Chemico-Vector and Mechanochemico-Vector Properties of Polarized Glass-Ceramic Silicophosphate of Narpsio

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ケイリン酸塩結晶化ガラス Narpsio のケミコベクトル及びメカノケミコベクトル特性

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Glass-ceramics of $\text{Na}_2\text{O}-\text{R}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ (Narpsio) consist of a skeleton structure of 12-tetrahedra-membered rings and exhibit a super Na^+ conductivity. Glass-ceramic Narpsio was proved to be electrically polarized through highly mobile sodium ions. Narpsio also shows relatively higher solubility in water. Taking into account of the water solubility and the chemical composition, the reactivity of polarized and non-polarized glass-ceramic Narpsio in the stimulated body fluid (SBF) were investigated in relation to bioactivity. After the 6 days' immersion of SBF, hydroxyapatite microcrystals aggregated semispherically were grown on the glass-ceramic Narpsio surfaces. Although the acceleration effects were under study, the growth rate was recognized to be higher in both of the negatively and positively charged surfaces. In analogy with polarized bioglasses, we confirmed the chemico-vector effects of glass-ceramic Narpsio for biomedical purpose. Additionally, glass-ceramic Narpsio, prepared by the locally biasing crystallization method, showed unreported microstructural changes of surfaces during chemical polishing with water, depending upon the direction of a biasing field. The phenomenon was interpreted as a mechanochemico-vector effect. [Recived August 22, 2005; Accepted November 17, 2005]

Key-words : Narpsio, Polarization, Chemico-vector, Mechanochemico-vector

1. Introduction

$\text{Na}_5\text{YSiO}_4^{(1),2)}$ -type sodium silicophosphates with the chemical formula of $\text{Na}_{3+3x-y}\text{R}_{1-x}\text{O}_3\text{P}_y\text{Si}_{3-y}\text{O}_9$. (R=rare earth ions) (denoted as Narpsio) are super Na^+ -conductors with a conductivity of 10^{-1}Scm^{-1} at 300°C and an activation energy of 20kJmol^{-1} .^(3)–8) Although the skeleton structure of Narpsio comprises 12- $(\text{SiO}_4)^{4-}$ tetrahedra-membered rings, the detailed structures of the glass ceramics are controllable by their nominal composition and condition of crystallization.^(3)–7)

Glass-ceramic Narpsio bears similarity in chemical formula to bioactive glasses and exhibits much higher electrical conductivity and relatively higher solubility in distilled water. Therefore, the glass-ceramic Narpsio could be electrically polarized at relatively lower temperature and intensity of the electrical field and has been supposed to be a candidate of bioabsorbable ceramic. The absorption rate was recognized to be controllable by both of its chemical composition and crystallization condition. Moreover, during crystallization process, application of electrical bias to the Narpsio could change into graded materials. In the present study, Na_5YSiO_4 -type glass-ceramic Narpsio (gc: Narpsio) has been developed as a candidate for a novel bioresorbable material. Moreover, the high ion conductivity leads us to the possibility of electrical polarization. Polarization is important in biomaterials, since we have more recently demonstrated by *in vitro* and *in vivo* tests that the charged surfaces of electrically polarized hydroxyapatite^(9),10) acquired enhanced osteoconductivities.^(11)–13) This study will demonstrate the electrical polarizability and *in vitro* biocompatibility or chemico-vector effect of gc: Narpsio.

In the development of Narpsio for a novel biomaterials, gc:

Narpsio crystallized in a local field was found to show two different mechanochemical reactions, depending upon the direction of the biasing field. The phenomenon can be classified as a mechanochemico-vector effect, which will also be shown in this report.

2. Experimental

Starting glasses were prepared from reagent-grade powders of Na_2CO_3 , Y_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, and SiO_2 according to the literature.⁽⁸⁾ The mixed powders of appropriate compositions were calcined at 900°C for 1 h, and then, melted at 1350°C for 1 h. The melts were quenched by pouring into a graphite die, and then, annealed at 500°C for 8 h. Crystallization procedure was carried out according to the previous reports.^(5),6) Some of the obtained bulk glasses were heated at an increasing rate of *ca.* $100^\circ\text{C}\cdot\text{h}^{-1}$ to the temperature of 50°C above the glass transition point. After being annealed for 1 h, the specimens were heated at 1100°C for 1 h, and then, slowly cooled in a furnace to room temperature (*RT*). The obtained glass-ceramic specimens were polished with diamond disks of 30, 15 and $6\mu\text{m}$ in turn for further experiments. The other bulk glasses were electrically biased with 50Vcm^{-1} throughout during crystallization up to 900°C (**Fig. 1**),⁽⁶⁾ then subjected to polishing after cooled down to room temperature. For observation of a mechanochemical effect, these specimens were not polarized.

