Transactions of the Materials Research Society of Japan 25 [1] 173-176 (2000)

Electrovectorial Effect of Poled Bioceramics on Dissolution and Crystallization

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In order to understand an effect of polarized hydroxyapatite (HAp) on crystallization and dissolution, growth phenomena of K_2SO_4 crystal on HAp ceramics were investigated as well as dissolving phenomena of HAp. The HAp ceramics polarized under dc fields of 1-8kV/cm at 300-500°C for 1h were immersed in a saturated alum ($KAl(SO_4)_2 \cdot 12H_2O$) basic solution with KOH at 60°C. During the solution cooled down to room temperature, K_2SO_4 crystals educed spontaneously and grew on surfaces of the HAp ceramics. The amount of crystals grown on the negatively charged surface was apparently larger than that on the positively charged one. This observation proved that HAp ceramics could have the ability to control the crystal growth by the polarization treatment. Polarized HAp ceramics also were immersed in a saturated alum ($KAl(SO_4)_2 \cdot 12H_2O$) acidic solution for investigation of dissolution phenomena.

Key words: ceramics, polarization, hydroxyapatite, crystal growth, dissolution

1. INTRODUCTION

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAp), a crystallographical analogue to calcified tissues of vertebrates, has been well developed as an implant material because of its outstanding biocompatiblity[1]. HAp also attracts great interest as candidate for its application to such fields as a liquid chromatographic column for the separation of proteins and nucleic acid, a catalyst for dehydration or dehydrogenation of some alcohol, powder carriers for removing heavy metal ions and chemical sensors for various gasses.

Recently, Yamashita *et al.* [2] reported that acceleration and deceleration of bone-like crystals grown in the simulated body fluid (SBF) were observed on the negatively charged surface (N-surface) and the positively charged one (P-surface) of HAp ceramics treated by electrical polarization, respectively. Biological behavior was also estimated by the cultivation of osteoblastic and fibroblastic cells on the surface of polarized HAp ceramics [3]. Cultured cells were found on the grown bone-like crystal layers for N-surface, while the cells were directly on the P-surface. Ohgaki *et al.* [3] reported, moreover, that N-surface of HAp ceramics had more adhered cultured cells than the P-surface. There is no description on the complete clarification of these phenomena under now. The investigation of these above-mentioned observations is very important in order to discover new potential function of HAp ceramics, and will lead to create a novel material processing [4].

In this paper, the authors mainly demonstrate heterogeneous growth phenomena on polarized HAp ceramics using K_2SO_4 crystallization. Effects of polarization treatment on crystallization will be discussed by reference to bone-like crystal (homogeneous) growth phenomena [2]. Using acidic $KAl(SO_4)_2 \cdot 12H_2O$ (mineral name; alum) solution, an observation of dissolution phenomena on polarized HAp ceramics is also described.

2. EXPERIMENTAL PROCEDURES

Materials

HAp powders were prepared by a precipitation reaction from calcium hydroxide and phosphoric acid. A suspension of calcium hydroxide was stirred and a solution of phosphoric acid was added in drop to product a gelatinous precipitate. The obtained slurry was filtered, dried, and calcined at 850 °C for 2h. The resulting powders were finely ground under 200 mesh. HAp ceramics were obtained by sintering of HAp powders at 1250 °C for 2h. The H_2O vapor stream was used as the sintering ambience in order to prevent the dehydration of HAp during heating [5]. The obtained HAp ceramics were characterized by X-ray diffracto-metry (XRD), infrared spectroscopy (IR), and scanning electron microscopy (SEM).

