

Nanoscale Activated Field on Ceramic Electret in Pseudobiological Environment

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ABSTRACT

A pseudo-biological environment using simulated body fluid (SBF) has been widely accepted as an osteobonding estimation of biomaterial surfaces. We have been demonstrated by SBF tests that the negative surface charges induced by an electrical polarization increased the overgrowth conductivity on the hydroxyapatite (HA) ceramic surface but that the positive charge diminished the overgrowth ability. Almost of the particles were deposited on each of the negatively charged ceramic substrate grain. The grain boundaries of the substrate clearly appeared as linear lacks of deposition. Therefore, the ~10 nanometer-scale morphological modification was attributed to the electrostatic force generated by the HA electret. The idea of the nano-scale activated field concerning the in vitro overgrowth should be extensible into the in vivo calcification reactions of the electrically polarized HA ceramics implanted in bone tissues.

Keywords: hydroxyapatite, simulated body fluid, surface charge, electret, electrical polarization

1 INTRODUCTION

We disclosed that hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HA) had an electrical polarizability due to proton transport [1, 2] and reported that the surface charges induced by electrical polarization affected interaction to surrounding environment. A pseudo-biological environment using simulated body fluid (SBF) has been widely accepted as an osteobonding estimation of biomaterial surfaces [3]. We have been demonstrated by SBF tests that the negative surface charges induced by an electrical polarization accelerated the overgrowth on the HA ceramic surface but that the positive charge decelerated it [1]. The enhanced osteobonding ability was revealed by in vivo implantation tests and corresponded the estimation by the SBF method [4,5]. However, it has not been clarified yet the phenomena of the microcrystal growth from SBF. In the present study, the morphologies of the deposited HA microcrystals were precisely observed on the HA electrets after SBF immersion. The nano-scale activated field was discussed in view of the electrostatic effects of HA ceramic electrets.

2 MATERIALS AND METHODS

2.1 Materials and Characterization methods

Powder of HA was prepared by a precipitation synthesis from calcium hydroxide ($\text{Ca}(\text{OH})_2$) aqueous suspension and phosphoric acid (H_3PO_4) at room temperature (RT) [6]. Suspension of calcium phosphate was precipitated by adding solution to aqueous suspension (0.5M) continuously at RT with vigorous stir using a propeller mixer. The calcium hydroxide obtained from reagent grade calcium carbonate (calcite, CaCO_3) fine powder (Wako, Japan) was dispersed in distilled water. The powder of calcium carbonate was calcined at 1100°C for 3h in air and then hydrolyzed by means of adding distilled water. The amount of phosphoric acid was adjusted so that no other phase than HA was detected in the product heated at 1100°C by XRD analysis. After the adjustment of phosphoric acid amount, the reaction suspension was aged for 4 days with continuous mixing. The obtained slurry was filtrated and then, dried at 60°C for 24 h. The powder calcined at 850°C was uniaxially pressed at 220 MPa. The pellets were sintered at 1250°C for 2 h in saturated water vapor [7]. The obtained dense HA ceramic disks with the size of 10 mm diameter and 0.7 mm thickness were identified by powder X-ray diffractometry (XRD) and FT-infrared spectroscopy (FT-IR).

2.2 Electrical Polarization Procedure and Verification Method

The HA ceramic disk cramped with a pair of Pt electrodes was polarized in air at a temperature ranging from 300 to 500°C for 1h in a dc electric field of 1 or 10 kVcm^{-1} . The thermally stimulated depolarization current (TSDC) spectra were examined with a handmade measurement cell shielded against stray field and a pico ammeter (Hewlett-Packard 4140B) from RT to 850°C at a heating rate of $5^\circ\text{C}/\text{min}$. The stored electrical charge (Q) was calculated by numerical integration from each of the measured current spectrum [2].

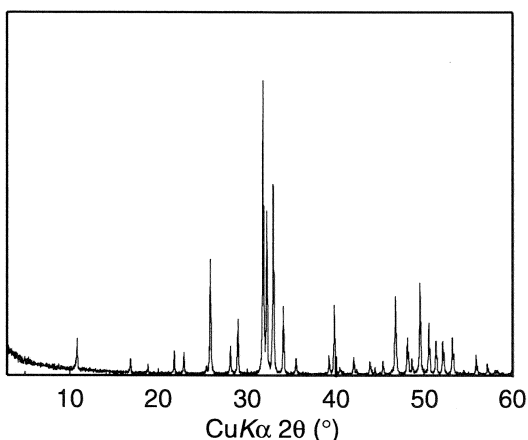


Fig.1 XRD pattern of HA ceramics.

