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DEVELOPMENT OF CALCIUM PHOSPHATE GLASS-CERAMICS FOR SURGICAL AND DENTAL USE

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Abstract Two types of glass-ceramics have been developed in the system of calcium phosphate without silica. The preparation conditions, crystallization processes, and some of physical properties are briefly reported. These glass-ceramics have high potential use for bone substitutes and dental materials such as dental crown, root and tooth.

INTRODUCTION

Great attention has been given on bioceramics in surgical and dental fields. The great majority of works on bioceramics have so far dealt with sintered products of ceramics such as alumina, hydroxyapatite and tricalcium phosphate. Generally ceramics are made by sintering powdery raw materials at high temperatures or by glass-ceramic processes. The purpose of the work reported here is to describe and review briefly characteristics in crystallization of calcium phosphate glasses, the resultant glass-ceramics and its potential application to bone implant and dental crown(root). All the glass-ceramics reported here have been developed in our laboratory.

CHARACTERISTICS IN CRYSTALLIZATION¹

Calcium metaphosphate glasses exhibit abnormal¹ crystallization behavior, i.e., these glasses crystallize easily at temperatures considerably lower than the glass transition temperature ($T_g \approx 500^\circ\text{C}$)², although glass does not normally crystallize below T_g . This behavior enables to produce unidirectionally crystallized glass-ceramics as shown below.

GLASS-CERAMICS

Two types of glass-ceramics have been developed in the system of $\text{CaO-P}_2\text{O}_5$ without silica.

(A). Unidirectionally Crystallized Glass-Ceramics (UDC)

$\text{CaO-P}_2\text{O}_5$ glass rod was heated at around T_g under a temperature gradient of $30\text{-}300^\circ\text{C/cm}$, so that $\beta\text{-Ca}(\text{PO}_3)_2$ crystalline fibers ($1\text{ }\mu\text{m}$ dia.) with very high aspect ratio were aligned in parallel to the longitudinal direction of the rod.³ The properties and microstructures depend on the $\text{CaO/P}_2\text{O}_5$ ratio of the specimen and heat-treatment conditions. They were found to exhibit a unique fracture behavior, that is to say, fracture does not occur catastrophically but proceeds step by step, even beyond the yield value. Generally, increasing the ratio of $\text{CaO/P}_2\text{O}_5$ of UDC, the chemical durability is improved and the orientation degree of the crystalline fibers decreases. For the purpose of improving chemical durability and biocompatibility, the surface layers of UDC were successfully converted by a chemical reaction with molten $\text{CaCl}_2\text{-Ca}(\text{NO}_3)_2$ mixture at about 420°C into apatite phase which was tightly bound on the UDC (Fig.1).

As seen in Fig.2, the Young's modulus of the resultant UDC is much lower than that of conventional ceramics. This is very much favorable as a bone implant material because the Young's modulus should be as close as possible to that of living bone.

(B). Randomly Crystallized Glass-Ceramics

A few kinds of glass-ceramics were prepared by volume crystallization of $\text{CaO-P}_2\text{O}_5$ glasses having additive components, while the binary calcium phosphate glasses themselves do not exhibit volume crystallization. The representative examples are as follows.

(B-1). $\text{CaO-P}_2\text{O}_5$ containing a small amount of Al_2O_3

Calcium phosphate glass-ceramics containing Al_2O_3 were developed with or without nucleating agents of a mixture of ZrO_2 and Y_2O_3 . The physical properties are close to those of natural dental enamel. For example, hardness ($H_V = 380\text{ kg/mm}^2$) and thermal expansion coefficient ($1.1 \times 10^{-5}/\text{deg}$) are almost the same.

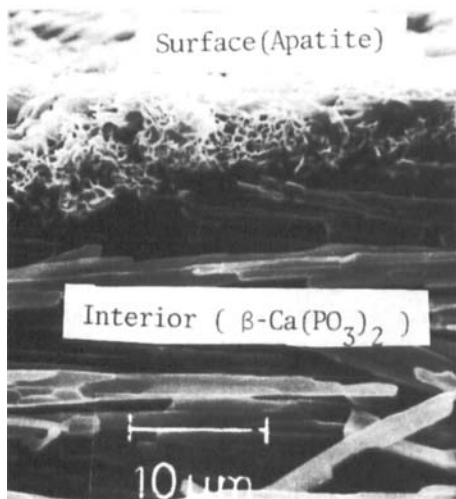


Fig.1. Photo of SEM of UDC
(Apatite is bound on surface)

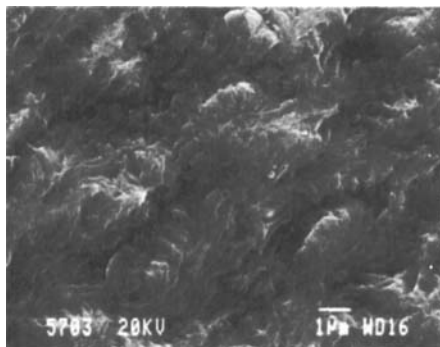


Fig.3. Photo of SEM of
 $45\text{CaO} \cdot 25\text{P}_2\text{O}_5 \cdot 30\text{P}_2\text{O}_5$ glass-
ceramic volume-crystallized

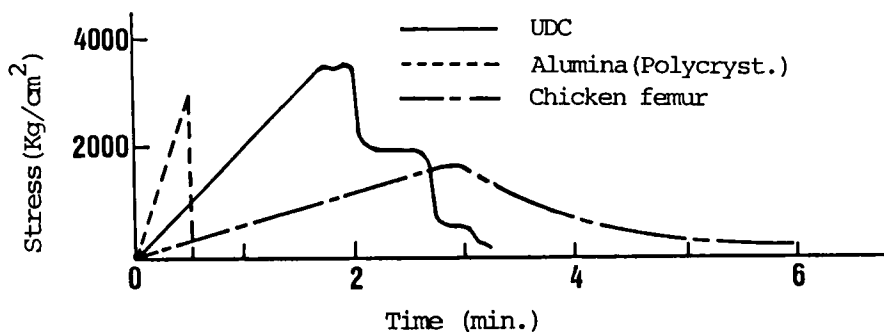


Fig.2. Bending test (Autograph) (Stress-Strain)
(Crosshead speed: 0.1 mm/min, Span: 25 mm)

Since a desired shape of these glass-ceramics can be produced with high accuracy, they are highly promising as dental crown materials.^{4,5} The clinical trials have been successfully finished for dental crown.

(B-2). $\text{CaO-TiO}_2\text{-P}_2\text{O}_5$

These have been just developed recently, having representative composition of $45\text{CaO}\cdot 25\text{TiO}_2\cdot 30\text{P}_2\text{O}_5$ (in mol %). This type of glass-ceramics consisting of very fine crystalline particles (Fig.3) has been found to have high bending strength (2000 kg/cm^2), high chemical durability and ivory appearance. It is expected that these glass-ceramics are available not only to dental crown, but to bone implant and condyle substitute material at hip joint.

Insertion of biomaterial in a living tissue essentially results in the creation of an artificial interface between the living tissue and the biomaterials. Studies of implantation of the calcium phosphate glass-ceramics into animal bone have been carried out by several investigators in orthopedic surgery,⁶ and are still in progress.⁷

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