Preparation of Calcium Phosphate Fibers

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Abstract β -calcium metaphosphate fibers were successfully extracted from crystallized glasses by leaching with distilled water or a dilute NaOH aqueous solution. The fibers of high aspect ratios (30~120) were obtained from the crystallized glasses of which molar ratio of $\text{CaO/P}_2\text{O}_5$ is slightly less than unity. It is expected that the fibers are available for new applications to biomedical fields.

Introduction

Calcium phosphate glasses and glass-ceramics¹⁻⁵ have high potential in use as biomedical materials. It has been reported that $\text{Ca}(\text{PO}_3)_2$ glass is nontoxic.¹ The unidirectionally crystallized glass-ceramic having fiber-reinforced composite structure was successfully produced by reheating a calcium phosphate glass rod around the metaphosphate composition under a temperature gradient around the glass transition temperature (T_g).^{2,3} The glass-ceramic composed of crystalline $\beta\text{-Ca}(\text{PO}_3)_2$ fibers (diameter; $\approx 1 \mu\text{m}$) shows high mechanical strength (400~600 MPa in bending) and low Young's modulus (70~120 GPa). This result implies that the $\beta\text{-Ca}(\text{PO}_3)_2$ fibers are of high-strength and flexibility. In addition, the glass-ceramic shows good biocompatibility.^{4,5} Therefore, it is expected that this fiber can be used for new composite-biomaterials. Our earlier works reported

that the β -Ca(PO₃)₂ fibers are successfully extracted from the crystallized product of a calcium phosphate glass by leaching with distilled water or a dilute NaOH aqueous solution.^{6,7} In this report the optimal glass composition to obtain the fiber will be discussed.

Experimental Procedure

Batch mixtures with CaO/P₂O₅=0.72~1.00 in molar ratio were prepared by using raw materials such as Ca(H₂PO₄)₂·H₂O and H₃PO₄. The mixtures were melted in a platinum crucible at 1250 °C for 2 h. The melts were poured onto a carbon plate and cooled to a room temperature. The resultant glasses were reheated at 600 °C for 48 h for crystallization. The crystallized glass blocks were crushed into powders below 850 μm using an alumina mortar. The powders (10 g) of the crystallized glasses were put into a tefron vessel filled with 200 ml of leaching solutions to extract β -Ca(PO₃)₂ fibers.⁶ Distilled water (DW) or an aqueous solution of 0.1 N NaOH were used as the solution. They were stirred at 70°~90 °C for 4~72 h. The resultant products were filtrated and dried at 150 °C in air. The crystalline phases in the glasses crystallized and the fibers obtained were identified by X-ray diffraction analysis (XRD). The morphologies of the fibers were observed by scanning electron microscopy (SEM).

Results and Discussion

Glass-ceramics which contain long fibrous β -Ca(PO₃)₂ can be prepared by reheating CaO-P₂O₅ glasses around the metaphosphate composition at the temperature around T_g.^{2,3,6,7} Glass-ceramics converted from the calcium ultraphosphate glasses (CaO/P₂O₅<1) consist of crystals such as β -Ca(PO₃)₂, Ca₂P₆O₁₇, and an ultraphosphate glassy phase.³ Figure

1 shows change in pH values of NaOH solution as a function of leaching time. The pH value decreased rapidly at the initial stage of leaching. The decrease in pH was caused by dissolution of phosphate ions from ultraphosphate glassy and crystalline phases.⁶ XRD analysis showed that a large amount of β -Ca(PO₃)₂ crystal exist in the crystallized product of CaO·P₂O₅ glass without the ultraphosphate crystals. It was difficult to obtain a large amount of fibrous products from the CaO·P₂O₅ crystallized glass by DW-treatment for 72 h. On the other hand, β -Ca(PO₃)₂ fibers were released preferentially from the matrix phase of the crystallized glass with CaO/P₂O₅=0.85. The ultraphosphate phases are much poorer in chemical durability than fibrous β -Ca(PO₃)₂ crystals. The existence of the ultraphosphate matrix phases in β -Ca(PO₃)₂-containing glass-ceramics is essential for this treatment.

Figure 2 shows SEM photographs of the fibrous products obtained by DW-treatment. From XRD analysis, these products contain β -Ca(PO₃)₂ and Ca₂P₆O₁₇. Fiber (A) obtained from the crystallized glass with CaO/P₂O₅=0.85 is smaller in diameter and larger in length compared to that (B) with CaO/P₂O₅=0.72. The β -Ca(PO₃)₂ crystals precipitated in the glass with CaO/P₂O₅=0.72 may be shorter in length than that with CaO/P₂O₅=0.85. Fiber (B) contains a large amount of Ca₂P₆O₁₇. The ultraphosphate matrix phases were not dissolved out successfully by this treatment. We have reported that Ca₂P₆O₁₇ is dissolved out almost perfectly by NaOH-treatment.⁶ The calcium metaphosphate fibers containing no ultraphosphate phases are obtained by NaOH-treatment of the crystallized glass with CaO/P₂O₅=0.85.

Summary

In this work we prepared the calcium metaphosphate fibers having high aspect ratios of 30~120 with diameters of 1~5 μ m from a crystallized

glass with $\text{CaO}/\text{P}_2\text{O}_5=0.85$. It is expected that the fibers are available to fillers for high-strength composite-biomaterials and for biomedical cushions such as a periodontal substitute.

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Figure 1. Change in pH values with treatment time at 80°C when the crystallized glass powders were immersed into 0.1 N NaOH aqueous solution. The numbers in the figure represent the $\text{CaO}/\text{P}_2\text{O}_5$ ratios (in mol) of the crystallized glasses.

Figure 2. SEM photographs of calcium phosphate fibers obtained by DW-treatment for 72 h. (A): Fibers obtained from the crystallized glass with $\text{CaO}/\text{P}_2\text{O}_5=0.85$. (B): Fibers obtained the crystallized glass with $\text{CaO}/\text{P}_2\text{O}_5=0.72$.

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