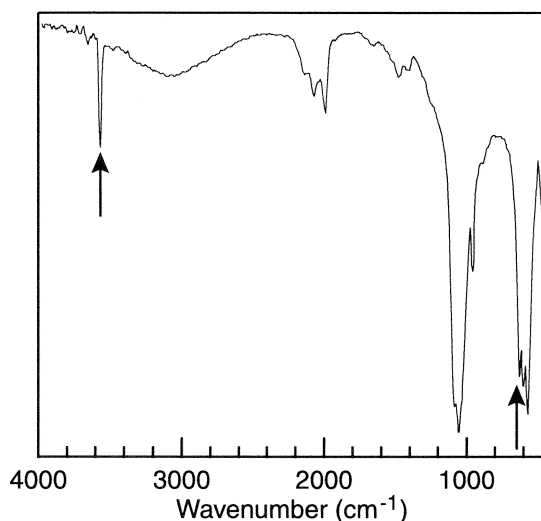


Fig.2 IR spectrum of HA ceramics. Arrows indicate OH⁻ absorption bands.

2.3 Crystal growth using SBF

The SBF with ion concentrations almost equal to those of human blood plasma was prepared according to the method described by Kokubo [3]. The HA samples were immersed in 10 cm³ of the SBF at 37.0°C up to 9 days. The immersed samples were washed with distilled-deionized water, and then dried at RT for SEM microstructure observation.

3 RESULTS AND DISCUSSION

3.1 Characterization of HA ceramics

The obtained HA ceramics had an average relative density of 98%. The mean grain size of the HA ceramics was 2 μm, based on SEM observation. The XRD pattern (Fig.1) of the HA specimen was well corresponded to the published data of HA (JCPDS No. 9-432). Therefore, it was verified that the ceramics consisted of pure HA phase.

The peaks at 3570 and 630 cm⁻¹ in the IR spectrum (Fig.2) were assigned to the stretching and bending absorptions of hydroxide ions, respectively. The wide absorption bands at 3400 and 1650 cm⁻¹ were attributed to adsorbed water.

3.2 Evaluation of stored charges

The TSDC spectra (Fig.3) of the HA ceramics polarized in a dc field of 1.0 kVcm⁻¹ at 300 and 400°C for 1h. The curve increased at ca. 180°C and reached maximum at 375 for the sample polarized at 300°C and 420°C for the sample

done at 400°C, and then decreased. The calculated charge storage (Q) was 3.92 and 15.1 μCcm⁻², respectively [8].

The TSDC spectrum showed that the polarized HA ceramics stored large electrical charges and that the decay process of depolarization was very slow. The electrical properties suggested that the electrically polarized HA was an electret [2, 8].

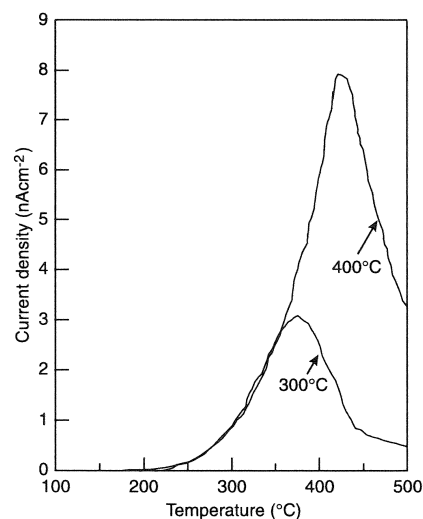


Fig.3 TSDC spectra of electrically polarized HA ceramics.