Electrical polarization was undertaken on the specimens with a pair of platinum electrodes according to the previous report.⁽¹⁰⁾ Platinum wire was attached to each of the electrodes. The wires insulated with $\alpha\text{-Al}_2\text{O}_3$ dense tubes were shielded with a stainless steel pipe. A measurement cell was placed in an electric furnace equipped with non-inductive

Fig. 1. Narpsio glass (a) and Narpsio glass-ceramic (gc: Narpsio).

coaxial heating elements. The specimen temperature was measured by a chromel-alumel thermocouple next to the specimen. During the polarization, the specimens were heated in air at 300°C for 1 h at the polarization temperatures at a heating rate of 100°C·h⁻¹ and then cooled to *RT* at a rate of *ca.* 100°C·h⁻¹. A d. c. electrical field was applied from the polarization temperature to *RT* using a Hewlett-Packard E3620A power supply. After the electrodes were short-circuited at *RT* for a sufficient time, the thermally stimulated current (TSC) measurements were carried out in air from *RT* to 750°C at a constant heating rate of 2.0°C·min⁻¹. The TSC method¹⁴⁾ involves the polarization of the samples by a static field at high temperature. The sample is then cooled to a temperature at which the external field is removed and heated at a constant rate. A current corresponding to dipole relaxation is recorded as a function of time and temperature. The depolarization current was measured with a Hewlett-Packard 4140B pA meter. All of the instruments were networked with an IEEE488 interface and controlled and monitored with a personal computer. The data were later analyzed with the appropriate software.

The reactivities on the surfaces of the polarized and the non-polarized gc: Narpsio were evaluated by immersing in simulated body fluid (SBF). The SBF with ion concentrations nearly equal to those of human blood plasma was prepared using the technique described by Kokubo¹⁵⁾ for precipitation of bone-like apatite. Specimens were immersed in 10 cm³ of SBF in plastic bottles at 37°C up to 6 d. The immersed samples were then removed from the SBF solutions and washed with distilled-deionized water. The obtained specimens were dried at *RT* for microstructural observations.

For the study of mechanochemical property, water-polished surfaces of polarized non-polarized gc: Narpsios as well as local-filed biased gc: Narpsio's (Fig. 1) were subjected to SEM observation. Polishing for SEM was carried out using diamond disk of 30 down to 6 μm in diameter with distilled water.

3. Results and discussion

3.1 Characterization

The obtained glass-ceramics were white opaque and had homogeneous appearance without any inclusion. The crystalline phase was verified to be Na₅YSiO₄-type single-phase by XRD analysis (Fig. 2). All the glass-ceramic specimens, whether or not crystallized under biasing field, were identified as a Na₅YSiO₄-type single phase in an XRD analytical accuracy.

The TSC curve (Fig. 3) of the polarized gc: Narpsio increased at *ca.* 100°C and showed noticeable 4 peaks at *ca.* 172, 350, 451, 620 and 730°C. The polarization charge calculated from numerical integration of the TSC spectrum was 55 mCcm⁻¹. According to the previous reports,^{4),5)} the ionic conduction through grain boundary was detectable above 195°C.

Fig. 2. XRD pattern of gc: Narpsio.

Fig. 3. TSC spectrum of gc: Narpsio electrically polarized at 300°C.

The first-peak temperature fairly agreeing with the characteristic temperature about conduction was interpreted to be the threshold temperature of transport length expanding of sodium ions. The third (451°C) and the fourth (620°C) temperatures giving peaks coincided with the glass transition and the crystallization temperatures reported in the literatures,^{4),5)} respectively. The fifth and largest peak was attributed to the relaxation of the Na⁺ ions shifted by the polarization treatment. Although the phenomena corresponded to the second peak at 350°C was not yet completely analyzed, the peak was attributable to structural changes and/or relaxations caused by thermal stimulation. The stored charge was recognized to be huge, compared to the polarized hydroxyapatite ceramics¹⁶⁾ and bioactive glasses,¹⁷⁾ and was attributed to the high electrical conductivity of gc: Narpsio. Taking into account of mobile Na⁺ ions in Na₅YSiO₄-type Narpsio structure, the ratio of Na⁺ ions taking part in polarization can be estimated as 100 ppm to 0.1% of all Na⁺ ions, including immobile ones, in the structure. This will be further mentioned to below.

3.2 Chemicovector effect

The negatively and positively charged surfaces of the electrically polarized gc: Narpsio's are denoted as *N*-surface and *P*-surface, respectively. The surface of the non-polarized gc: Narpsio is denoted as 0-surface.

Morphologies of overgrown crystals on gc: Narpsio surfaces after the immersion in SBF for 6 d are shown in SEM photographs (Fig. 4). The XRD patterns of the immersed gc: Narpsio surfaces including a small 002 peak and a broad peak assignable to 211, 112 and 300 reflections of hydroxyapatite.

