Transactions of the Materials Research Society of Japan 29[6] 2683-2685 (2004)

SBF evaluation of bioactivity of polarized ceramic apatite solid solutions

Keiichirou Shinohara, Satoshi Nakamura, Nobuo Kieda*, and Kimihiro Yamashita
Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10, Surugadai, Kanda, Chiyoda, Tokyo 101-0062, Japan
Fax: 81-3-5280-8005, e-mail: yama-k.bcr@tmd.ac.jp
Shonan Institute of Technology, 1-1-25, Tujidounishikaigan, Fujisawa, Kanagawa 251-8511, Japan
Fax: 81-466-36-1594, e-mail: kieda@mate.shonan-it.ac.jp

ABSTRACT
Formation rate of the bone-like apatite layer can be controlled on electrically polarized ceramics: Bone-like apatite formation was accelerated on negatively charged surfaces of the electrically polarized hydroxyapatite ceramics, while the formation was decelerated on positively charged surfaces. Pure (HAp) and yttrium-doped (Y-HAp) hydroxyapatite ceramics were obtained by sintering at 1250°C under H_2O vapor atmosphere. These ceramics were sandwiched between platinum electrode plates, and then, electrically polarized in a direct current field. The polarized Y-HAp ceramics was depolarized at temperatures of 100° to 400°C. The stored electrical charge estimated from the integration of the TSDC spectrum with respect to time was $0.4\mu C\cdot cm^{-2}$. In the SBF immersion experiment, the bone-like apatite formation was accelerated on the negatively charged surfaces of the polarized Y-HAp ceramics but decelerated on the positively charged surfaces of the polarized Y-HAp ceramics, compared with the non-polarized surfaces of Y-HAp. The tendency of the Y-HAp was almost similar to HAp. Therefore, the Y-HAp should be applicable to novel biomaterial device.
Key words: hydroxyapatite, yttrium, SBF, polarization

1. INTRODUCTION

Bioactive materials have been well known to bond directly to living bone in the body via formation of bone-like apatite layer on their surfaces. Hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$) ceramics were noted in terms of electrically controllability. We have investigated the electrically characteristics of the surfaces of polarized HAp.[1,2] Moreover, we discovered that the electrostatic force of polarized HAp ceramics influenced the surrounding cells, bacteria and ions.[1-6] The polarized HAp ceramics controlled for the bone-like apatite layer formation in simulated body fluid (SBF).[1] Cultivation experiments of osteoblast-like cells on negatively charged surface of polarized HAp have demonstrated that both cell adhesion and cell growth, and accelerate of bacteria proliferation.[3,4] Moreover, *in vivo* examination, the electrically polarized HAp was enhanced of direct born bonding and new born formation.[5,6] Apatite solid solutions can accommodate oxygen ions and considerable amount of hydroxyl vacancies beside native hydroxyl ions at the lattice sites along the c-axis surrounded ions by cations.[7,8] The ionic conduction properties were established of the predominated conductions of protons and the mixed conduction of protons and oxygen ion in various apatite solid solutions.[8] HAp doped with yttrium was reported that osteoblast adhesion was increased.[9] Here we report that phenomena of the electrostasic force of polarized Y-HAp ceramics for bone-like apatite formation.

2. EXPERIMENTS

HAp and yttrium-doped hydroxyapatite (Y-HAp: $[Ca_{10-x}Y_x](PO_4)_6\ [(OH)_{2-x-2y}O_{x+y}\square_y]$powder were synthesized by precipitation method. Phosphoric acid was dropped, pH of solution was kept at 10.5 by dropping NH_4 solution. The reactant slurry was filtered, dried by freeze drying for 24 h, and calcined at 850°C for 2 h. The obtained powder was identified as a single phase of HAp by X-ray diffraction (XRD; Phillips PW1700). The HAp powder was finely ground to under 200 mesh, and formed to the pellets for approximately 140MPa pressure. Dense HAp ceramics were obtained by sintering of HAp green pellets at 1250°C for 2 h under H_2O vapor atmosphere. The shape of dense ceramics was disk of 1.1 mm in diameter and 0.7 mm in thickness. The specimens were sandwiched between platinum electrode plates, heated to polarization temperature of 300°C in air and electrically polarized in a dc field of $5.0kV\cdot cm^{-1}$ for 1 h (Fig.1). The samples were cooled at room temperature during polarization treatment. The negatively charged surface and positively charged surface of the polarized HAp ceramics were denoted as N-surface and P-surface, respectively. A part of these specimens were used thermally stimulated depolarization current (TSDC) measurement to confirm the stored charge of the surface. The surface of the HAp ceramics without polarization was denoted as 0-surface. The bioactivity on the surface of polarized HAp ceramics was evaluated for simulated body fluid (SBF), which has nearly equal ion concentrations and pH to those of the human blood plasma immersion test. Each specimen was immersed in 30 ml of 1.5 times SBF in bottles at 36.5°C.