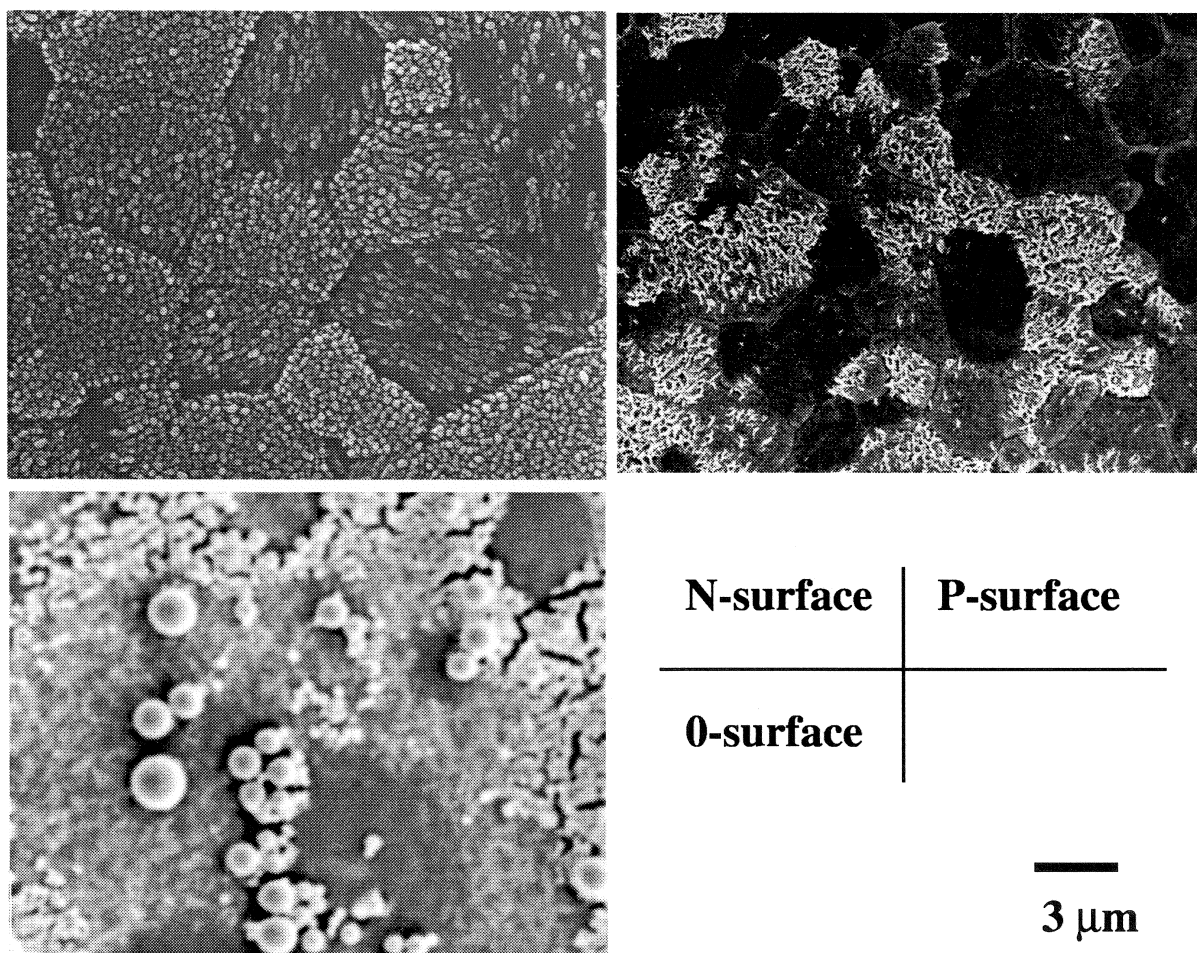


Fig. 4 SEM microphotographs of overgrown HA crystals on ceramic electrets after SBF immersion. (a) N-surface after 2days' immersion, (b) P-surface after 8days' immersion, and (c) 0-surface after 7days' immersion

The number of the migrated protons, which the electrical polarization was attributed to, was estimated as less than 0.5% of the total number in the HA ceramic substrate [2]. Moreover, no significant difference in XRD patterns and FT-IR spectra was found before and after polarization under any condition. Therefore, the chemical changes in the surface properties were possible to neglect.

3.3 Morphological observation of overgrown microcrystals

Figure 4a shows HA overgrowth on the negative charge induced surface (N-surface) of HA ceramic electret substrate after 2 days' immersion of SBF. Although no overgrown particle was found on the some part of the ceramic substrate, HA crystals with the size of *ca.* 50 nm were entirely overgrown on the N-surfaces of the ceramic

electrets. The particles were deposited on some of the ceramic substrate grain. The grain boundaries of the substrate clearly appeared as linear lacks of deposition. The majority of the overgrown crystals were spheroidal and uniformly orientated, whereas the orientation direction was not able to be decided.

Although no significant overgrown particles was observed on the positively charged surfaces (P-surfaces) after the immersion of the same duration, the tendency of the overgrowth behavior after 8 days' immersion was recognized to be similar to the N-surface (Fig.4b).

On the non-polarized surface (0-surface) of the HA ceramic substrates, many spheroidal particles with various diameter less than 3 μm were randomly aggregated after 7 days' immersion, while neither the individual overgrowth on each of the substrate grain nor the orientation of the crystals was observed on the 0-surfaces (Fig.4c).

The microstructural observation revealed that the negative surface charges accelerated overgrowth but that the positive charge decelerated it, as described in the published data [1]. Moreover, the induced surface charges of the HA electrets affected the overgrowth conductivities of the individual substrate grains. The domain phenomenon regulated by grains was not found in the overgrowth on the 0-surface. Therefore, the nanometer-scale morphological modification was attributed to the electrostatic force generated by the HA electret.

4 CONCLUSION

The microstructural observation revealed that the induced surface charges of the HA electrets affected the overgrowth phenomenon. The orientation of the crystals overgrown on the electrically polarized HA ceramic substrates demonstrated that the nanometer-scale heterogeneous nucleation was affected by electrostatic force of the charge induced surfaces.

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REFERENCES

- [1] K. Yamashita, N. Oikawa and T. Umegaki: *Chem Mater* 8, 2697, 1996.
- [2] S. Nakamura, H. Takeda and K. Yamashita: *J. Appl. Phys.* 89 5386, 2001.
- [3] T. Kokubo, *et al*: *J. Biomed. Mater. Res.* 24, 331, 1990.
- [4] T. Kobayashi, S. Nakamura and K. Yamashita: *J. Biomed. Mater. Res.* 57, 477, 2000.
- [5] S. Nakamura, T. Kobayashi and K. Yamashita: *J. Biomed. Mater. Res.* 61, 593, 2002.
- [6] S. Nakamura and K. Yamashita: *Phosphorus Research Bulletin* 11, 1, 2000.
- [7] K. Yamashita, K. Kitagaki and T. Umegaki; *J. Am. Ceram. Soc.* 78, 1191, 1995.
- [8] M. Ueshima, S. Nakamura and K. Yamashita: *Adv. Mater.* 14, 591, 2002.