Methods

Specimens for immersion experiment were disk-like shape with 10mm in diameter and 0.7mm in thickness. These specimen were sandwiched between platinum plates, heated up to 300-500°C in air, then subjected to the polarization treatment in dc fields of 1-8kV/cm for 1h, and thereafter cooled to room temperature under polarization. The thermally stimulated depolarization current (TSDC) method [6-8] was applied as a technique for confirming the polarization treatment. Polarized HAp specimens were immersed in a saturated alum+KOH solution with pH=11-13 at 60°C. KOH was added to prevent the dissolution of HAp ceramics. During the solution cooled down to room temperature, crystals educed spontaneously and grew on surfaces of HAp ceramics. The crystalline grown on HAp ceramics was analyzed by XRD, SEM, and electron dispersive spectroscopy (EDS). Moreover, polarized HAp specimens also were immersed in a saturated alum solution with pH=3 at 60 °C for 12h. The etched surfaces were observed analyzed by XRD and SEM.

3. RESULTS AND DISCUSSION

3.1. Preparation of polarized HAp ceramics

HAp ceramics used in this study were confirmed as pure HAp phase by XRD and IR. The relative density of the HAp ceramics was approximately 96 %. The grain size was identified as 1-3μm by SEM observation. No difference of XRD profiles, IR spectra and SEM analyses was observed between non-poled HAp ceramics and those polarized under a dc field of 6kV/cm at 400 °C for 1h.

Fig.1 shows the TSDC profile of the HAp ceramics for immersing experiment, which was polarized under a dc field of 8kV/cm at 500 °C for 1h. The TSDC spectrum has high peak (20μA/cm^2) at around 700°C, and showed that relaxation of polarization was carried out in the HAp ceramics by heating. Although the mechanism of polarization in HAp at high temperature was discussed in ref.[8], the detail was not cleared under now.

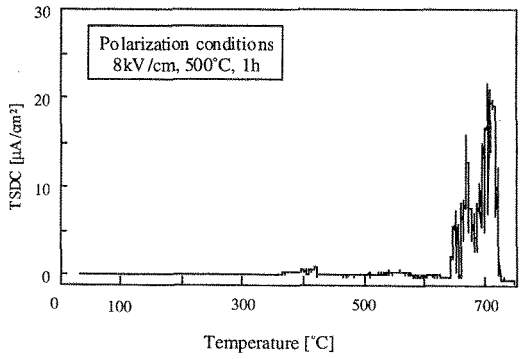

Fig.1 Thermally stimulated current profiles of the HAp ceramics, which was polarized under a dc fields of 8kV/cm at 500°C for 1h, measured at the heating rate 2°C/min.

3.2. Crystallization phenomena

A substance was confirmed by SEM observation to be adhered on all surfaces of the HAp ceramics after immersion. The result of EDS showed that crystals grown on the HAp surfaces consisted of K_2SO_4 phase. Although we firstly attempted to observe the effect of polarization treatments on crystallization of alum, K_2SO_4 precipitated instead of the desired crystals from alum solutions with high pH. However, since this result was not so important for our essential purpose of this study, the saturated alum+KOH solutions were used.

Fig.2 phenomenologically demonstrates the effect of polarization on the crystal growth on the HAp ceramics after immersed in the alum+KOH solution with pH=13 for the cooling time 24h. Small K_2SO_4 crystals with the dimension of ~1μm were observed on non-polarized HAp ceramics surface

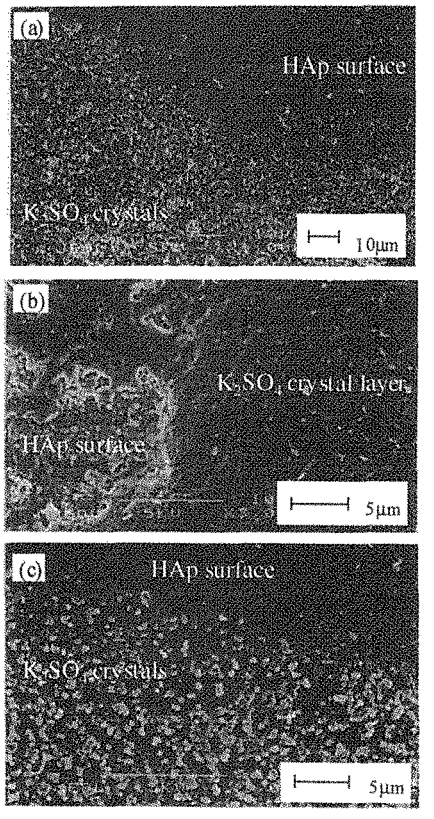

Fig.2 Scanning electron micrographs of (a) non-polarized, (b) negatively and (c) positively polarized surfaces of HAp ceramics specimens immersed in the alum+KOH solution with pH=13 for 24h (cooling from 60 to 6°C).

