in Fig.2. The steel-rods were attached to HAp body and HAp/Ti body using epoxy resin in order to prepare standard core specimens.

Results and Discussion

After NaOH treatment, the Ti disks had colored surface in all condition. It seemed Ti disks had some kinds of reaction layers by NaOH solution treatment. In reference [7], the reaction layer produced by only immersion (condition: A) was so weak as to delaminate from Ti substrate easily. According to this structurally defects, the Ti disks were needed the heat treatment at 600°C after the immersion (condition: B). While the reaction layer of condition: C had strong structure in spite of only immersion. From these results, it could be said that using NaOH solvo-thermal reaction on Ti surface treatment had the advantage in the view point of reducing the processing procedures.

SEM images of Ti surface treated with the condition of B and C were shown in Fig.3 and Fig.4 respectively. The difference between the treatment conditions could be found. The surface in Fig.4 was looked like a sponge. On the other hand, the surface in Fig.5 is looked like flowers.

The results of Raman spectroscopy analysis were shown in Fig.5 and Fig.6 respectively to characterize these reaction layers. The result of no treatment Ti surface put in Fig.5 in order to compare by Ti surface of no treatment. In the reaction layer of the condition B, the peaks could be found of rutile and a little narium titanate. In the condition C, the peaks could be found of anatase, rutile and natrium titanate.

The samples processing conditions is shown in Fig.7. HAp/Ti bonding bodies were achieved in all conditions of NaOH treatments. HAp/Ti interface toughness data obtained from 3-point bending tests. In terms of presenting K_{IC} , The data given in Table2 are average value obtained from at least five specimens. In case of A and B conditions, the interface toughness was slightly lower than the value of no treatment [6]. The interface toughness data of condition: C was higher than that of no treatment [6]. From these results, NaOH treatments on Ti surface were useful in obtaining HAp/Ti bonding body. Especially, NaOH solvo-thermal treatment on Ti surface could be enhanced the HAp/Ti interface toughness.

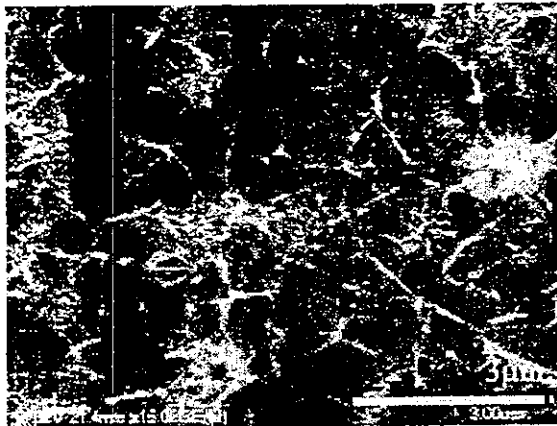


Fig.3 SEM image of Ti surface treated in NaOH (condition: B).

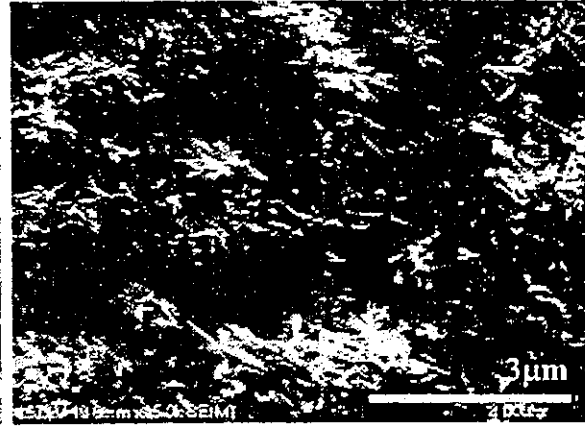


Fig.4 SEM image of Ti surface treated in NaOH (condition: C).

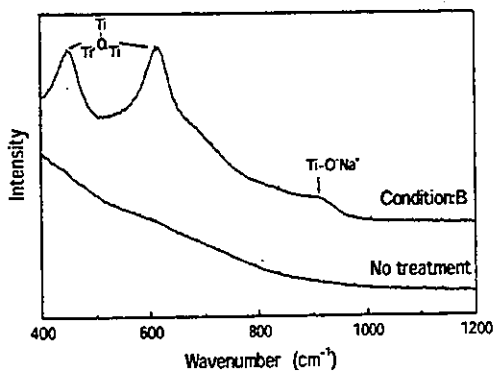


Fig.5 FT-Raman spectroscopy analysis of Ti surface (condition: B).

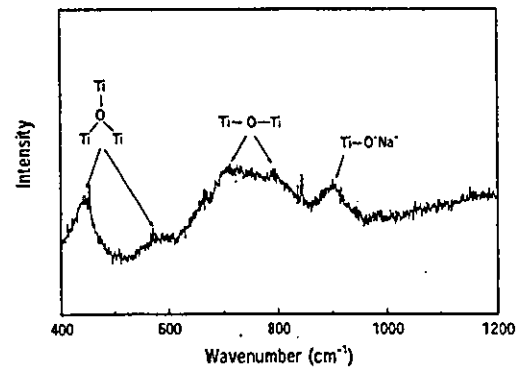


Fig.6 FT-Raman spectroscopy analysis of Ti surface (condition: C).

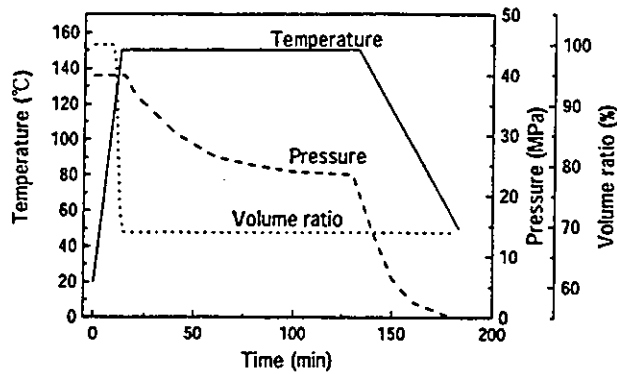


Fig.7 The indication of the temperature, shrinking behavior and pressure during HHP treatment.

Table2. Critical stress intensity factor K_{Ic} (MPam^{1/2})

	A	B	C	No treatment
K_{Ic}	0.22	0.21	0.35	0.25

The reaction layers were made on Ti surface in order to improve the joining properties of HAp/Ti by NaOH solution treatments. The properties of the reaction layers were not uniformity, depended on treatment conditions. It is needed appropriate treatment conditions should be found in order to enhance fracture toughness of HAp/Ti interface. Investigation of NaOH treatment condition and analysis of the reaction layer toward depth are in progress.

Conclusions

NaOH solvo-thermal treatment on Ti surface was very effective to bonding strength of hydroxyapatite and titanium. HAp/Ti interface fracture toughness could be enhanced with NaOH solvo-thermal treatment on Ti surface.

Acknowledgement

T.O. was supported by Research fellowship of the Japan Society for the Promotion of Science for Young Scientists.

