Modification of Yttrium-Stabilized Zirconia Ceramics Using Calcium Phosphate

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ABSTRACT

A biomimetic approach was applied for the chemical deposition of calcium phosphate (CaP) coatings on 3 mole% yttrium-stabilized zirconia [3YSZ] powders. The solid-state reaction of 3YSZ powders with the addition of CaP was investigated for the development of biodegradable zirconia ceramics. The solid-state interaction between the 3YSZ matrix powders and the CaP additives differed from the behavior of commercial zirconia matrix powders. The 3YSZ powders were chemically reacted with precursors for the CaP formation. 3YSZ powders were mixed in an aqueous solution of Ca-P precursors and the CaP was precipitated on the surface of the 3YSZ matrix powders. The CaP-doped YSZ powders were calcined at 1100°C and shaped powder blocks were then fired at 1600°C for 2 h. The CaP phase formation was investigated using FE-SEM and XRD analysis.

Key words : Calcium phosphate, Zirconia, Solid-state interaction

1. Introduction

Yttrium-stabilized zirconia (YSZ) has been used as a dental laminate material due to its good mechanical properties, biocompatibility, and for patient-oriented esthetic reasons. Zirconia is bioinert, and this leads to the poor fixation of a ceramic implant in the bone. The incorporation of CaP into the zirconia matrix has been attempted in an effort to determine if the controlled release of calcium and phosphate ions can have an osteoinductive effect.[1-3] For an implant application, the biodegradable modification of YSZ ceramics has been investigated; the incorporation CaP into the zirconia matrix can potentially increase the osteo-inductivity of the scaffold and therefore promote osteo-genesis when implanted in vivo.[4-6] Zirconia powders are coated with thin layers of calcium phosphate (CaP), which is known to be bioactive and osteoconductive, leading to good bone-bonding ability and support bone-tissue in-growth.[7-9] Hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP) ceramics have been used in the development of bone scaffolds and have been shown to increase the levels of osteoconductivity (support cell attachment). Calcium and phosphate ions have been postulated to be osteogenic factors that enhance osteoblast differentiation and mineralization.

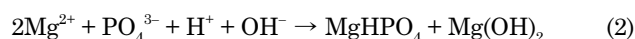The aim has been a combination of the excellent mechanical properties (toughness, wear resistance) of CaP-coated zirconia with the biocompatibility and osteocon-ductive potential of CaP. These applications have involved the use of nano-metric or micrometric-sized zirconia and CaP powders obtained by wet precipitation methods. Stabilized zirconia is most commonly formed by pressing and sintering at temperatures ranging from 1300°C to 1600°C. The selected sintering temperature must be kept as low as possible because CaP decomposes in β-tricalcium phosphate, $(Ca_3(PO_4)_2)$ TCP, at temperatures higher than 1000°C. This process affected with the ratio of the CaP addition into the YSZ matrix, through a reaction between both phases. In this report, a solid-state reaction between YSZ powders and CaP additives was investigated using commercially well-known zirconia powders and a dental block.
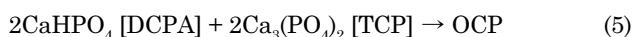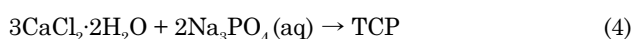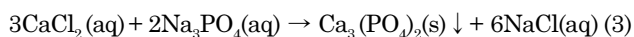
2. Experimental Procedure

2.1. Sample Preparation

As YSZ matrix commercial powders, KZF-3Y (Kyoritz, Japan) and TZ-3Y (Tosoh, Japan) were used. The precursors for the CaP formation were $MgCl_2 \cdot H_2O$ (Hayashi), $CaCl_2$ (Aldrich), and Na_3PO_4 (TSP, Aldrich). On the basis of the YSZ matrix, the amounts of precursors were calculated for the formation of octacalcium phosphate (OCP) or tricalcium phosphate [TCP] powders. In these experimental calculations, the total amount of YSZ matrix with CaP additives was based on 10 g batches.

The chemical reactions for the formation of calcium phosphate (CaP) can be written as follows:

$$MgCl_2 \cdot 6H_2O + TZ\text{-}3Y(s) \rightarrow YSZ\text{–}Mg(OH)_2 + Cl^- + H^+ \quad (1)$$

$$2Mg^{2+} + PO_4^{3-} + H^+ + OH^- \rightarrow MgHPO_4 + Mg(OH)_2 \quad (2)$$

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$$3CaCl_2(aq) + 2Na_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) \downarrow + 6NaCl(aq) \quad (3)$$

$$3CaCl_2 \cdot 2H_2O + 2Na_3PO_4(aq) \rightarrow TCP \quad (4)$$

$$2CaHPO_4 [DCPA] + 2Ca_3(PO_4)_2 [TCP] \rightarrow OCP \quad (5)$$

In this experiment, the calculated amounts of zirconia matrix and OCP as an additive were 9.9242 g and 0.0758 g, respectively. The OCP phase is formed through a solid-state reaction in a mixture of 2DCPA and TCP, as shown in Eq. (5). In order to make the OCP-modified YSZ ceramics, the calculated amounts of DCPA and TCP were 0.02338 g and 0.05433 g, respectively. The respective amounts of $CaCl_2 \cdot 2H_2O$ and Na_3PO_4 were 0.07725 g and 0.05743 g for the formation of 0.0543 g of TCP.

