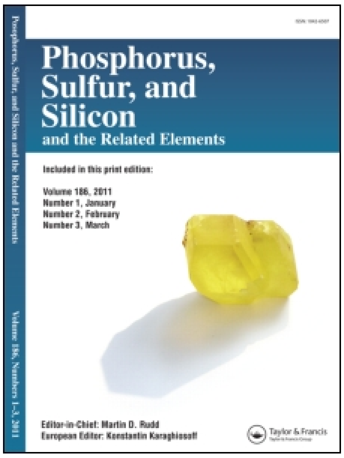

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Bioceramics Composed of Calcium Polyphosphate Fibers

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Bioceramics Composed of Calcium Polyphosphate Fibers

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Abstract High-strength glass-ceramics consisting of crystalline fibers were synthesized by controlled crystallization of glasses in the $CaO-P_2O_5$ system. Their unique microstructure and mechanical properties are reported. The fibers are also successfully extracted from the glass matrix. These glass-ceramics and ceramic fibers are proposed for new applications to bio-related fields.

Introduction

Calcium phosphate ceramics have great potential for biomedical applications, because their chemical compositions are close to that of living hard tissues. High-strength and high-toughness biomaterials with low elastic modulus are requisite for wide applications. Toughness of ceramic or polymer materials is effectively improved by introducing some fibers to matrix. The fibers for toughening biomaterials should be biocompatible and not toxic. It has been reported that $Ca(PO_3)_2$ glass-ceramics exhibit biocompatiblity.[1,2] Calcium polyphosphate crystals of metaphosphate composition are nontoxic fibers.[3] Therefore, we expect that the $Ca(PO_3)_2$ crystals have high potential uses as new applications to bio-related fields. The objective in this paper is to synthesize new ceramics consisting of crystalline calcium polyphosphate fibers as new bioceramics.

Calcium Phosphate Glass-Ceramics

Fiber-containing calcium phosphate ceramics were produced by reheating and crystallizing the $CaO-P_2O_5$ glasses.

Volume-Crystallized Glass-Ceramics

It was found that some $CaO-P_2O_5$ glasses exhibit volume-crystallization by adding nucleating agents. Figure 1 shows a SEM photograph of the glass-ceramic containing a small amount of Al_2O_3, Y_2O_3, and ZrO_2. Note that this glass-ceramic consists mainly of fine dendritic δ-$Ca(PO_3)_2$ crystals. The bending strength and the fracture toughness of this glass-ceramic were 150 MPa and 1.8 MPa·$m^{0.5}$, respectively, and were two to three times higher than those of conventional ceramic materials for dental use such as porcelain and crown. It is available for applications to this field.

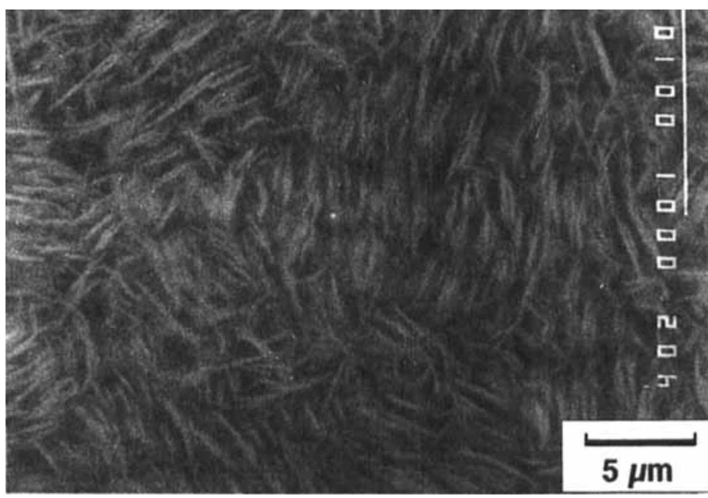


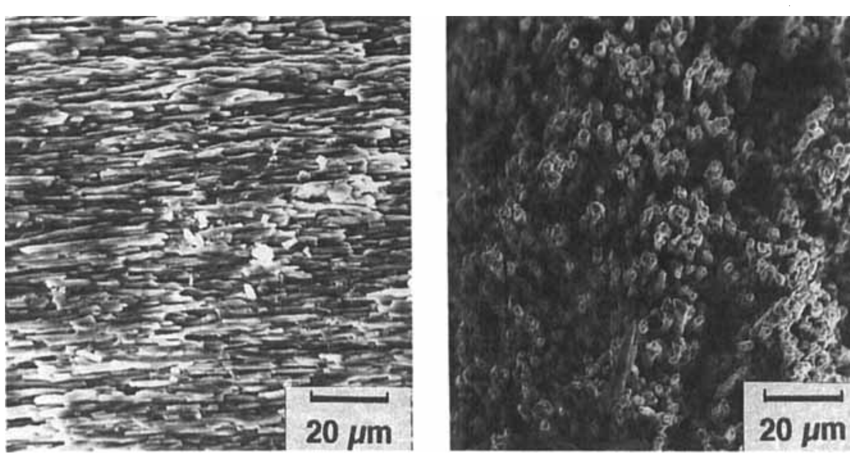
Figure 1 SEM photograph of 52CaO $46P_2O_5$ $2Al_2O_3$ (mol%) containing small amounts of ZrO_2 and Y_2O_3.