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骨置換材料のための水熱ホットプレス法による ハイドロキシアパタイトセラミックス-チタン接合体の作製

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Bonding hydroxyapatite ceramics and titanium by hydrothermal
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Key words: Hydrothermal hot-pressing method (水熱ホットプレス法),
Hydroxyapatite (ハイドロキシアパタイト),
Titanium (チタン), Bonding strength (接合強度),
Diffusion zone (拡散構造)

Solidification of hydroxyapatite (HA) and its bonding with titanium (Ti) was achieved simultaneously by using a hydrothermal hot-pressing method at temperatures as low as 150°C. A mixture of calcium hydrogen phosphate dihydrate 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 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 .

目 的

ハイドロキシアパタイト: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
(以下 HA と省略)は生体骨の主な無機成分であり、骨と直接的に結合する¹⁾。よって HA セラミックスは生体活性セラミックスと呼ばれ、骨

修復材料として用いられているが、HA セラミックス単体では機械強度が不足しており、大腿骨など大きな荷重の加わる部位には使用できない。一方、Ti 系金属材料は高い生体適合性を有する金属材料であり骨置換材料として用いら

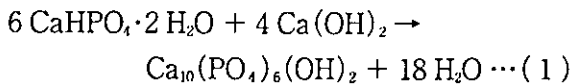
れているが、骨との直接的な結合は期待できない。そこでTi系材料にHAをプラズマ溶射コーティングしたものが人工関節、人工歯根に使用されている。しかしながら、溶射によるHAコーティング層は基板金属に本質的には接合しておらずHA/Ti界面強度が不足していること、また超高温プロセスであることによるHAの熱分解等が指摘されており、これら問題の解決が望まれている。

本報においては、水熱ホットプレス法（以下HHP法と省略）による新たなHAセラミックスとTiの接合法を報告するとともに、その接合強度と界面構造について検討を行った。

方 法

本研究において、HA/Ti接合体を作製するにあたり、HHP法を用いて、式(1)の化学反応を利用してHAを合成・固化し、同時にTiとの接合を試みた。

HHP法とは自然界に存在する堆積岩の生成過程であると言われている溶解および沈積現象を実験室レベルで模擬し、加熱および加圧することでこれらの現象を人工的に短時間で再現し、固体粉末から岩石のような強固な固化体つまりセラミックスを作製する意図のもとに開発された方法である²⁾。



出発原料はリン酸水素カルシウム二水和物($\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$: KANTO CHEMICAL CO., INC. 鹿1級・純度98.0%)と水酸化カルシウム($\text{Ca}(\text{OH})_2$: KANTO CHEMICAL CO., INC. 鹿1級・純度95.0%)をHAの化学量論組成である $\text{Ca}/\text{P}=1.67$ となるように秤量し、乳鉢で30分混合した。Hosoi et al. は、この式(1)の反応を用い、リン酸水素カルシウム二水和物(DCPD)と水酸化カルシウム($\text{Ca}(\text{OH})_2$)とを Ca/P 比が1.67になるように調整した混合粉を

オートクレーブ内に装填し、圧力40 MPaに保持し、150℃にて水熱ホットプレス処理することにより、HAを固化させることに成功している³⁾。この反応の特徴は、DCPDの結晶水が約65℃で解離を始めるため、この解離した結晶水を水熱反応溶媒に利用することにある⁴⁾。このため本法では通常水熱反応処理において必要とされる水は添加されておらず、見かけ上ドライパウダーの焼結手順と同じであるが現実には機械的圧縮効果に加えて水熱反応を活用する方法である。本研究で目的としているHAと金属の接合においても水を添加せず、DCPDから解離する結晶水を利用するものとする。これにより150℃の低温でHAセラミックスが得られる。

HAに接合させる金属材料は工業用純Ti(純度99.5%)であり、直径20mm、高さ10mmの円柱状に切り出し、表面を1500番まで耐水研磨紙で仕上げた後純水およびアセトンで超音波洗浄を行った。これを出発原料とともにオートクレーブ中(図1)に配置しHHP処理を行った。

HHP法による固化・接合体作製条件については、圧力40 MPaを維持し、昇温速度10℃/min.で150℃に達した後この温度を2h保持した。詳しい固化体作製状況を図2にまとめた。HA固化体の体積収縮についてはオートクレーブのピストン部分の移動距離 Δh を計測することによ

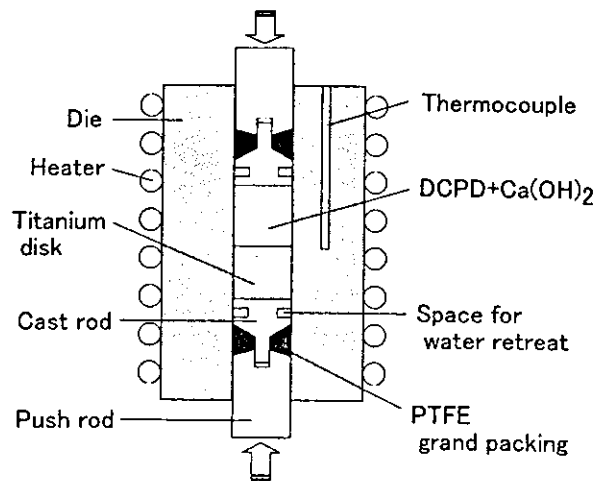


図1 水熱ホットプレス法のオートクレーブ概略図

り、HA 固化体の体積収縮率 V (%) を算出した。 V は昇温開始時の出発原料の高さを h_i と Δh から、以下の式 (2) で算出した。

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

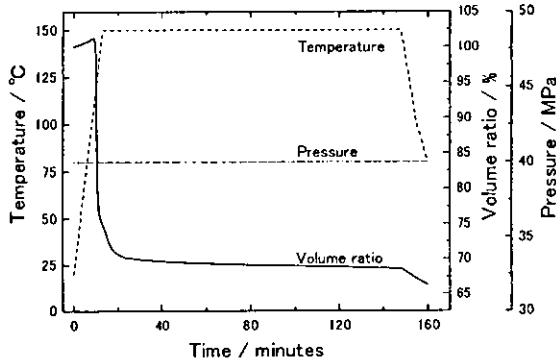


図2 試験片作製条件

HHP 法にて作製された HA / Ti 接合体の界面接合強度は、室温にて一軸引張および3点曲げ試験による破壊靱性を求めることにより応力拡大係数 K ($\text{MPam}^{1/2}$) に基づき評価した。

引張試験においては、ユニバーサルジョイントを使用することで、材料にかかるねじり等の効果を低減した。

3点曲げ試験片の模式図を図3に示す。これは典型的な脆性材料である岩石の破壊試験規格である ISRM 規格を応用した試験片である⁵⁾。予き裂が HA / Ti 界面に導入されている。 K は式(3)により算出される。 Y'_c は無次元応力拡大係数、 F は荷重、 S はスパン長、 D は試験片直径である。破壊靱性値すなわち限界応力拡大係数 K_k は式(3)の荷重に破断時の荷重を代入することにより求めた。

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

また得られた HA / Ti 接合体について界面部分の元素組成を詳しく調査するため、HA 表面から Ti 方向に向かってマーカス型高周波グロー放電発光表面分析装置 (HORIBA JY-500 RF:GD-OES) による深さ方向への元素組成分析を行った。