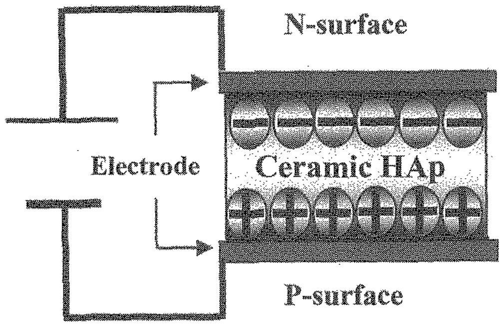


Figure 1. Schematic illustration of sample arrangements for electrical polarization.

3. RESULTS AND DISCUSSION

The XRD patterns of the obtained HAp and Y-HAp specimens consisted of a single phase of HAp as shown in Fig.2.

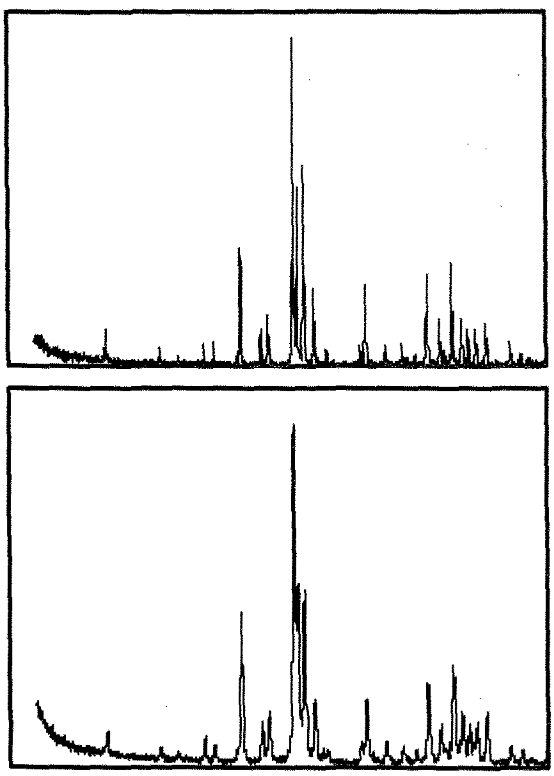


Figure 2. XRD patterns of HAp and Y-HAp ceramics sintered at 1250°C for 2 h. (a):ceramic HAp, (b): ceramic Y-HAp

After polarization, the stored charge surface of Y-HAp was confirmed for TSDC measurement (Fig.3). The polarized Y-HAp ceramics was depolarized at temperatures of 100° to 400°C. The TSDC curve of the polarized Y-HAp ceramics increased at 100°C and reached first peak point, and increased again for the maximum point, and then gradually declined the stored electrical charge estimated from the integration of the TSDC spectrum with respect to time was 0.4μC·cm^{-2}.

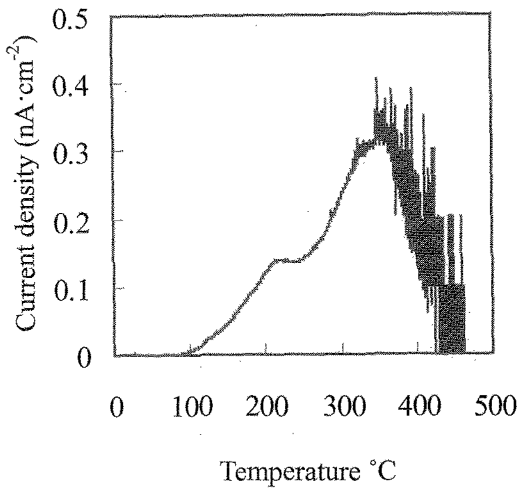
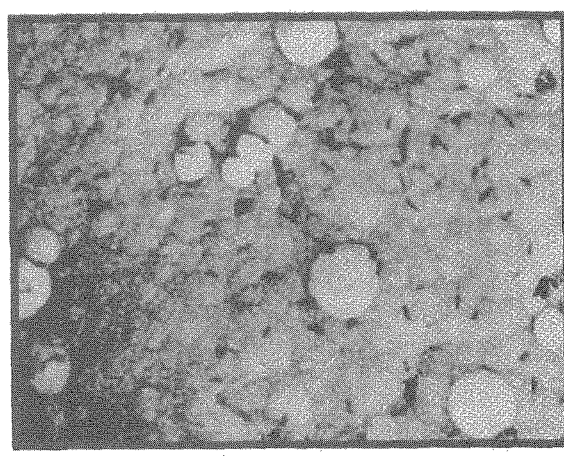


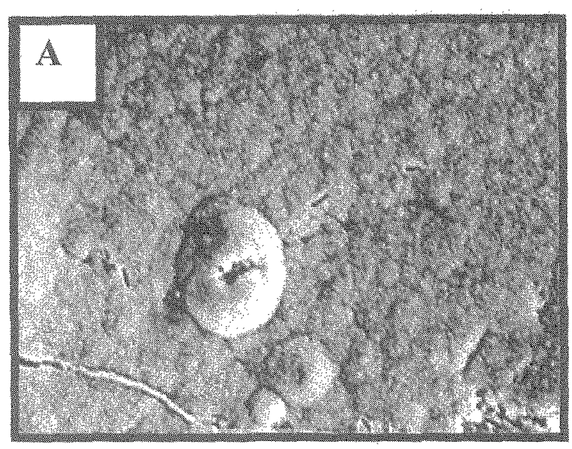
Figure 3. TSDC spectrum of Y-HAp ceramics polarized in dc field of 5kV·cm^{-1} for 1 h at 300°C.

