POLARIZED YTTRIA-STABILIZED ZIRCONIA IMPROVES DURABILITY FOR DEGRADATION AND APATITE FORMATION IN SIMULATED BODY FLUID

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Abstract: Yttria-stabilized zirconia is currently used as an orthopedic and dental material, because of its excellent mechanical properties. In this study, we have improved the bioactivity of yttria-stabilized zirconia by a combination of electrical polarization and chemical treatment. The phase transformation from tetragonal to monoclinic ZrO_2 after alkaline treatment was inhibited on positively charged yttria-stabilized zirconia surfaces compared with negatively charged and conventional surfaces. During polarization, some oxide ions move from the positively charged surface to the negatively charged surface, leading to an increase in oxygen vacancies on the positive surface and hence greater formation of Zr-OH when this surface was exposed to alkaline solution. The bioactivity was assessed by immersing the samples in simulated body fluid and evaluating the growth of apatite on the surfaces. The combination of polarization and alkaline treatment increased the bioactivity *in vitro*.

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INTRODUCTION

Since the late 1960s, yttria-stabilized zirconia (YSZ), especially 3 mol% Y_2O_3 -doped zirconia, has been shown to be a biomaterial with excellent mechanical properties, and YSZ ceramics are currently used as ball heads in artificial hip joints and post-crowns in dental applications [1-2]. YSZ is however bioinert, meaning that no direct bonding of YSZ to natural bones occurs *in vivo*. In the present study, we have addressed this shortcoming by employing chemical treatments with the aim of increasing the bioactivity of YSZ.

We have recently demonstrated that the ceramic hydroxyapatite (HA) [3] may be polarized via proton migration [4], and that the polarized surfaces of HA enhanced tissue regeneration of both hard [5] and soft [6] tissues *in vivo*. Additionally, the polarized HA also accelerated protein adsorption [7] and cell adhesion through improved wettability of water [8]. Thus electrical polarization can have excellent chemical, biological, and biomedical effects.

Another serious problem with YSZ lies in its instability due to a tetragonal (t) to monoclinic (m) phase transformation at relatively low temperatures of ($< 400^\circ\text{C}$) in moist air or hot water [9]. These phenomena are usually termed low temperature degradation (LTD). Kobayashi et al. have reported that the annealing treatment of zirconia at $65\text{--}400^\circ\text{C}$ in water for a long time spontaneously gave rise to the transformation of tetragonal into monoclinic phase [10]. This t-m phase transformation in YSZ is reportedly accompanied by cracking on the surface

due to the volume expansion of about 4-5% and degradation of mechanical strength, which can cause critical accidents in medical applications.

It is crucial to inhibit the LTD of YSZ in medical and structural applications and also to understand the role of moisture in LTD. We observed that our polarization process successfully inhibited LTD in the chemical treatments of YSZ ceramics. This report details the bioactivation and LTD-inhibition of polarized YSZ ceramics and discusses the polarization mechanisms.

MATERIALS AND METHODS

Yttria-partially stabilized zirconia powder (TZ-3Y, Tosoh, Japan) was pressed into a mold at 120 MPa. The YSZ compacts were sintered in air at 1400°C for 1 h. The relative density values of the sintered YSZ compacts were *ca.* $99.2 \pm 0.1\%$. The sintered YSZ samples were electrically polarized as previously described [4] with a pair of platinum electrodes at 200°C in a direct-current (d.c.) electric field of $20\text{ V}\cdot\text{cm}^{-1}$ for 30 min in air. The electrically polarized YSZ samples were treated with alkaline ($5\text{ mol}\cdot\text{dm}^{-3}$ NaOH at 95°C for 24 h) solution in commercial glass tubes. After chemical treatment, the samples were washed with deionized water and dried at 60°C for 3 h. The unpolarized YSZ with and without alkaline treatment were designated as O and YSZ, as the controls, respectively. The negatively charged YSZ and positively charged YSZ surfaces after the alkaline treatment were designated as N and P,

Fig. 1 (A) XRD pattern of YSZ was highly consistent with tetragonal ZrO₂ (closed circles), indicating that the as-polarized YSZ surfaces consisted of a single phase of tetragonal ZrO₂. The surfaces after the alkaline treatment consisted of both tetragonal ZrO₂ and monoclinic ZrO₂ (open circles) phases. (B) Extents of phase transformation from tetragonal ZrO₂ into monoclinic ZrO₂ after alkaline treatment. (*<0.001)

respectively.