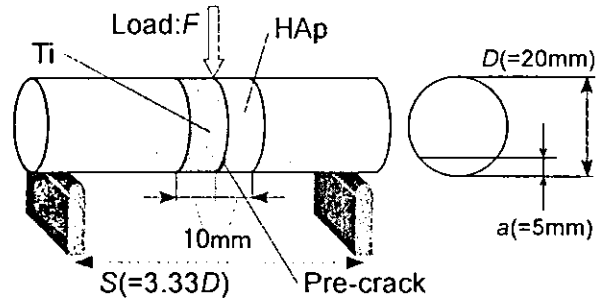


図3 3点曲げ試験片の概略図

結果

本研究で用いた HHP 処理条件により、HA セラミックスと Ti バルク体との接合体を作製することができた。得られた HA / Ti 接合体の写真を図4に示す。水熱反応を利用することにより、150°C という比較的マイルドな温度条件で HA セラミックスと Ti を接合できることがわかる。

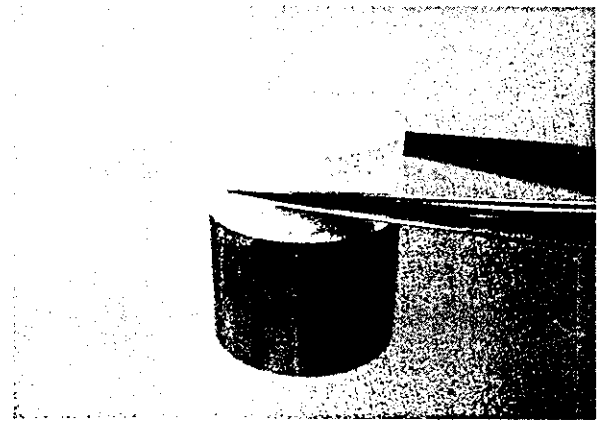


図4 得られた HA / Ti 接合体

一般にセラミックス/金属接合体において界面強度試験を行うとセラミックス/金属界面が破壊のサイトとなることが多いが、本報で作製された HA / Ti 接合体の引張試験における破壊サイトは、HA / Ti 界面ではなく HA 中であった。図5に引張試験後の試験片の写真を示す。引張における破断時の応力は約 10 MPa であった。これは5本の試験片の平均値であり、全ての試験片において図5に見られるように HA セラミックス中で破断しているのが観察された。

そこでより正確に界面強度を評価するため

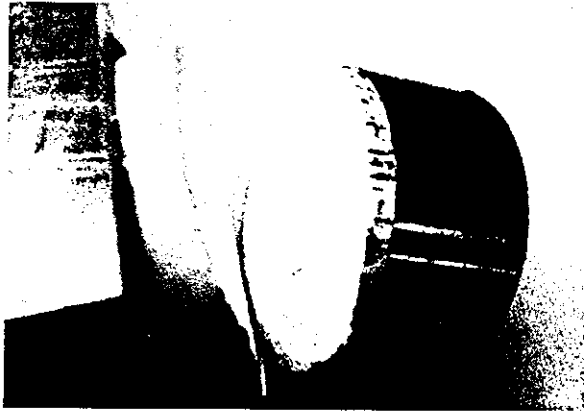


図5 引張試験後の破面

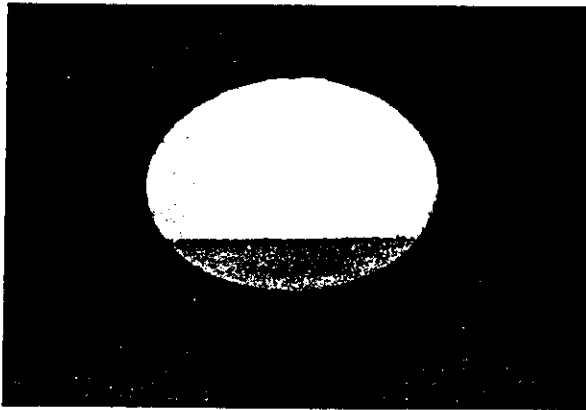


図6 3点曲げ試験後の破面

に、界面に予き裂を導入した3点曲げ試験を行ったが、図6に見られるように、引張と同様HA中で破壊し、Ti上にHAが多く付着・残留していることが確認された。

3点曲げ試験結果から導出される破壊靱性値 K_{Ic} の値は $K_{Ic} = 0.30 \text{ MPam}^{1/2}$ であった。

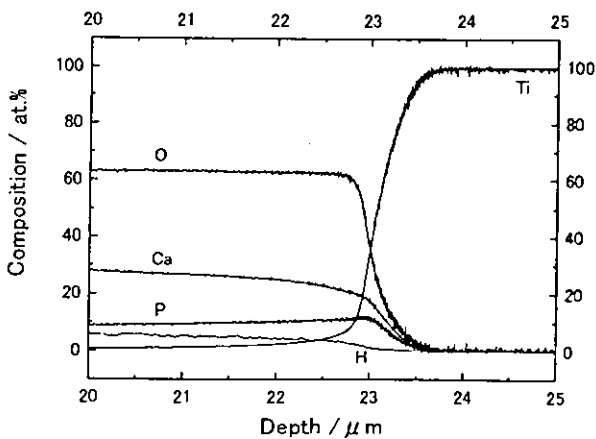


図7 HA/Ti界面の元素分析結果

GD-OESによる深さ方向への元素組成分析を行った結果を図7に示す。これによれば、HA/Ti界面近傍での $1 \mu\text{m}$ 程度の範囲にわたり、TiとHAの構成元素であるCa, P, O, Hの質量比が変化している拡散層が観察され、反応層がHA/Ti界面に形成されていることが示唆される。

考 察

DCPDと水酸化カルシウムの混合粉末をHAの出発原料としHHP法を用いることで、 150°C の低温でのHAセラミックスとTiとを強固に接合させることが可能であることがわかった。接合強度評価のための引張および3点曲げ試験において、き裂進展経路はHA/Ti界面ではなくHAセラミックス中であることから、HHP法により接合されたHA/Ti界面の破壊靱性はHHP法により作製されたHAセラミックスと同等ないしそれ以上であると思われる。具体的にはHA/Ti界面強度を破壊靱性値で評価すると $K_{Ic} = 0.30 \text{ MPam}^{1/2}$ 以上であると見積もられる。というのは、この値はき裂がHAセラミックスを進展したときの値であるため、HA/Ti界面の破壊靱性はこれよりも大きいことが予想されるためである。また引張3点曲げいずれの試験においてもHAセラミックス中で破壊したことから、異なる材料負荷モード、初期欠陥の有無にかかわらずHAセラミックス中で破壊することからも、HA/Ti界面の破壊靱性はHAセラミックスよりも大きいことが示唆される。

HHP法によるHA/Ti接合は、水熱環境下における化学反応によるHAセラミックス生成とTi表面の不働体被膜形成とが同時に起き、また圧縮がかかることでTiとHAの構成元素であるCa, P, O, Hの拡散層が形成されるものと推察され、これがHA/Ti接合に大きく寄与しているものと考えられる。