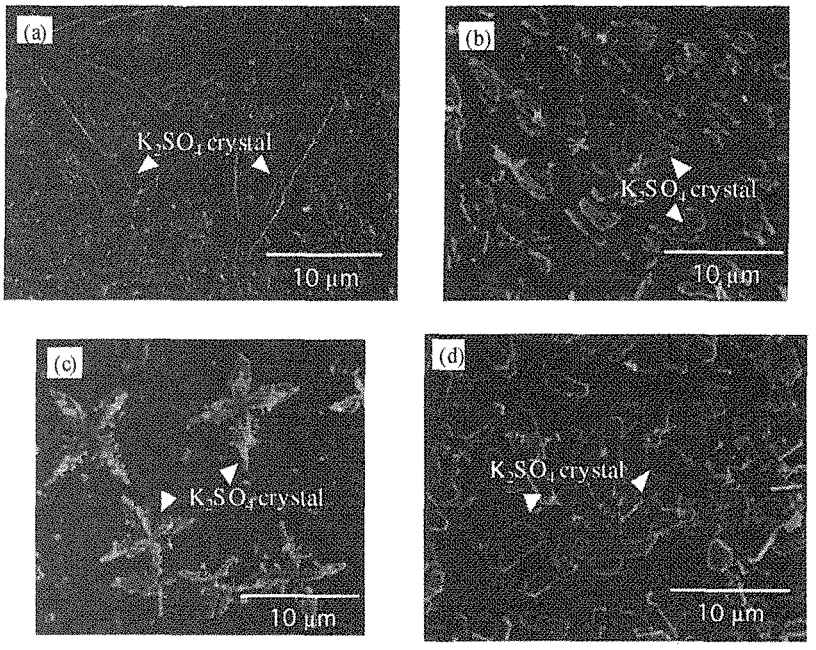

Fig.3 Scanning electron micrographs of K_2SO_4 crystals grown on (a) non-polarized, (b & c) negatively and (d) positively polarized surfaces of the HAp ceramics specimens immersed in the alum+KOH solution with pH=11 for 72h (cooling from 60 to 6°C).

(Fig.2a). K_2SO_4 crystals had two kinds of shapes; rectangular parallelepiped and scaled ones. These features were very similar to the observation on P-surface of HAp ceramics (Fig.2c). On the other hand, K2SO4 crystals were in layers on N-surface (Fig.2b). The amount of crystals grown on N-surface were apparently lager than others. The acceleration of crystal growth, therefore, was identified on the N-surface of the HAp ceramics.

K_2SO_4 crystals grown on surfaces of HAp ceramics, which were immersed in the alum+KOH solution with pH=11 for the cooling time 72h, were shown in Fig.3. Sword-like crystals with ~10μm in length (Fig.3a) were observed mainly on non-polarized HAp ceramics. These sword-like crystals were also identified on N-surface but not on P-surface. Moreover, on N-surface, K_2SO_4 crystals with scale-like (Fig.3b) and dendritic (Fig.3c) shapes were observed. These two shapes were not found on other surfaces. Aggregations of idiomorphic K_2SO_4 crystals, which belongs to the orthorhombic symmetry at <587°C [9], were observed only on P-surface. Since dendritic crystals were produced at a higher growth rate [10], it was cleared that the crystallization on the N-surface of the HAp ceramics were evidently accelerated compared with other surfaces. This morphological change seemed to be considerably attractive, because this result would lead to the synthesis of crystal with desired orientation and shape without using substrate.

