	り じゅん ごあ
氏名	李 俊 国
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指導教官	東北大学教授 橘田 俊之
論文審査委員	主査 東北大学教授 橘田 俊之　東北大学教授 山崎 仲道 東北大学教授 川崎 亮

論文内容要旨 (Abstract)

Chapter 1 Introduction

There is a great tendency for biomaterials to replace diseased or damaged parts of bone. Hydroxyapatite (HAp) exhibits excellent biocompatibility, bioactivity and osteoconductivity. Thus, HAp ceramics is highly expected to be used as bone and tooth implants. However, to our knowledge, some problems remain to be solved for fabrication of HAp ceramics with desirable properties. For example, higher temperatures (>1000°C) are commonly needed for sintering HAp ceramics with sufficient strength. But HAp dehydrates at high temperatures (>800°C), and this will cause an inevitable decrease in its biocompatibility. Additionally, the fracture toughness of the HAp ceramics sintered at high temperatures is still insufficient for the use as bone replacement. On the other hand, the mechanical properties of HAp ceramics prepared at low temperatures are very poor. In this study, an attempt to improve the mechanical properties of HAp ceramic has been made through preparing a HAp ceramic with a lamellar structure by hydrothermal hot-pressing method at low temperatures (<300°C).

Chapter 2 Solidification of hydroxyapatite ceramics from various calcium phosphates by hydrothermal hot-pressing process

In this chapter, firstly, calcium phosphates (such as DCPD, OCP and HAp) were synthesized, consisting of platelike crystals. Then, using these calcium phosphate as starting material (additionally, α-TCP was also used) and $Ca(OH)_2$ or ammonia water as reactant, the preparation and solidification of HAp was carried out by hydrothermal hot-pressing under conditions of 300°C, 40MPa, 2h. When $Ca(OH)_2$ was used as reactant, calcium phosphate and $Ca(OH)_2$ dissolved in water and then HAp precipitated, resulting in HAp ceramics with a homogeneous structure. When ammonia water was used as reactant, the samples prepared from DCPD and OCP exhibited a lamellar structure, while the sample fabricated from α-TCP was homogeneous with needlelike HAp crystals. It was concluded that OCP was the most suitable material to form lamellar structure in HAp ceramics by hydrothermal hot-pressing method. The lamella is stacked by platelike HAp crystals with the c crystal axis normal to the loading direction (Fig.1).

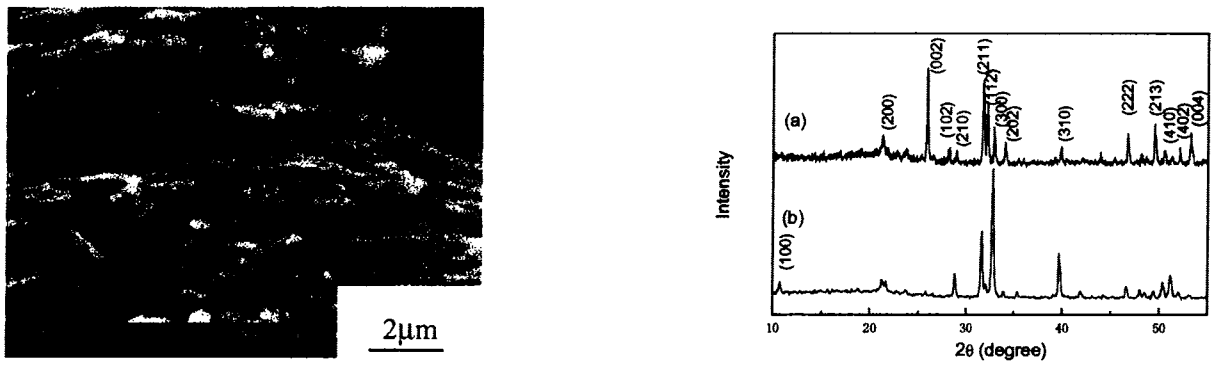

Fig.1 SEM photograph (a) and XRD pattern (b) of the sample fabricated from OCP and ammonia water

Chapter 3 Effects of hydrothermal hot-pressing conditions on the formation of lamellar structure

In chapter 3, using OCP as the starting material, the effects of HHP conditions, such as pH value of medium, NH_4^+ concentration and amount in medium, treatment temperature, applied pressure, and treatment time, on the formation of lamellar structure of HAp ceramics by HHP were investigated. A lamellar structure of HAp ceramics can be formed by using OCP powder as a starting material and using NH_4^+–containing medium when the pH value is higher than 7.0 and the temperature is higher than 200°C. Moderate amount of high concentration ammonia water, high pressure and long treatment time are necessary for high degree of