ま と め

1. 水熱ホットプレス (HHP) 法を用いることでハイドロキシアパタイト (HA) セラミックスとチタン (Ti) バルク体との接合体を作製することができた。その温度は150℃, 圧力 40 MPa, 反応時間は 2 h であった。
2. HHP 法により作製された接合体の HA/Ti 界面破壊靱性は HA セラミック ($K_{Ic} = 0.30 \text{ MPam}^{1/2}$) と同等ないしそれ以上である。
3. HA/Ti 界面近傍の約 $1 \mu\text{m}$ にわたる領域に構成元素比の変化する拡散層の存在を見出し, 水熱ホットプレス法による HA/Ti 接合は反応層の形成によるものであることが示唆された。

謝 辞

本研究の一部は, 厚生労働省科学研究費補助金萌芽的研究先端医療技術推進事業 (H14-ナノ-021) ならびに日本学術振興会特別研究員事業の助成によるものである。関係者各位に謝意を表す。

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Role of NH_4^+ on the formation of hydroxyapatite ceramics with lamellar structure by hydrothermal hot-pressing

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Key words : Hydroxyapatite, Lamellar structure, Hydrothermal hot pressing

Hydroxyapatite ceramics was prepared by hydrothermal hot-pressing from octacalcium phosphate. Various solvents were added to octacalcium phosphate powder and then treated by hydrothermal hot-pressing at 300°C, 40 MPa for 2 hours. The effects of the solvent were investigated. When the solvent contained NH_4^+ and pH value was greater than 7, the hydroxyapatite ceramics with lamellar structure could be obtained. The degree of hydroxyapatite crystals alignment became higher with the increasing NH_4^+ concentration. The bending strength became larger with the increasing degree of hydroxyapatite crystals alignment. The maximum bending strength reached approximately 70 MPa.

1. Introduction

One of the most important requirements for artificial implants is biocompatibility, viz. acceptance to the tissue surface. Hydroxyapatite (HAp) has excellent biocompatibility with tissue because it is the main inorganic part of the hard tissue. Thus, HAp ceramics is regarded as one of the most suitable biocompatible materials for replacement implants¹⁾.

The conventional method for preparing HAp ceramics is a sintering technique where high temperature (1000-1500°C) is commonly used. However, the biocompatibility of HAp may decrease due to high temperature treatments²⁾. Thus, a low temperature technique may be more appropriate to prevent or alleviate the decrease of biocompatibility. One of the issues in the application of conventional HAp ceramics is their fracture property is poorer than human bones^{3,4)}.

The formation of lamellar structures is expected to improve the fracture strength of

the material, as observed, for example, in shells. In fact, human bones also have a lamellar structure and its HAp crystals are composed of slender needles 200-400 Å long by 15-30 Å thick in collagen fiber matrix, and these fibrils are arranged into lamellar sheets. The structure of human bones provides the excellent mechanical property. For example, their bending strength is in the range of 50-150 MPa. In this study, a hydrothermal hot-pressing (HHP) method is employed to prepare HAp ceramics from octacalcium phosphate (OCP), and the effect of different solvents on the texture of the HAp ceramics is examined with the objective of forming a lamellar structure in the HAp ceramics.

2. Experimental procedure

2.1 Preparation of HAp ceramics

The starting powder material, OCP was prepared by hydrolysis of $\alpha\text{-Ca}_3\text{PO}_4$ in a mixture solution of CH_3COONa , CH_3COOH , and water

with $\text{pH}=4.7$ at 70°C for $6\text{ h}^{5)}$. The precipitation was filtered and washed by ion-exchanged water, and then dried at 50°C . Schematic of the apparatus used for hydrothermal hot-pressing is shown in Fig. 1. The inner diameter of the cylindrical reaction chamber was 20 mm . Different solvents were used to prepare HAp ceramics from the OCP. The pH and concentration of NH_4^+ in each solvent are shown in Table 1, along with the sample No. The OCP powder (5 g) was placed into the middle portion of the reaction chamber, as shown in Fig. 1. Then, solvent (0.5 g) was added to the OCP powder. A pressure of 40 MPa was applied to the sample through the loading rods from the top and bottom. While keeping the applied pressure, the sample was heated to 300°C at a rate of $10^\circ\text{C}/\text{min}$, and then the temperature was kept constant for 2 h , followed by natural cooling down to room temperature.

2.2 Determination of the HAp crystal alignment

X-ray diffraction (XRD) analyses were conducted employing $\text{CuK}\alpha$ at 40 kV and 40 mA , in order to examine the phase and texture of the solidified bodies by the HHP method. The XRD analyses were made by using two mutually orthogonal planes: the plane parallel with the applied load direction (hereafter, designated by plane (a)), and the plane normal to the applied load direction (designated by plane (b)). The degree of the crystal alignment is estimated by the following parameter:

$$\eta = \frac{I_{(002)}^a}{I_{(300)}^a} \frac{I_{(300)}^b}{I_{(002)}^b} \quad (1)$$

where $I_{(002)}^a$ and $I_{(300)}^a$ are the intensity of (002) and (300) reflections on plane (a), respectively. $I_{(002)}^b$ and $I_{(300)}^b$ are the intensity of (002) and (300) reflections on plane (b), respectively. In this

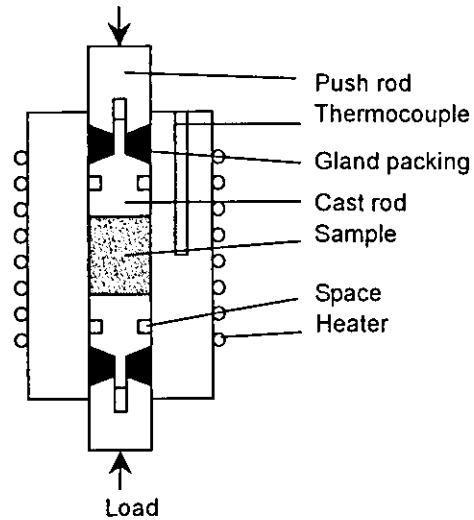


Fig. 1 Schematic of the apparatus used for HHP process

Table 1 Solvents used for HHP process

Sample No.	Solvent	pH	NH_4^+ concentration (mol/l)
S 1	$\text{CH}_3\text{COONH}_4$	4	3.42
S 2	$\text{C}_6\text{H}_5(\text{COOK})(\text{COOH})$	4	0
S 3	H_2O	7	0
S 4	$\text{Na}_2\text{BO}_3\text{O}_7$	9	0
S 5	$\text{NH}_4\text{HCO}_3 + \text{NH}_3\text{H}_2\text{O}$	9	3.49
S 6	$\text{NH}_4\text{HCO}_3 + \text{NaOH}$	10	2.32
S 7	$\text{NH}_3\text{H}_2\text{O}$	10	0.00075
S 8	$\text{NH}_3\text{H}_2\text{O}$	14	16.59

study, the XRD parameter η defined by the above equation is used to obtain a measure of the degree of crystal alignment in the solidified bodies.

2.3 Determination of the bending strength

The bending strength was measured by conducting 3-point-bending tests (Fig. 2). The dimensions of the specimens were 3.1 mm width, 4.8 mm height, and $16\sim 18\text{ mm}$ length, respectively. Stainless steel blocks (30 mm long) were attached to both ends of the HAp ceramics prepared by HHP process, using epoxy resin, in order to prepare a standard bending specimen.