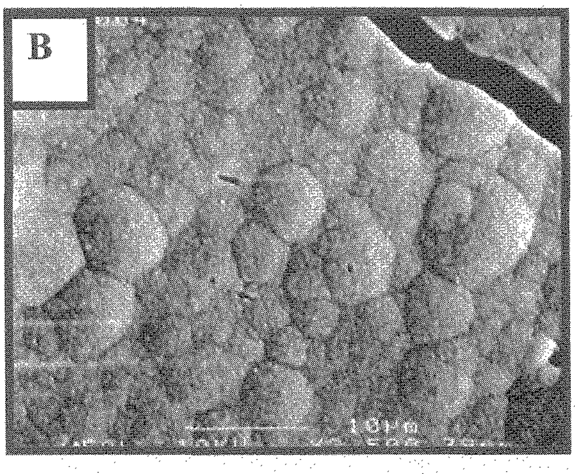
Fig.4. show SEM photograph of the surface of HAp ceramics soaked in the 1.5SBF for 5days. The HAp ceramics surface was covered by deposition of bone-like apatite.

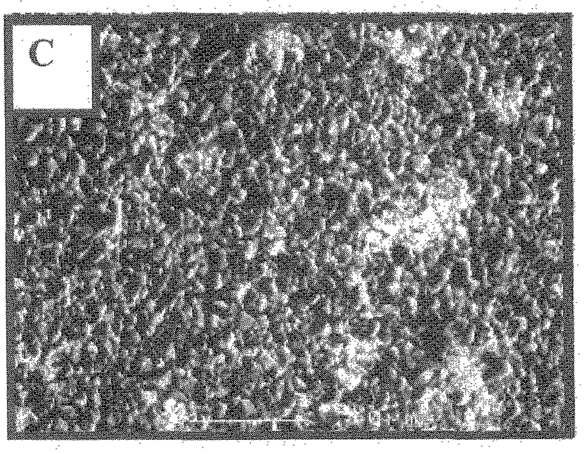


10μm

SEM photographs of the 0-, N-, and P-surfaces of the polarized Y-HAp ceramics soaked in 1.5SBF for 5days







10μm

were shown in Fig.5 (A-C). It can be seen from Fig.5 that large crystals of 4 to 10μm in diameter covered the N-surface of polarized Y-HAp. And only surface of Y-HAp ceramics could be observed in P-surface of polarized Y-HAp. As a result, the bone-like apatite formation was accelerated on the N-surface of the polarized Y-HAp ceramics but decelerated on the P-surface of the polarized Y-HAp ceramics, compared with the 0-surface of Y-HAp. Formation rate of the bone-like apatite crystal growth was almost same on the Y-HAp ceramics as HAp ceramics. It is suggested that the doped yttrium ions affect the structure of hydroxyl vacancies. Polarized treatment added values for in this character.

The tendency of the Y-HAp was almost similar to HAp. Therefore, the Y-HAp should be applicable to novel biomaterial device.

ACKNOWLEDGMENT

This work was partly supported by a Grants-in-Aid from the Japan Society for the Promotion of Science (#15360338), the Mitsubishi Foundation, the Murata Scientific Foundation, a grant for Development of Advanced Medical Technology from the Ministry of Education, Science, Sports and Culture of Japan

REFERANCE

[1] K.Yamashita, N.Oikawa, T.Umegaki, Chem.Mater., 8,2697-2700 (1996)
[2] S.Nakamura, H.Takeda, K.Yamashita, J Appl Phys., 89.5386-5392 (2001)
[3] M.Ohgaki, T.Kizuki, M.Katura, K.Yamashita., J.Biomed.Mater.Res.,57.366-373 (2001)
[4] M.Ueshima, S.Tanaka, S.Nakamura, K.Yamashita., J.Biomed.Mater.Res.,60.578-584 (2002)
[5] T.Kobayashi, S.Nakamura, K.Yamashita., J.Biomed.Mater.Res.,57.477-484 (2001)
[6] S.Nakamura, T.Kobayashi, K.Yamashita., J.Biomed.Mater.Res.,61.593-599 (2002)
[7]K.Yamashita, K.Kitagawa, T.Umegaki., J.Am.Ceram.Soc.,78.1191-1197 (1995)
[8]K.Yamashita, H.Owada, T.Umegaki, T.Kanazawa. K.Katayama., Solid State Ionics 40/41.918-921(1990)
[9] T J.Webster, C.Ergun, R H.Doremus, R.Bizios., J.Biomed.Mater.Res.,59.312-317 (2002)

(Received October 13, 2003; Accepted May 5, 2004)