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Biomimetic apatite coating on yttria-stabilized tetragonal zirconia utilizing femtosecond laser surface processing

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ABSTRACT

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) have been used in orthopedic and dental implants because of their excellent physicochemical properties. In this study, we developed an apatite coating technique with low thermal effects for Y-TZP ceramics based on a biomimetic process using a supersaturated calcium phosphate solution (CP solution) as a coating medium. To achieve this, we performed femtosecond laser processing with low thermal effects as a surface pre-modification tool for Y-TZP ceramics. By changing the laser scanning mode, we fabricated two different submicro-/micro-structures on the Y-TZP sample. Both laser-treated samples showed increased water wettability due to ablation plasma and partly formed an apatite layer on their surfaces in the CP solution within 7 days. To further enhance the apatite-forming ability, we applied an alternate dipping process to the laser-treated sample in order to precoat the sample with apatite precursors. The laser-treated and precursor-precoated sample successfully formed an apatite layer on the entire surface in the CP solution within a shorter time period (24 h). The thus-coated apatite layer adhered to the sample so strongly that the layer remained on the sample even after the tape-detaching test. This strong adhesion may be attributed to the mechanical interlocking effects due to laser-induced surface roughening. Our proposed apatite-coating technique using the laser- and precursor-assisted biomimetic process would be useful for the creation of apatite-coated Y-TZP ceramics for orthopedic and dental applications.

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) are fine engineering ceramics with the advantages of high chemical durability, mechanical strength, fracture toughness, abrasion resistance, and esthetic appearance [1–3]. In addition, zirconia ceramics could show unique electrical and optical properties [4,5]. Owing to these advantageous characteristics, zirconia ceramics have been applied as not only industrial materials but also biomaterials such as hip joint balls, knee joint components, and esthetic crowns [6–8]. However, despite the increasing importance in clinical applications, zirconia ceramics are intrinsically bioinert and generally cannot form a direct bond with the surrounding living bone tissue. Therefore, zirconia ceramics with bone-bonding ability have been sought for particular implant applications that require integration with the bone tissue.

The use of apatite coating is a well-established method for impairing bone-bonding ability to base artificial materials. This is because apatite, a calcium phosphate (CaP) compound found in human bone mineral, exhibits direct bone-bonding ability *in vivo* [9]. Among the various apatite coating techniques, low temperature biomimetic processes [10–14] based on pseudo-biomineralization reactions in supersaturated CaP solutions are particularly suitable for coating Y-TZP ceramics compared with conventional high temperature processes such as plasma spraying [15] and sputtering [16]. This is because the high temperature processes can induce partial thermal decomposition of apatite [15] and the transformation from the tetragonal phase to the monoclinic phase in Y-TZP, possibly leading to mechanical deterioration of Y-TZP ceramics [17,18].

Since the early 2000's, a variety of biomimetic apatite coating techniques have been developed for stabilized zirconia ceramics [10–14]. For example, Uchida et al. proposed acid and alkaline treatment methods to induce apatite formation on zirconia/alumina nanocomposite ceramics in a simulated body fluid (SBF) with ion concentrations approximating those in the body fluid [11]. Takemoto et al. applied heat and CaP precoating treatments to acid-treated zirconia/alumina nanocomposite ceramics to induce apatite formation in SBF [12]. Zain et al. employed polydopamine precoating to induce apatite formation on yttria-stabilized zirconia ceramics in 1.5SBF with ion concentrations 1.5 times higher than those of SBF [13]. Klopčič et al. modified the composition of the supersaturated CaP solution to obtain rapid apatite

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coating on zirconia ceramics [14]. On the other hand, we developed a plasma- and precursor-assisted biomimetic process for the formation of apatite coating on polymeric materials [19–22]. In this process, a polymeric material is first treated with oxygen gas plasma, and then precoated with apatite precursors to induce apatite formation on the surface in supersaturated CaP solutions. It was revealed that the plasma-induced surface wetting [19] and roughening [20–22] are the major factors affecting the apatite-forming ability of the polymeric material and the adhesion of the coating to the material surface. While such a gas plasma treatment is effective in increasing the surface wettability of zirconia ceramics, it is generally unable to change the surface morphology owing to the higher physicochemical stability of zirconia compared with that of polymeric materials.

Recently, femtosecond laser processing with the high peak power and low thermal effects [23] has shown to be effective in producing microstructures on Y-TZP ceramics *via* laser ablation [24,25]. More recently, we fabricated a periodic grating submicro-structure in a checkered micro-pattern on a Y-TZP surface by femtosecond laser processing without a noticeable increase in the monoclinic phase content at the surface (~1 vol%) [26]. In this study, we applied this femtosecond laser processing to Y-TZP ceramics as a surface pre-modification tool in the precursor-assisted biomimetic apatite coating process. Our hypothesis was that the femtosecond laser processing should be effective in producing Y-TZP surfaces with increased surface roughness and wettability *via* ablation plasma, and this should enable the formation of strongly bonded apatite coatings on Y-TZP ceramics.