The load was applied to the specimen so that the load direction was parallel to the axial load used for the HHP process. The specimens were loaded to complete failure at a constant crosshead speed of 0.5mm/min. The bending strength was calculated by using the following equation :

$$\sigma = \frac{3PL}{2bh^2} \quad (2)$$

where P is the load, L (=50mm) span, b (=3.1 mm) and h (=4.8mm) the width and height of the specimen, respectively.

The fracture surface was observed by a scanning electron microscope (SEM).

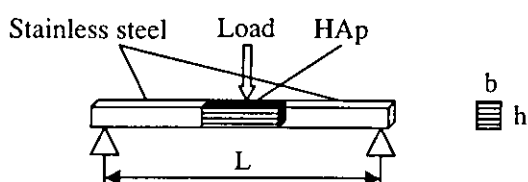


Fig. 2 Schematic of the 3-point-bending test

3. Results and Discussion

The XRD patterns of the solidified bodies are shown in Fig. 3. The results obtained on planes (a) and (b) are shown for each sample. The majority of the peaks are those of HAp, whereas the peaks underlined in the figure correspond to CaHPO_4 . It is seen that the primary phase of the solidified bodies is HAp. The XRD patterns of the samples, which are processed with the solvents containing no NH_4^+ ion (samples : S2, S3, and S4), is similar for the orthogonal planes, regardless of the orientations with respect to the applied load direction. However, it is noted that the NH_4^+ -containing solvents (samples : S5, S6, S7, S8) produce a marked different XRD pattern for the orthogonal planes, when the pH value is greater than 7. When the NH_4^+ concentration is increased, on plane (a), the relative intensity of the peak (002) becomes larger while the peak (300) decreases.

The results show that the HAp crystalline produced by the HHP process with the NH_4^+ -containing solvents has an anisotropic structure : the c crystal axis of the HAp is normal to the applied load. The XRD parameter η is plotted as a function of the NH_4^+ concentration in Fig. 4. It is clearly shown that the degree of the aligned c crystal axis tends to be higher with the increasing NH_4^+ concentration. It should be noted that when the pH value is less than 7 (sample S1), no anisotropic feature appears in the XRD pattern.

SEM observations of the fracture surfaces (Fig. 5) show that the orientation of HAp grains is random when the solvents include no NH_4^+ ion (sample S2, S3, S4). However, the samples prepared with high concentration of NH_4^+ ion exhibit a lamellar structure. These observations are consistent with the XRD patterns described above. Thus, NH_4^+ plays an important role in the formation of HAp ceramics with the lamellar structure.

The bending strength of the samples is plotted in Fig. 6, as a function of the XRD parameter η . It is demonstrated that the bending strength becomes larger with the increasing η . This result indicates that the formation of the lamellar structure is useful to improve the fracture strength of HAp ceramics. The maximum bending strength achieved by the HHP process reaches approximately 70 MPa.

4. Summary

A lamellar structure of HAp ceramics can be produced using OCP powder as a starting material and NH_4^+ -containing solvents with the hydrothermal hot-pressing technique. The lamellar structure is formed by stacking HAp thin layers. The formation of the lamellar structure enhances the fracture strength of HAp ceramics.

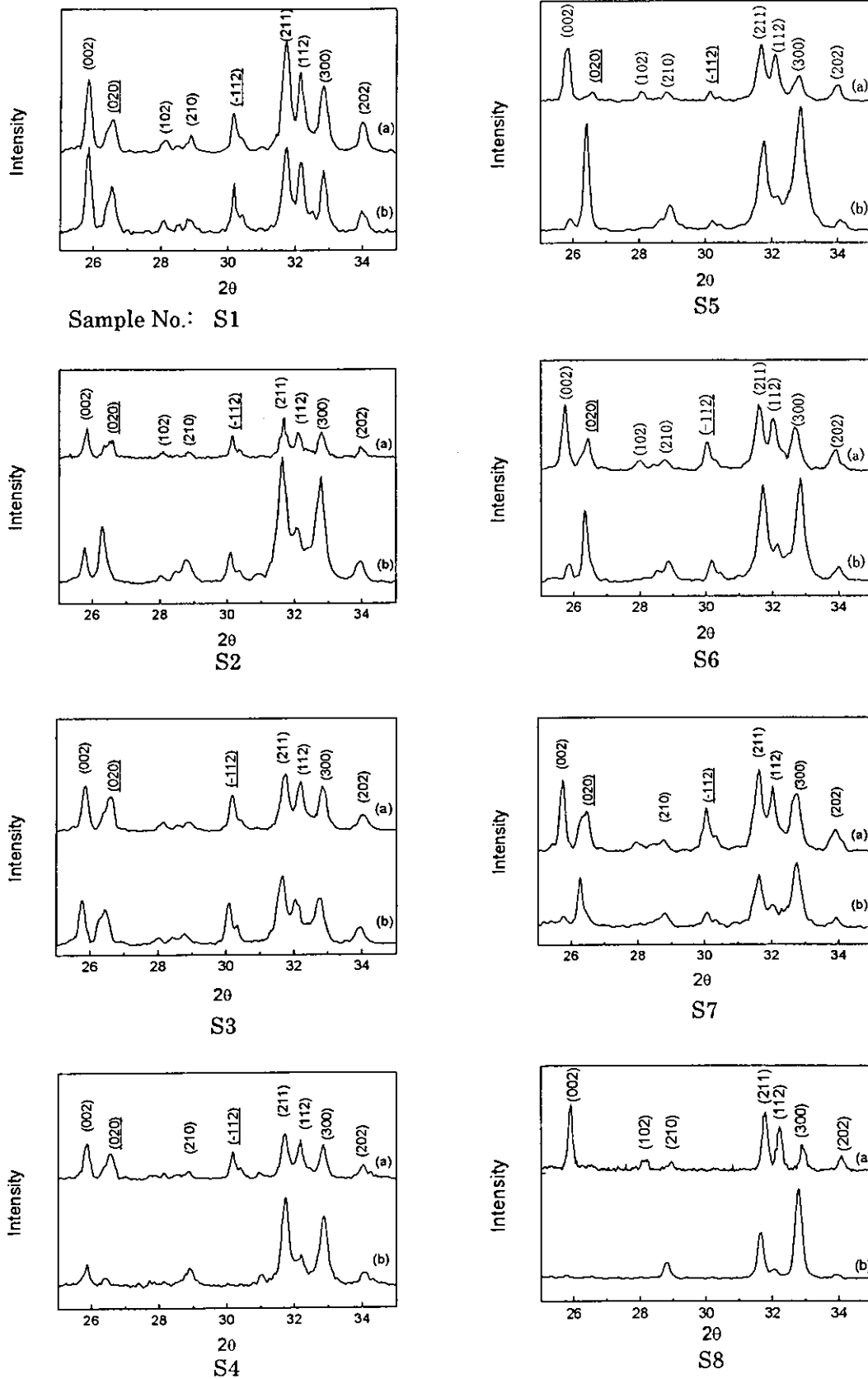


Fig. 3 XRD patterns on plane (a) (parallel with the applied load direction) and, plane (b) (normal to the applied load direction). The peaks are HAp, except the underlined cryptographic plane which correspond to CaHPO₄