X-ray diffraction (XRD) measurements for phase analysis of the alkaline-treated YSZ surfaces were performed at (RT) temperature with Cu-K α radiation at 40 kV and 40 mA on a Philips PW 1700 diffractometer equipped with a graphite monochromator. The extents of phase transformation were calculated using the equation of Garvie and Nicholson [11]. Compositional analysis was carried out using x-ray photoelectron spectroscopy (XPS) on a JPS-90SX spectrometer (Japan) with Al K α x-rays at an analytical angle of 45°. The C 1s peak was used for calibration of the binding energies by setting its binding energy to 284.6 eV to correct for sample charging.

The YSZ samples were immersed in simulated body fluid (SBF) with pH 7.4 at 37 °C for 4 and 6 days. SBF solution was prepared using the technique described by Kokubo et al. [12, 13]. After immersion in SBF, the samples were washed with deionized water and ethanol, and then dried at RT in air. The surfaces were sputtered with Pt-Pd using an ion coater (Eiko Engineering IB-2). The sputtered surfaces were observed using a scanning electron microscope (SEM, Hitachi S-2400).

RESULTS & DISCUSSION

The XRD patterns of the YSZ surface was highly consistent with the published data for ZrO₂ (ICDD no. 79-1796), indicating that the surfaces consisted of a single phase of tetragonal ZrO₂ (Fig. 1A). As shown in Fig. 1A, the XRD patterns for the O, N and P surfaces after the alkaline treatment consisted of the phases of tetragonal ZrO₂ and monoclinic ZrO₂ (ICDD no. 37-1484). The extents of the phase transformation from tetragonal ZrO₂ to monoclinic

ZrO₂ after alkaline treatment were 9.6, 10.4 and 1.5 mol %, for O, N and P surfaces, respectively (Fig. 1B). The phase transformation was significantly inhibited on the P surface. Thus alkaline treatment promotes t→m transformation on each surface of O, N and P surfaces, while the P surface was proven to be remarkably resistant to LTD in alkaline solution.

Figure 2 shows the detailed XPS scans for oxygen 1s of O, N and P surfaces after the alkaline treatment. The peak in binding energies of oxygen appeared for the alkaline-treated surfaces from 530-532 eV, which was decomposed into two peaks: 532 eV for H₂O or OH groups and 530 eV for ZrO₂ [14]. The ratios of the areas of H₂O or OH group to total oxygen in O, N and P surfaces were 47.3, 52.7 and 61.2 %, respectively (Fig. 2B). As with the alkaline treatment, more hydroxyl groups were formed on the P surface, compared with the O and N surfaces.

Sato et al. concluded that the phase transformation resulted from Zr-OH formation from chemical reactions between ZrO₂ and H₂O on the YSZ surfaces instead of the release of zirconium and yttrium ions even in corrosive solutions at 95°C [15]. The mechanism of Zr-OH formation on the YSZ surface was reported to progress in three stages: (1) the formation of hydrogen bonds between the protons of water molecules and the oxygen atoms of Zr; (2) two concerted coupling reactions: first between the proton of water molecules and the oxygen atom of Zr and a second between the oxide ions of water molecules and the Zr atoms; (3) the cleavage of the Zr-O-Zr bonds and the formation of Zr-OH by the phase transformation [15-17]. During the phase transformation, both the binding forces and the strain energies were decreased due to microcrack formation by the cleavage of Zr-O-Zr bonds [15, 18].