The above results agreed well with bone-like crystal growth on polarized HAp ceramics in SBF

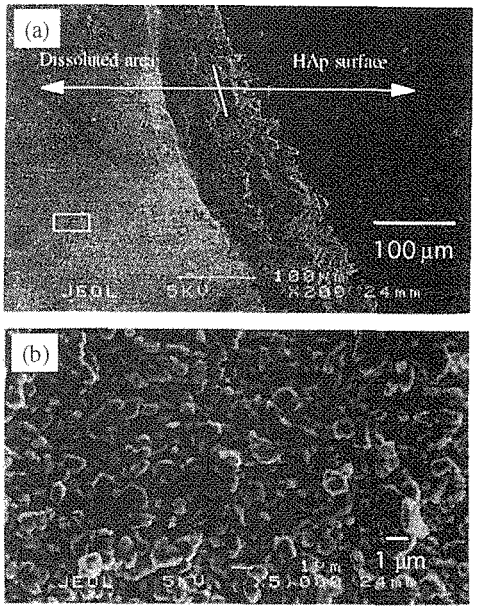

Fig.4 Scanning electron micrographs of non-polarized surfaces of the HAp ceramics specimens after immersed in the Alum solution with pH=3 for 12h (cooling from 60 to 30°C). The enlarged photo (b) is a part of open rectangle in the micrograph (a)

[2]. The accelerated and decelerated growth models proposed in ref.[2] are summarized as follows;

(i) On N-surface, metallic cations are more rapidly adsorbed than other surfaces. Nucleation takes place among these

supersaturated ionic groups, and the remaining dipole moments accelerate the growth of nuclei due to the attraction of these ions.

(ii) On P-surface, chloride ions appear to be mainly adsorbed, which may be unfavorable for crystal growth.

On the basis of this model, in this study, K^+ ions were predominantly adsorbed on N-surface compared with others. Therefore, on N-surface, it was presumed that the nucleation and growth rate were accelerated, and then that dendritic K_2SO_4 crystals were grown.

3.3. Dissolution phenomena

Fig.4 shows the surface of non-polarized HAp ceramics specimens immersed in the alum solution with pH=3 for 12h during cooling from 60 to 30°C. It was found that HAp dissolved in this solution (Fig.4a) and original grains appeared on the etched surface (Fig.4b). The dissolved distance was approximately 100μm. These features of non-polarized HAp ceramics were not different from those of N- and P-surfaces. Since the dissolving rate was too high to detect the difference of dissolution phenomena on each surface, optimum solution and immersion time would be necessary. This immersion experiment is now under further study.

4. CONCLUSION AND OUTLOOK

To clarify an effect of polarization treatments on crystallization over bioceramics, an attempt was made to grow heterogeneous crystals on surfaces of the HAp ceramics. The results showed that acceleration and deceleration of K_2SO_4 crystals grown in alum+KOH solution were observed on N- and P-surfaces of the HAp ceramics, respectively. Polarized HAp ceramics, moreover, were immersed in a saturated alum acidic solution, and investigated for understanding the effect on dissolution.

It is noted that our results in this study seem to be important, because HAp ceramics could have the ability to control the heterogeneous crystal growth through simple treatment process such as the electrically polarization. These results should be considered as a novel material processing, which brings out the latent faculties in conventional and well-known dielectric materials. Real applications for such material shown in this study are not evident at present. However it is assumed that ideas related to develop new smart materials for medical, environmental and biochemical applications, etc.

ACKNOWLEDGEMENT

This work was financially supported by Grant-in-Aid for General Scientific Research (A)-10305047, (C)-11650855 and (C)-10895015 of the Ministry of Education, Science and Culture of Japanese Government. The authors would also like to express their thanks to Kato Kagaku Shinko-kai for the supply of the grant for their study.

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(Received December 16,1999 ; Accepted January 31,2000)