Fig. 4. Morphologies of overgrown crystals on gc: Narpsio after immersed in SBF 6 d; *N*-surfaces (upper left), *P*-surfaces (upper right), and *O*-surfaces (lower left). Scale bars indicate 100 μm . Insets of highly magnified photographs (Scale bars indicate 1 μm) showed that overgrown layers consisted of nanosized crystals. XRD pattern (lower right) of overgrown layer on *N*-surface.

The overgrown crystals were densely aggregated and formed layer structures with cracks, while the thickness was varied in accordance with surface charges. The thickness was not able to be statistically compared because of wide deviations of estimated values from SEM observation. The unclearness was attributed to the high solubility of the gc: Narpsio. The concealment of surface charge effects by high solubility was reported in the case of bioactive glass of 45S5 type.¹⁸⁾

In the *N*-surfaces, the layered overgrown deposits were observed with semispherical grains of 10–50 μm in diameter. The thickness was recognized to indicate the highest value among the surfaces, based on an estimation from the step thickness of peeled off overgrowth layers. The grains were homogeneously sporadic on the entire layers. Based on the highly magnified SEM images, the layer consisted of 50–100 nm granular crystals. In the *P*-surfaces, the layers were remarkably porous, compared to the *N*-surfaces. The diameter of the pores found in the entire layers was ranging from 0.5 to 3 μm . No semispherical grain was found in any views. The nanosized crystals forming the layers were similar to those in the *N*-surfaces. In the *O*-surfaces, the overgrown layers were porous, similar to the *P*-surfaces, and together with the semispherical grains, similar to the *N*-surfaces. The few number of the cracks revealed that the overgrown layers were thin. The nano-sized crystals were same as those of the other surfaces in size but different in shape. The shape of the crystals was tabular, while the dominant face and crystallographic direction were unclear. The effects of the electrical polarization were obvious in nano and micro structures of the overgrown crystals, while the influences on the growth rate of the crystals were not well delineated. The gc: Narpsio indicated the for-

mability of apatite crystals in SBF regardless to the electrical polarization and gave rise to the view that gc: Narpsio was osteoconductive and capable to apply to biomedical devices.

3.3 Mechanochemico-vecro effect

The polarization and locally biased crystallization were phenomenologically proved to have significant influences on the mechanochemical reaction (Figs. 5a–e): Figure 5 demonstrates the different mechanochemical reactions on *N*-, *P*- and *O*-surfaces. Although a small amount of whiskers were projected on *O*-surface, *N*-surface promoted overall the growth of whiskers with 5 μm length and 1 μm diameter, and there were reversely very few whiskers on *P*-surface. Although we attempted to identify the whiskers by XRD, the analysis has not yet been completed so far because of the limited quantity of grown whiskers in the present study. Although estimation of the amount of the migrated Na^+ ions was difficult because of their nonuniform spatial distribution after the crystallization process with the bias, the amount must be small enough to preserve the skeleton structure of Narpsio.

The difference in whiskers growth was also observed between the parallel and perpendicular surfaces (denoted as // and $\perp$ -surfaces, respectively) to the applied dc field of Narpsio crystallized under biasing field (Figs. 5d and e): The whiskers with 5 to 10 μm in length were densely observed on // surface, whereas there were whiskers on $\perp$ -surface.

The above mentioned phenomena are presently attributed to some mechanochemical reactions of surfaces with different chemical compositions derived by polarization. As both polarization and biasing crystallization take place due to mobile Na^+ ions in Narpsio, polarized and biasing crystallized states are considered to correspond to local fluctuation in the

Fig. 5. Morphologies of electrically polarized surfaces (a: *N*-surfaces, and b: *P*-surfaces), non-polarized surfaces (c), and locally biased surfaces (d: surfaces parallel (//) and e: surfaces perpendicular ($\perp$) to bias direction). Insets indicate higher magnified images.

concentration of Na^+ ions. In the case of polarized surface, the concentration is considered as

$$P\text{-surface} > 0\text{-surface} > N\text{-surface}.$$

Biasing crystallization is thought to give rise to the Na^+ concentration fluctuation as

$$\perp\text{-surface} > //\text{-surface}.$$

Because of the decrease of Na^+ ions, the structural rigidity of both *N*- and *//*-surfaces were degraded to decomposition through a mechanochemical reaction with water during mechanical polishing. Generally, superionic conductors such as β -alumina, Nasicon and Narpsio tend to be water soluble because of mobile Na^+ ions. These phenomena can be classified as mechanochemico-vector effect.¹⁹⁾

4. Conclusion

Glass-ceramic Narpsio of a super sodium ion conductor was proved to be electrically polarized. The effects of the electrical polarization were obvious in morphologies of the overgrown crystals, while those on the growth rate were vague. Based on the SBF tests, glass-ceramic Narpsio was recognized to be

osteoconductive regardless to the electrical polarization.

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