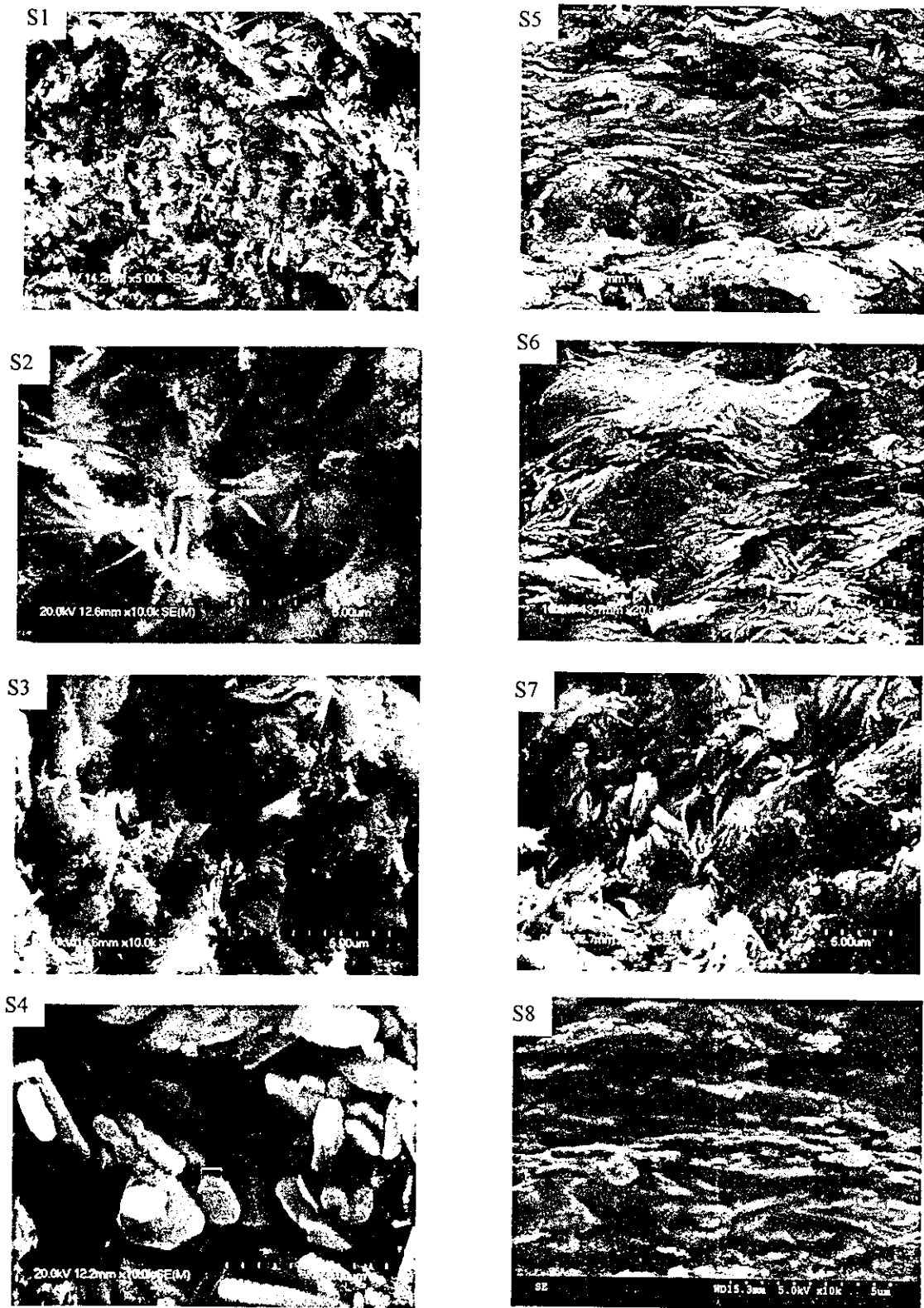


Fig. 5 SEM of the fracture surfaces

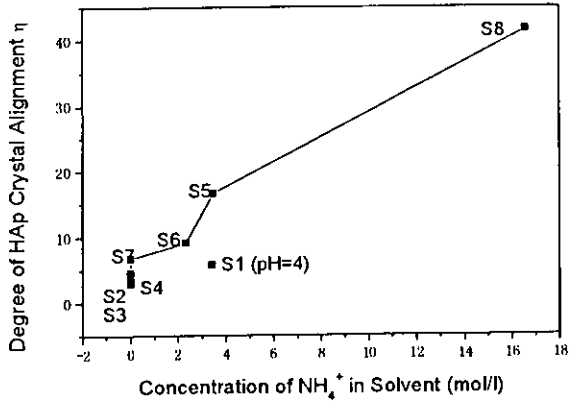


Fig. 4 Relationship between the degree of HAp crystal alignment (η) and NH_4^+ concentration

Acknowledgements

This study was supported in part by the Japan Ministry of Health, Labor and Welfare under Grants-in Aid for Research on Advanced Medical Technology.

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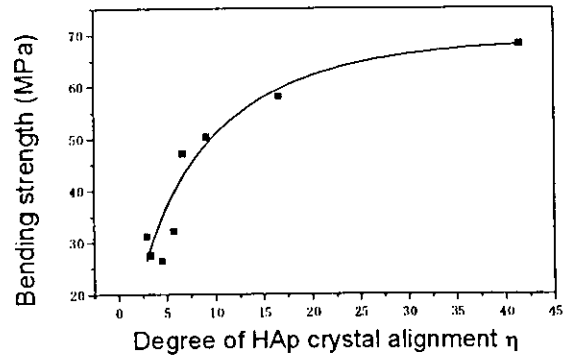


Fig. 6 Relationship between the bending strength and η

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和文抄録

水熱ホットプレス法による層状構造を有するハイドロキシアパタイトセラミックスの作成と NH_4^+ イオンの役割

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Key words: ハイドロキシアパタイト, 層状構造, 水熱ホットプレス

本研究は、リン酸八カルシウム (OCP) を出発原料として、機械的圧搾効果と同時に水熱反応を利用する水熱ホットプレス法を用いることによりハイドロキシアパタイト (HAp) を作製し、その高強度化に関する検討を行った。作製条件は、反応温度 300°C 、反応時間 2 hrs、加圧力は 40 MPa であった。本条件で OCP から HAp セラミックスを作製できることを示すとともに、種々の溶媒を用いた固化実験を行うことにより、 NH_4^+ イオンを含んだアルカリ性の溶媒を

用いることにより層状構造を有する HAp セラミックスを生成できることを見出した。 NH_4^+ イオンを含んでいても酸性溶液では層状構造は形成されなかった。X線解析の結果を用いて層状構造を特徴づけるパラメータを考案し、本パラメータと測定した3点曲げ強度の間に良い相関関係があることを示し、層状構造の形成が HAp セラミックスの高強度化に有効であることを明らかにした。本研究で得た最高の曲げ強度は約 70 MPa であった。

JOINING HYDROXYAPATITE CERAMICS AND TITANIUM ALLOYS BY HYDROTHERMAL METHOD

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Keywords: Hydroxyapatite, Titanium alloy, Hydrothermal method, NaOH solution, Joining.