Unidirectionally Crystallized Glass-Ceramics

$Ca(PO_3)_2$ glass having a chain structure crystallizes even at temperatures below the glass transition temperature (Tg).[4] The growth rate of β-$Ca(PO_3)_2$ fibrous crystal is extraordinarily high at around Tg, since the crystal growth proceeds without accompanying the breaking and reforming of P-O-P bonds (non-reconstructive-type crystallization). On the other hand, the nucleation rate is low at around Tg. In the CaO-P_2O_5 glass, crystallization usually begins in several places on the surface of the specimen when it is heated isothermally. When the glass was heated in a furnace under a temperature gradient of 3~33°C/mm at around Tg, preferred-oriented crystalline fibers continued to grow from the higher-temperature edge of the rod toward their lower-temperature edge.[5,6] The unidirectionally crystallized glass-ceramics consisting of β-

$Ca(PO_3)_2$ crystalline fibers with ≈1 μm diameter were produced by reheating the glasses having the compositions of CaO/P_2O_5=0.9~1.13 in mol ratio. Glassy phase and crystals such as $2CaO{\cdot}3P_2O_5$ and $4CaO{\cdot}3P_2O_5$ lay as matrix between the crystalline fibers.

Figure 2 shows SEM photographs of the fracture surfaces after a bending test. The glass-ceramics showed high strength of 400~600 MPa in bending and low Young's modulus of 70~120 GPa. Their fractures proceeded non-catastrophically, but their behaviors varied with composition of the glass-ceramics. The glass-ceramics derived from the glasses with $CaO/P_2O_5<1$ were broken step by step even beyond a maximum bearable stress, while those from the glasses with $CaO/P_2O_5>1$ exhibited a half stable fracture. The behaviors depend on the length of the fibers and the bonding strength between fibers and matrix phases. The length of the fibers precipitated in the glasses with $CaO/P_2O_5>1$ were shorter than that in the glasses with $CaO/P_2O_5<1$. The unidirectionally crystallized glass-ceramics are available for biomedical applications which require high-strength and flexibility, example for, bone grafting, bone anchoring, and so on.



(a) (b)

Figure 2 SEM photographs of the fracture surfaces of unidirectionally crystallized glass-ceramics ($45\,CaO \cdot 55\,P_2O_5$).

(a) The cross-section parallel to the growing direction of ß-$Ca(PO_3)_2$ crystals.
(b) The cross-section perpendicular to the growing direction of ß-$Ca(PO_3)_2$ crystals.

Calcium Polyphosphate Fibers for New Applications

The mechanical properties of the above-mentioned glass-ceramics suggest that β-$Ca(PO_3)_2$ is a high-strength fibrous crystal. We expect that this fiber will be used for new composite-biomaterials.

One of the methods for producing the fibers is to extract them from the matrix phases of the glass-ceramics. The crystallized glasses were effectively leached with dilute NaOH aqueous solutions (≈0.1N) at 60°~70°C. The fibers were filtrated from the solutions and then dried at 150°C. β-$Ca(PO_3)_2$ fibers obtained by this method have high aspect ratios (30~120) with diameters of 1~5 μm as shown in Figure 3. We expected that the fibers are available to bioabsorbable carriers which stabilize bone morphogenetic proteins or medicaments for treatments and to fillers for biomedical cushions such as a periodontal substitute. In biotechnological field, the fiber-composite materials with porosity may be also significant materials for supporting microbe immobilization or tissue culture.

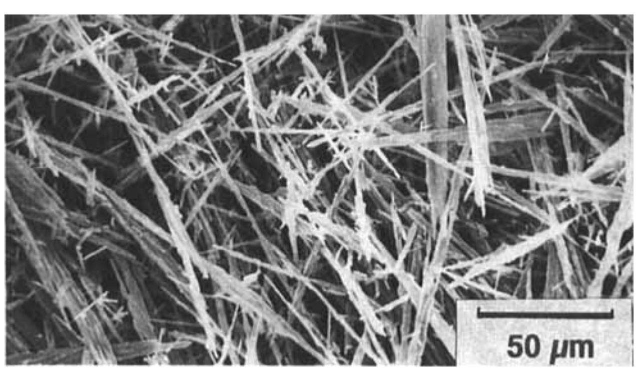


Figure 3 SEM photograph of β-$Ca(PO_3)_2$ fibers extracted.

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