HAp crystals alignment (η). The formation of the lamellar structure is useful to improve the bending strength of the HAp ceramics (Fig.3). The lamellae-forming process can be described as follows: OCP reacts with ammonium to form $NH_4H_2PO_4$ and platelike HAp crystals. When the temperature is higher than the melting point of $NH_4H_2PO_4$, the platelike HAp crystals will suspend in the melted $NH_4H_2PO_4$. On the other hand, the melted $NH_4H_2PO_4$ will be pressed out under pressure. The HAp crystals suspended in $NH_4H_2PO_4$ will come down because of the two factors, the applied pressure and the pressing-out of the $NH_4H_2PO_4$, accompanied with the formation of a lamellar structure. Obviously, $NH_4H_2PO_4$ plays an important role in the formation of the lamellar structure.

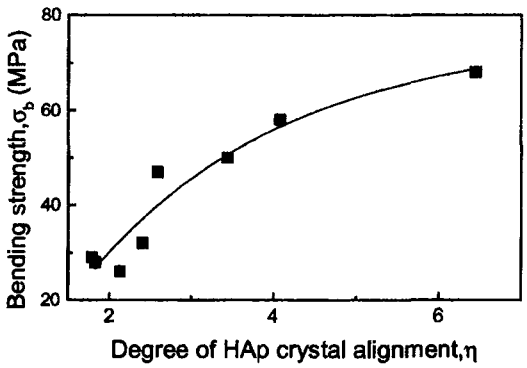

Fig.2 Relationship between bending strength and degree of HAp crystal alignment

Chapter 4 Fabrication of HAp/polymethylmethacrylate composites

In order to obtain the biomaterial with a similar structure to human bone, HAp/polymer composite with a lamellar structure was prepared. In this chapter, PMMA was chosen for the preparation of HAp/polymer composites because PMMA polymer exhibits high thermal resistance, good mechanical properties and excellent biocompatibility. HAp/PMMA composites were prepared by PMMA addition through two different routines: (1) mixing PMMA powder and OCP powder and (2) mixing OCP powder with a solution of methyl methacrylate monomer and α,α'-Azobisisobutyronitrile. The mixture was put into the autoclave. Afterwards, ammonia water with 10% amount of the OCP was dripped into the mixture, and then a pressure of 40MPa was applied to it. After 3 minutes, the sample was heated to 200°C at a rate of 10°C/min and then kept at 200°C, 40 MPa for 2 hrs. When PMMA was added through routine 1, the PMMA impeded the formation of lamellar structure. The resulted bending strength was lower than pure HAp ceramics. When PMMA was added through routine 2, a small amount (5%) of addition of PMMA enhanced the orientation of HAp crystals, resulting in an improvement of the bending strength. In contrast, an excessive amount of PMMA would prevent the formation of lamellar structure because the PMMA particles tended to connect with each other and to form a network, which in turn prevented the pressing-out of $NH_4H_2PO_4$, resulting in a decrease of the bending strength.

Chapter 5 Reinforcement by in-situ formation of HAp whiskers

In chapter 4, the strength of the composites is still insufficient because the low heat resistance of the PMMA limits the processing temperature. In this chapter, the HAp ceramics was reinforced by in-situ formation of HAp whiskers. The HAp/HAp-whisker composite was successfully fabricated through mixing OCP and α–TCP powder with ammonia water media by hydrothermal hot pressing at 300°C, 40MPa for 4h. The α–TCP can transform completely into HAp whiskers/rods under the hydrothermal hot pressing conditions. The composite prepared by addition (30%) of α-TCP still possesses a lamellar structure. In this case the bending strength and fracture toughness in the direction parallel to the lamellae reach 101 MPa, 1.84 $MPa \cdot m^{1/2}$ respectively.

The progress in reinforcing HAp ceramics in this study was shown in Fig.3. Both the bending strength and the fracture toughness are greatly enhanced by the formation of the lamellar structure at the treatment temperature of either 200°C or 300°C. At the treatment temperature of 200°C, the bending strength is further improved by the addition of PMMA. For the treatment temperature of 300°C, the bending strength and the fracture toughness in the direction parallel with the lamellae are further enhanced by in-situ formation of the HAp whiskers. In such a case the whole toughness is more approaching to that of human bone.