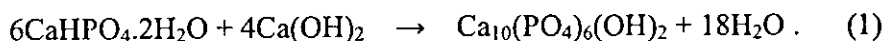
Abstract. Solidification of hydroxyapatite (HA) and its bonding with titanium (Ti) alloys was achieved simultaneously by using a hydrothermal hot-pressing (HHP) method. The reaction temperature used for the HHP treatment was as low as 150 °C. Two types of Ti alloys; Ti-15Mo-5Zr-3Al and Ti-6Al-2Nb-1Ta were tested to examine the effect of NaOH hydrothermal treatment. The NaOH treatment was shown to be useful to enhance the interface fracture property in the bonded HA/Ti body for both Ti alloys. The use of Ti-15Mo-5Zr-3Al was more effective in the NaOH treatment and the bonded HA/Ti body provided approximately three times higher interface toughness compared with that for the non-treated Ti alloy.

Introduction

Titanium (Ti) and its alloys are widely used as orthopedic and dental implant materials because of their high mechanical strength, low modulus and good corrosion resistance [1]. However, when embedded in the body, a fibrous tissue encapsulates the implant, isolating it from the surrounding bone. Some bioactive ceramics such as hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (HA), bioglass and glass ceramics can directly bond to living bones when used as a bone replacement materials [2]. The mechanical properties of HA only allow its applications in the small non-loaded structures. The possibility of HA deposited into the films and its bioactive properties exploited in the structural prostheses, for instance teeth root, hip, knee and shoulder joint replacement. Therefore, the HA is used as coating materials of those prostheses surface in order to prepare the bioactive layers on the Ti alloys. The HA surface improves the fixation of the implants due to the penetrative growth of the bone into the coating, forming a mechanical interlock.

Plasma spraying techniques traditionally have been used in process of hydroxyapatite coating [3]. However, this high temperature method results in a number of significant problems, including phase and chemical decomposition of the HA, absence of a chemical interface/bond between the HA coating and substrate.

We have recently reported a new method for bonding HA ceramics and pure Ti disk by using a hydrothermal hot-pressing (HHP) [4]. The hydrothermal reaction of calcium hydrogen phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$; DCPD) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) occurs in a liquid phase as follows:



The water of crystallization in DCPD is slowly lost below 100 °C is well known phenomena [5]. If the released water can be utilized as a reaction solvent during the HHP treatment, then the synthesis and solidification of HA and joining the HA to metal can be achieved simultaneously under the hydrothermal condition.

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 [6]. This paper describes a new bonding technique of HA ceramics and Ti alloys and discusses the effects of the NaOH solution treatment on the interface property of bonded HA/Ti alloy bodies in HHP method.

Experimental

Sample preparation. Firstly DCPD powder is used as a starting material 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%, Japan) and 1.0M diammonium hydrogen phosphate solution ($(\text{NH}_4)_2\text{HPO}_4$; Kanto Chemical Co., Inc.,

98.5%, Japan). The mixing was carried out at a room temperature (approximately 20°C). The precipitate from the mixture was filtered and washed with deionized water and acetone. The washed filter cake was oven-dried and then ground to a powder.

Two kinds of Ti alloys rods (Ti-15Mo-5Zr-3Al, Ti-6Al-2Nb-1Ta; Kobelco, Japan), 20mm in diameter, were used as a substrate material. The Ti alloy rods were cut into disks with a thickness of 10mm, and were cleaned in deionized water and acetone by using an ultrasonic cleaner. The Ti alloys disks were treated with alkali solution (5M NaOH). The conditions of a NaOH solution hydrothermal treatment were conducted at 150°C for 0h, 2h and 24h respectively. After the hydrothermal treatments, the Ti alloys disks were washed by deionized water, and then dried in air. The surfaces, the surfaces of the NaOH treated Ti alloy disks were observed using scanning electron microscopy (Hitachi FE-SEM S-4300).

DCPD and calcium hydroxide ($\text{Ca}(\text{OH})_2$; Kanto Chemical Co., Inc., 95.0%, Japan) were mixed in a mortar for 30min with a Ca/P ratio of 1.67. The powder mixture and Ti alloys disks were placed into the middle of the autoclave, as shown in Fig.1. The autoclave has a pistons-cylinder structure with an inside diameter of 20mm. 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 PTFE was fixed between a cast rod and a push rod, and it was deformed by pressure from the top and bottom to prevent leakage of the hydrothermal solutions.

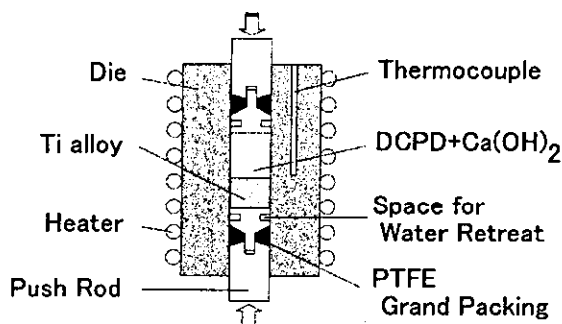


Fig.1 The schematic illustration of the autoclave for Hydrothermal Hot-Pressing (HHP).

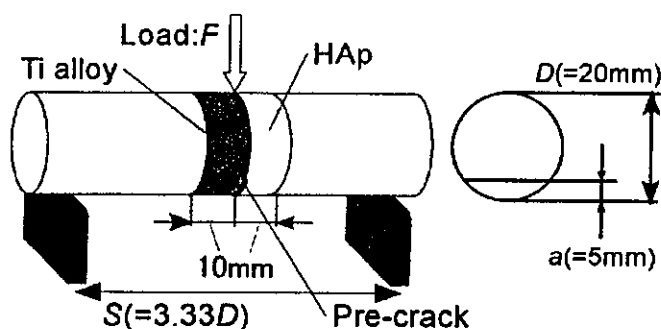


Fig.2 Schematic illustrations of 3-point bending test.

A pressure of 40MPa was initially applied to the sample through the loading rods from the top and bottom at room temperature. After the initial loading the autoclave was heated to 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 a room temperature naturally, and the sample removed from the autoclave. 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 the initial sample height, and Δh is the relative displacement during the heating process.

Bonding strength evaluation. Uniaxial tension tests and 3-point bending tests were conducted to obtain an estimate of the fracture toughness for the HA/Ti alloy interface. In the 3-point bending tests, core-based specimens were used to determine for the fracture toughness. The configuration of the core-based specimen used is shown in Fig.2. Two steel rods were attached to the HA/Ti body using an epoxy resin in order to prepare the standard core specimens.

A pre-crack was introduced along the interface of the bonded HA/Ti alloy specimens. The stress intensity factor K was employed to evaluate the bonding property of the HA/Ti alloy specimens. K was computed using the following equation [7]:

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

where D is the diameter of the specimen ($=20\text{mm}$), S ($=3.33D$) is supporting span, F is load, Y'_c is dimensionless stress intensity factor. The value of Y'_c can be found in Ref.[7] as a function of the relative length, a/D .