Deposits of bone-like apatite crystals had formed

Fig. 2 (A) Detailed XPS scans for oxygen 1s of O, N and P surfaces after the alkaline treatment. (B) Ratios of the areas of H₂O or OH groups to oxygen in YSZ samples after alkaline treatment. (*<0.01)

and grown to *ca.* 2 μm in diameter on the alkaline-treated P surface after immersion for 4 days, whereas there were no deposits on the alkaline-treated O and N surfaces (data not shown). After the immersion for 6 days, deposits of bone-like apatite crystals were also observed on the alkaline-treated O and N surfaces (Fig. 3A). As shown in Fig. 3B, the XRD patterns of the deposited bone-like apatite crystals consisted of the phase for HA (ICDD no. 9-432).

The YSZ surfaces after alkaline treatment showed the phase transformation from tetragonal ZrO₂ to monoclinic ZrO₂ and the deposition of bone-like apatite crystals after immersion in SBF. These results, when combined with the mechanism proposed by Sato et al. [15], suggest that the Zr-OH formed on the P surface by the alkaline treatment induced the nucleus formation of apatite crystals when the surfaces were immersed in SBF solution. However, although the amount of OH groups was larger on the alkaline-treated P surface than the alkaline-treated O and N surfaces, the phase transformation was inhibited on the chemically treated P surface. This result is incompatible with the mechanisms proposed by Sato et al.. On the other hand, Uchida et al. showed that apatite crystals were deposited on chemically treated Ce-TZP/Al₂O₃ by the formation of Zr-OH without phase transformation [13, 19]. Thus, the Zr-OH formation on our YSZ surfaces must result not only from the aforementioned mechanism proposed by Sato et al. but also from some other mechanism.

Hydroxide ions have been reported to penetrate into the oxygen vacancies on the surface and in the lattice of 2.66 (mol %) yttria-partially stabilized zirconia samples sintered at 1450 °C for 2 h after

hydrothermal treatment at high pressure, based on the measurement of the lattice constant [20].

Thus, the alkaline treatment induced a reaction on the P surface and formed oxygen vacancies (V_O) as described below [16]:

Since there are oxygen vacancies in the YSZ structure, the likely carrier of polarization in YSZ is oxide ions. During the polarization treatment of YSZ, the oxide ions migrate to the oxygen vacancies near the negatively charged surface induced at the cathode, resulting in an increase in concentration of oxygen vacancies near the positively charged surface induced at the anode.

By the definition of Bronsted-Lowry, water molecules exist as oxonium ions or hydroxide ions in alkaline solution. Thus, the hydroxide ions are attracted to the oxygen vacancies near the positively charged YSZ surface and may enter these vacancies, inducing the formation of Zr-OH on the P:

The LTD resistance of the P surface was attributed to lower cleavage of Zr-O-Zr bonds via the adsorption of water molecules.

This formation of Zr-OH groups on both the O and N surfaces was consistent with the results of the extent of phase transformation after the chemical treatment (from XRD) and the equal amount of hydroxyl groups (from XPS). The formation of Zr-OH groups was accelerated on the P surface by the selective attraction of hydroxide ions into the oxygen

Fig. 3 (A) SEM images of the surfaces of YSZ samples after SBF immersion. Deposition of bone-like apatite crystals of around 1 μ m in diameter was observed on the surfaces of the acidic-treated O, N and P surfaces after SBF immersion for 6 days. (Bar=1 μ m) (B) The XRD patterns of the deposited bone-like apatite crystals consisted of the phase for tetragonal ZrO₂ (closed circles), monoclinic ZrO₂ (open circles) and HA (closed square) phases.

vacancies in comparison with the O and N surfaces. The Zr-OH groups were considered to contribute to the nucleus formation during the deposition of bone-like apatite crystals from SBF solution.

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