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Effect of ZnO addition on bioactive $CaO–SiO_2–P_2O_5–CaF_2$ glass–ceramics containing apatite and wollastonite

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Abstract

Some ceramics show bone-bonding ability, i.e. bioactivity. Apatite formation on ceramics is an essential condition to bring about direct bonding to living bone when implanted into bony defects. A controlled surface reaction of the ceramic is an important factor governing the bioactivity and biodegradation of the implanted ceramic. Among bioactive ceramics, glass–ceramic A–W containing apatite and wollastonite shows high bioactivity, as well as high mechanical strength. In this study, glass–ceramics containing zinc oxide were prepared by modification of the composition of the glass–ceramic A–W. Zinc oxide was selected to control the reactivity of the glass–ceramics since zinc is a trace element that shows stimulatory effects on bone formation. Glass–ceramics were prepared by heat treatment of glasses with the general composition: $x\mathrm{ZnO} \cdot (57.0 - x)\mathrm{CaO} \cdot 35.4\mathrm{SiO_2} \cdot 7.2\mathrm{P_2O_5} \cdot 0.4\mathrm{CaF_2}$ (where $x = 0$–14.2 mol.%). Addition of ZnO increased the chemical durability of the glass–ceramics, resulting in a decrease in the rate of apatite formation in a simulated body fluid. On the other hand, the release of zinc from the glass–ceramics increased with increasing ZnO content. Addition of ZnO may provide bioactive $CaO–SiO_2–P_2O_5–CaF_2$ glass–ceramics with the capacity for appropriate biodegradation, as well as enhancement of bone formation.

Keywords: Glass–ceramics; Bioactivity; Apatite; Zinc; Simulated body fluid

1. Introduction

Artificial materials implanted into bone defects are generally encapsulated by fibrous tissue isolating them from the surrounding bone [1]. This is the normal response of the body towards inert artificial materials. However, some ceramics, such as Bioglass® [2], glass–ceramic A–W [3] and sintered hydroxyapatite [4], form bone-like apatite on their surfaces in the living body and bond to living bone through this apatite layer. This bone-bonding ability is called bioactivity. These bioactive ceramics are already used clinically as important bone-repairing materials. Their bone-bonding ability is achieved by the formation of a biologically active apatite layer after reaction of the ceramics with the surrounding body fluid [5,6]. A controlled surface reaction of the ceramic is an important factor governing its bioactivity, as well as its biodegradability.

Of the bioactive ceramics, the glass–ceramic A–W shows high bioactivity and high mechanical strength [3,7]. In the present study, we expected that addition of zinc oxide to the bioactive glass–ceramic would control the reaction between the glass–ceramic and the surrounding body fluid. Zinc oxide was selected to control the reactivity since zinc is an essential trace element that has stimulatory effects on bone formation [8]. The zinc ions released from the glass–ceramic may enhance bone regeneration. With regards to ceramics designed to release zinc ions, Ito et al. [9,10] recently developed calcium phosphate ceramics containing zinc. However, they used polycrystalline ceramics, so the range where zinc can be incorporated is limited and the behaviour of their materials is expected to be different from the glass-based materials. There are no reports on the effect

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of ZnO addition on apatite-forming ability and zinc release of glass-based materials. The effect of the addition of ZnO to $CaO–SiO_2–P_2O_5–CaF_2$ glass–ceramics on their apatite-forming ability, chemical durability and zinc release was examined during this study.

2. Materials and methods

2.1. Preparation of glass–ceramics

The composition of the glass was based on a modification of the glass–ceramic A–W. Glass was prepared with a composition of $x\mathrm{ZnO} \cdot (57.0 - x)\mathrm{CaO} \cdot 35.4\mathrm{SiO_2} \cdot 7.2\mathrm{P_2\text{-}O_5} \cdot 0.4\mathrm{CaF_2}$ (where $x = 0.0$, 0.7, 3.6, 7.1 or 14.2 mol.%), as shown in Table 1, using a conventional melt-quenching technique. Batch mixtures of these compositions were prepared from ZnO, $CaCO_3$, SiO_2, $CaHPO_4 \cdot 2H_2O$ and CaF_2 (Nacalai Tesque Inc., Kyoto, Japan). The reagent $CaHPO_4 \cdot 2H_2O$ was pre-heated at 1000 °C for 4 h to obtain $Ca_2P_2O_7$, which was then used. The powder mixture was put into a platinum crucible and heated in a $MoSi_2$ furnace at 1450 °C for 2 h. The molten material was poured onto a stainless steel plate to be quenched. Transparent glasses were obtained for all compositions.