Results and Discussion

Sample preparation. An example of the HHP processing conditions is shown in Fig.3. The temperature and pressure histories are shown in the figure along with the volume ratio data. It was shown that lowering of the pressure after the completion of the volume change is useful to produce a better bonding property. Thus, the pressure was decreased as indicated in Fig.3 for all the tests. The

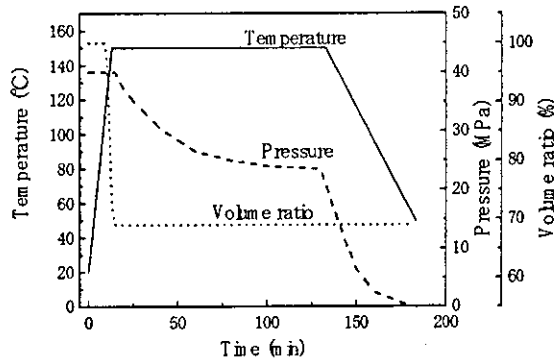


Fig.3 The indication of the temperature, shrinking behavior and pressure during HHP treatment.



Fig.4 Photo of Ti-15Mo-5Zr-3Al surface treated with NaOH hydrothermal solution for 2h.

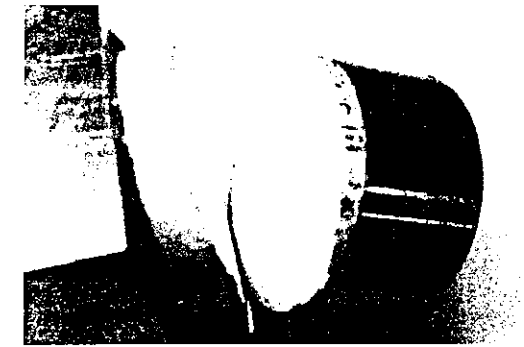


Fig.5 Photo of no treated Ti-15Mo-5Zr-3Al specimen after tensile test.

Bonding strength evaluation. The tensile strength of the bonded HA/Ti bodies measured and the fracture location observed. The bonded body of the Ti-6Al-2Nb-1Ta alloy without treatment fractured along the interface and showed an only lower value of tensile strength, 1.0MPa. On the other hand, the Ti-15Mo-5Zr-3Al alloy without NaOH treatment produced the improved bonding property compared with the case of the Ti-6Al-2Nb-1Ta alloy. The bonded specimen of Ti-15Mo-5Zr-3Al alloy after tension test is shown in Fig.5. It can be seen that the fracture took place in the HA ceramics and the interface remained undamaged. The tensile strength for the bonded body was 1.0MPa. This value corresponds to the range of tensile strength of the HA ceramics that is reported in previous literatures. The above-mentioned observation suggests that the interface may have higher fracture property than the HA ceramics itself. These results also suggest that the NaOH treatment of Ti surfaces may improve the interface fracture property in the bonded HA/Ti bodies.

In order to access more directly the interface fracture property, the bonded HA/Ti bodies with a pre-crack were subjected to 3-point bending fracture toughness tests. The values of the critical

bonded bodies were obtained for the two Ti alloys in both the cases of the NaOH solution treatment and non-treatment. An SEM image of the Ti-15Mo-5Zr-3Al alloy surface treated with NaOH for 2hours is shown in Fig.4. The treated surface exhibit a sponge-like morphology which is totally different from smooth non-treated initial surface. It has been shown by Raman spectroscopy that a reaction layer consisting of titanium oxide and sodium titanate was formed on the treated Ti surfaces. Thus, the sponge-like surface as in Figure 4 may reflect the formation of titanium oxide and sodium titanate.

stress intensity factor K_c are shown in Fig.6, as a function of the NaOH treatment time. The toughness data plotted in the figure are average values obtained from at least five specimens. The Ti-6Al-2Nb-1Ta alloy without treatment showed an extremely lower fracture toughness. It is noted, however, that the NaOH treatment allows us to improve the interface fracture property. The treatment of 24hrs appears to further increase the interface fracture toughness relative to the 2 hrs treatment. Based on the SEM observation and Raman spectroscopy, the reaction layer formed on Ti surface may be responsible for the improved interface toughness in the NaOH treated bodies. The Ti-15Mo-5Zr-3Al alloy is shown to produce the enhanced interface toughness compared with that of Ti-6Al-2Nb-1Ta. It is particularly noted that the treatment of 2hrs is most effective and provides approximately three times higher interface toughness than that for the non-treated Ti alloy. The fracture surface of the surface treated body for 2hrs is shown in Fig. 7. It is seen that the fracture initiates at the pre-crack tip and propagates not along the interface but into the HA ceramics. This observation clearly indicates that the bonded interface achieved by the HHP method possess a significantly enhanced fracture property. As shown in Fig. 6, the prolonged treatment of 24hrs provide no further increase in the interface toughness and rather cause a toughness reduction for Ti-15Mo-5Zr-3Al alloy in contrast with Ti-6Al-2Nb-1Ta. Optimal surface treatment conditions should be found in order to enhance the fracture toughness of the HA/Ti alloy interface. Further investigation of NaOH treatment conditions and detailed chemical analysis of the reaction layer are in progress.

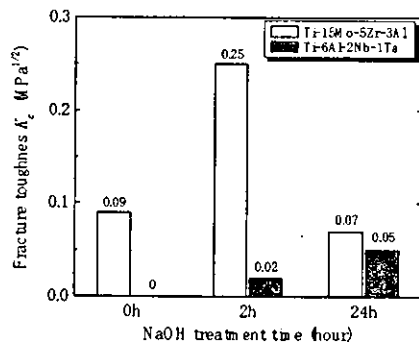


Fig.6 Fracture toughness calculated from 3-point bending test.

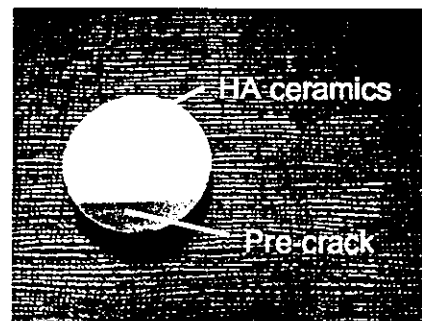


Fig.7 Photo of Ti-15Mo-5Zr-3Al specimen treated with NaOH for 2h after 3-point bending test.

Conclusions

It has been demonstrated that HA ceramics can be bonded to Ti alloys by using a hydrothermal hot-pressing method. Fracture toughness tests revealed that the interface fracture property of the bonded HA/Ti bodies can be significantly improved by means of NaOH hydrothermal treatment of Ti surfaces. It appears that the use of Ti-15Mo-5Zr-3Al alloy is more useful to enhance the interface fracture property, relative to Ti-6Al-2Nb-1Ta.

Acknowledgements

Author T.O. was supported by research fellowship of the Japan society for the promotion of science for young scientists.

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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

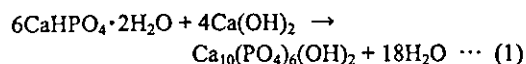
1. INTRODUCTION

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 (CaHPO₄·2H₂O; 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 Ca²⁺ and PO₄³⁻ at the stoichiometric ratio of Ca/P=1.67 in HA. For example, the chemical reaction of DCPD and calcium hydroxide (Ca(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