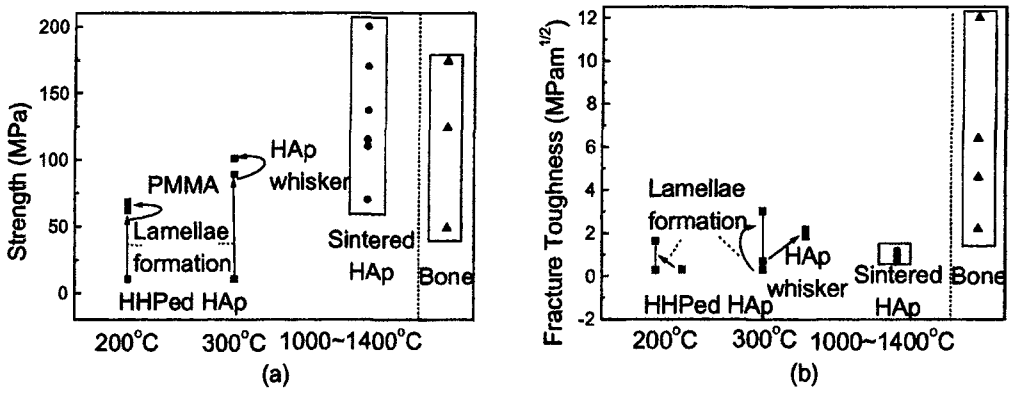

Fig.3 Strength (a) and fracture toughness (b) of the hydroxyapatite ceramics

Chapter 6 Conclusions

From this study, the following points are clarified:

1. Formation of lamellar structure is favorable to the mechanical properties of the HAp ceramics.
2. It is feasible to prepare HAp composites with good mechanical properties at low temperatures (<300°C) by hydrothermal hot-pressing method.

論文審査結果の要旨

生体活性を有するハイドロキシアパタイト（HAp）は，人工骨や人工歯根などへの適用が期待され，活発な研究対象となっている．従来の焼結法などで作製された HAp は人骨と同程度の強度特性を有する一方，未だ靭性は小さく荷重担体部位への広範な適用は制限されているのが現状である．また，高温焼結により HAp 本来の生体活性が低減することや，有機物との複合化が困難である課題もある．

本論文は，高強度で高靭性を有する HAp セラミックスを低温で作製することを目的として，水熱ホットプレス法を用いた固化法ならびにその複合化に関する検討を行い、それらの結果をまとめたもので全編６章よりなる。

第１章は序論であり、本研究の背景を述べている。

第２章では、６種類の出発原料ならびに反応溶媒の組み合わせに対して，水熱ホットプレス法を用いた固化実験を行い，破壊特性評価および生成相，破面観察の結果に基づき，破壊特性の向上に効果的な出発原料と反応溶媒の組み合わせを見出している．これにより，出発原料としてリン酸８カルシウム(OCP),反応溶媒としてアンモニア水を用いることで微細な層状構造を有する HAp セラミックスを 300℃という比較的低温で作製できることを示している．これは，重要な知見である．

第３章では，第２章の知見に基づき，OCP とアンモニア水の系に焦点を当てた合成条件の最適化に関する系統的な検討を行っている．層状構造を形成するためには反応溶媒がアンモニアイオンを含みかつ pH が 7.0 以上の反応溶媒であることが要求されるとともに，X 線解析の結果に基づきアンモニアイオン濃度が大きくなるにつれ層状構造の配向が顕著になり破壊特性が向上することを明らかにしている．300℃の温度条件で作製した HAp セラミックスは，従来の 1000℃を超える焼結法で作製された場合と比較して約２倍の破壊靭性値と同程度の強度特性を有することを示している．

第４章では，水熱ホットプレスと同時に，200℃の条件下で溶液反応により重合した PMMA を HAp セラミックス中にほぼ均一に分散させることに成功している．これにより，PMMA の無添加の場合よりもさらに層状構造の配向度を高め，破壊特性を増大できる最適の添加量が存在することを見出している．

第５章では，α型第三リン酸カルシウム(α-TCP)と OCP を出発原料として用いることで HAp ウィスカーにより複合化した HAp セラミックスを作製できることを見出している．これにより層状構造における層間の破壊特性を顕著に向上させるとともに，層状構造に垂直な方向に対しても等方材に比較して高い破壊特性を有する複合体を作製できることを示している．これは有用な知見である．

第６章は結論である．

以上要するに本論文は，生体親和性が高くかつ破壊特性に優れた HAp セラミックスを低温で作製することを目的として微細な層状構造を創成する方法ならびにその複合化の方法を提案したものであり，地球工学ならびに材料工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。