The thermal properties of these glasses were examined by differential thermal analysis (DTA, TG-DTA2020S, MAC Science Co., Tokyo, Japan) from room temperature to 1000 °C at a rate of 5 °C/min.

The obtained glasses were pulverized to a particle size of less than 45 μm. Compacts of the glass powders approximately 16 mm in diameter and 2 mm in thickness were heated up to 930 °C at a rate of 5 °C/min and held at this temperature for 4 h for sintering and crystallization, followed by natural cooling in the furnace. Their surfaces were polished with No. 2000 silicon carbide abrasive paper. The surface structures of the glass–ceramics were examined by thin-film X-ray diffraction (TF-XRD, MXP3V, MAC Science Co.) and scanning electron microscopy (SEM, S-3500N, Hitachi, Tokyo, Japan).

2.2. Soaking in SBF

In order to estimate the bioactivity of the glass–ceramics obtained, they were soaked in 40 mL of a simulated body fluid (SBF) at pH 7.25 with ion concentrations nearly equal to those of human blood plasma at 36.5 °C, following the procedure reported by Kokubo et al. [11,12]. The composition of SBF, in comparison with that of human blood plasma, is shown in Table 2. Apatite formation on bioactive materials in the body can be reproduced in SBF. The surface structures of the glass–ceramics were examined before and after soaking in SBF, by TF-XRD and SEM.

The elemental concentration of SBF after soaking the glass–ceramics was examined by inductively coupled plasma atomic emission spectroscopy (ICP, Optima 2000DV, PerkinElmer, Boston, MA, USA), in order to examine the chemical durability of the glass–ceramics and their zinc release.

Table 1
Compositions of prepared glasses

Notation	Composition (mol.%)				
	ZnO	CaO	SiO_2	P_2O_5	CaF_2
Zn0	0.0	57.0	35.4	7.2	0.4
Zn0.7	0.7	56.3	35.4	7.2	0.4
Zn3.6	3.6	53.4	35.4	7.2	0.4
Zn7.1	7.1	49.9	35.4	7.2	0.4
Zn14.2	14.2	42.8	35.4	7.2	0.4

Glass–ceramic A–W: $7.1\mathrm{MgO} \cdot 49.9\mathrm{CaO} \cdot 35.4\mathrm{SiO_2} \cdot 7.2\mathrm{P_2O_5} \cdot 0.4\mathrm{CaF_2}$ (mol.%).

Table 2
Ion concentrations of human blood plasma and simulated body fluid (SBF)

Ion	Concentration/mol m^{-3}	
	Blood plasma	SBF
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	103.0	147.8
HCO_3^-	27.0	4.2
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

3. Results

Fig. 1 shows the DTA curve of the glass Zn7.1. Glass transition and crystallization temperatures determined from DTA results are summarized in Table 3. All the samples showed two crystallization temperatures less than 1000 °C, except for Zn0. For the sample without zinc (Zn0), two peaks might have overlapped since the exothermic peak was broad. Both the glass transition and the crystallization temperatures decreased with increasing ZnO content. The differences in crystallization temperatures

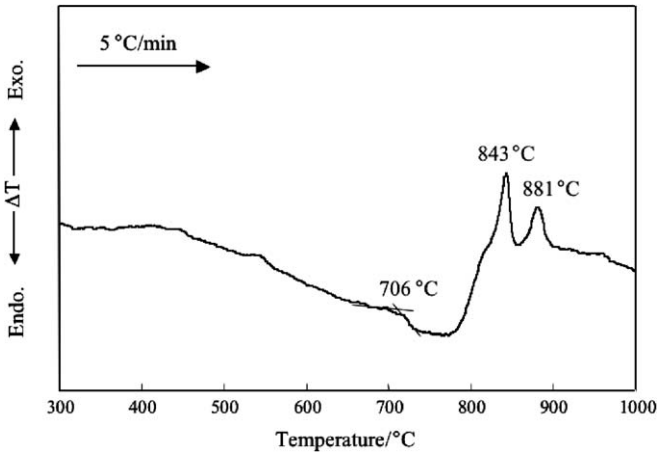

Fig. 1. DTA curve of Zn7.1.

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