We fabricated two different submicro-/micro-structures on the Y-TZP sample by changing the scanning mode of the femtosecond laser processing. The laser-treated samples and the samples that were further subjected to the alternate dipping process in Ca and P solutions (CaP dipping process) were immersed in a supersaturated CaP solution (so-called CP solution [27]) to enable the formation of an apatite layer on the surfaces (Fig. 1). These samples were compared to the Y-TZP sample that was subjected to the conventional oxygen gas plasma treatment followed by the CaP dipping process. The surface coverage and adhesion to the sample surface of the obtained apatite coatings were then characterized and discussed in terms of surface structures and wetting properties of the samples.

2. Material and methods

2.1. Sample preparation

Raw Y-TZP powders doped with 3 mol% yttria (TZ-3YB-E) were obtained from Tosoh Corp., Japan. Square Y-TZP plates with a thickness of 1 mm and lateral dimensions of 10 mm × 10 mm were prepared by sintering the raw Y-TZP powders at 1350 °C followed by square-cutting and wet-polishing to mirrored surfaces (Ra < 0.05 μm). The Y-TZP plates were ultrasonically washed three times with acetone and then dried in air. The resulting plates are hereafter referred to as the untreated Y-TZP samples.

2.2. Femtosecond laser processing for surface pre-modification

For the femtosecond laser processing, we employed a laboratory-made Ti:sapphire chirped-pulse amplification system that generates linearly polarized 810-nm-centered 80-fs full width at half maximum (FWHM) pulses at a repetition rate of 570 Hz. The laser beam was focused on the surface of the sample placed on an xyz-stage using a beam shaper (Focal π shaper 9TiS, AdlOptica GmbH, Germany) and a lens with a focal length of 300 mm. The xyz-stage controlled the irradiation position in the x- (horizontal) and y- (vertical) directions.

The focused laser profile was measured by a beam profiler consisting of a CCD camera and an analyzing software. The focused beam was elliptical because of the astigmatism of the laser beam. The intensity profile on the sample was adjusted with the beam shaper to be near-Gaussian with a homogeneous part around the beam center. The peak fluence F_{peak} of the near-Gaussian beam was estimated using

$$F_{peak} = 2E/(\pi {r_{eff}}^2) \quad (1)$$

$$r_{eff} = (r_x \cdot r_y)^{0.5}, \quad (2)$$

where E is the pulse energy, r_{eff} is the effective beam radius, and r_x and r_y are the horizontal and vertical beam radii at 86.5% energy transmission, respectively. By controlling the pulse energy E using a variable attenuator and the effective beam radius r_{eff} using the z position of the sample, the peak laser fluence F_{peak} was set to ~4 J/cm^2 per pulse; based on the previous work, this is higher than the ablation threshold (1.5 J/cm^2 per pulse) and falls within the effective range (2.7–7.7 J/cm^2 per pulse) for the production of the periodic grating structure on the surfaces of Y-TZP ceramics [26]. The effective range of the peak laser fluence was experimentally determined by changing the laser energy and the focused beam size on the Y-TZP sample followed by surface morphological observation [26].

Laser irradiation was conducted on the sample in ambient air with two different scanning modes: the stamp-scan mode and the line-scan mode. In the stamp-scan mode [26], 40 pulses were irradiated onto the same focused region of the sample surface without moving the sample. Irradiation using this stamp-mode generated an ablated elliptical crater on the sample surface with lateral dimensions of ~75 μm (x-direction) × ~105 μm (y-direction) and a depth of ~8 μm. After each stamp-mode irradiation, the sample was repeatedly moved by 60 μm steps in the x-direction. When the horizontal stamp scanning was finished at the edge of the sample, the sample was moved by 90 and 30 μm in the y- and x-directions, respectively, to irradiate the next row in the same manner.

In the line-scan mode, the focusing position was continuously moved in the x-direction at a constant speed of 0.7 mm/s. The primal line-scan irradiation generated an ablated line with a width of ~105 μm and a depth of ~8 μm on the sample surface. When the horizontal line scan was finished at the edge of the sample, the sample

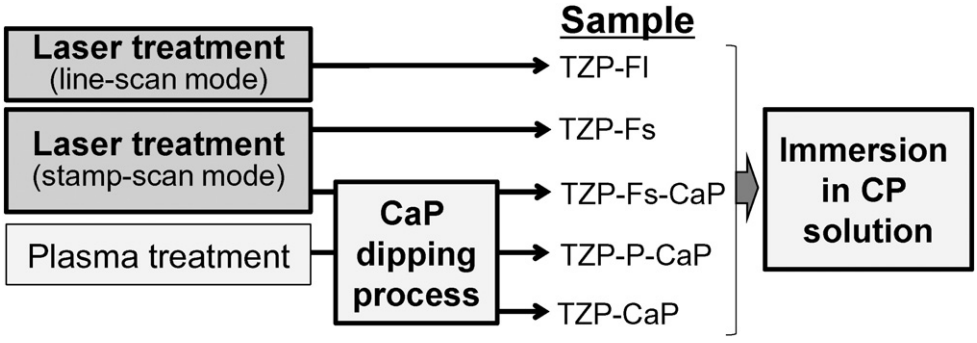

Fig. 1. Diagram of the experimental procedure.