A small amount of $MgCl_2 \cdot 6H_2O$, as shown in Fig. 1, was added to the zirconia powders of TZ-3Y or KZF-3Y and mixed in DI H_2O while stirring for an hour to form $Mg(OH)_2$, which would be attached onto the zirconia powders, as shown in Eq. 1. As expressed by Eq. 2, magnesium phosphate may be formed with an $Mg(OH)_2$ layer on YSZ powder. The precipitation of CaP, i.e., TCP, HAP or OCP from the solution, is a base uptake process. The amount of zirconia matrix powder is 9.9242 g, and the 3YSZ powders were stirred in a beaker with DI water for 1 h. The respective amounts of tri-sodium phosphate (TSP) used here were 0.05743 g, 0.0678 g and 0.07758 g for 0.75 CaP, 1.0 CaP and 1.25 CaP doping on YSZ powders. The TSP powders were dissolved in DI water while stirring and the aqueous solutions were dropped into an aqueous mixture of $CaCl_2$ at 0.7725 g, DCPA ($CaHPO_4$, dicalcium phosphate anhydrous) at 0.02338 g and $MgCl_2$ at 0.007566, which were preliminary stirred with zirconia matrix powders at 37°C for 30 min. During the dropping of the TSP aqueous solutions, the mixture solution was stirred at 90°C to activate the TCP phase formation on the surface of the zirconia powders. The slurry mixture was settled down after the precipitation of TCP and the DCPA powders were then added to the slurry solution while stirring. Normally, DCPA is not completely dissolved in water [10] and therefore some time is needed to ensure a clear mixture. DCPA is a mildly acidic and soluble (at the physiological pH) calcium phosphate (CaP) phase. The dissolution kinetics of $CaHPO_4$ in water at 37°C[11] showed that Ca^{2+} and HPO_4^{2-} ions were initially released from the DCPA; this completely stopped after four days in contact with the water at 37°C. The dissolution of DCPA is known to be incongruent,[11] which would be caused by the formation of a thin apatitic (apatite-like) calcium phosphate (HAp-CaP) layer on the surfaces of CaHPO4 particles through a topotactic reaction, which hindered further dissolution. Some self-hardening CaP pastes contain, for instance, approximately 25 wt% CaHPO4 in their powder components. After filtration and drying, a binder solution was added to the powders. In order to make the binder solution, 0.2 g of PVA and 0.1 g of glycerin were dissolved in 10 mL DI H_2O. The shaped sample body was fired at 1550°C or

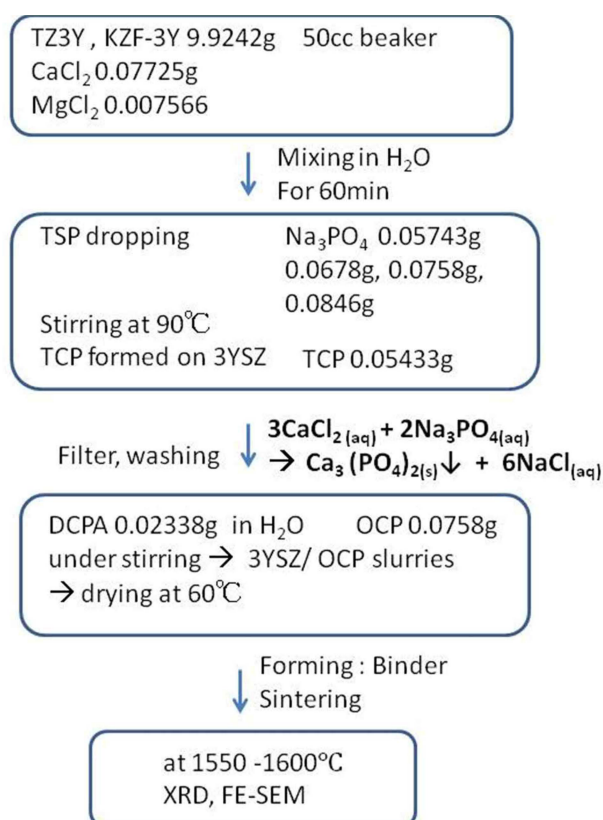**Fig. 1.** Flow diagram of the precipitation of calcium phosphate into the zirconia powders. TZ-3Y and KZF-3Y were used.

1600°C for 2 h.

Figure 1 shows the CaP coating process for the zirconia powders. The assumed amounts of formed OCP and zirconia matrix were 0.0758 g and 9.9242 g, respectively. Through the wet precipitation process, 0.07598 g of the OCP powders may be formed in the 9.9242 g of KZF-3Y zirconia powders. The aqueous binder solution was added to the mixed powders, and after drying, the hardened paste was ground by a pestle to be used for forming. The sample body was sintered at 1550°C or 1600°C for 2 h. The precipitation condition was precisely controlled to obtain the YSZ powders, which were uniformly coated by CaP phase and $Mg(OH)_2$. Through the wet precipitation method, the resulting CaP-doped YSZ ceramics showed a property change in terms of their density and microstructure. In particular, the microstructure of the CaP-doped YSZ ceramics was compared with that of a Prettau® sample body, which is a well-known esthetic dental laminate material.

In dental applications, zirconia powders are shaped and fired at 1100 - 1200 °C to make the primary dental block. Normally, a commercially supplied dental block is machined in a dental laboratory using CAD/CAM according to the patient-oriented tooth design, as required by the dentist. The machined block is fired at 1400-1600°C and the sintered zirconia block is finally polished and color-stained for the final tooth design. Prettau is commercially well-known

as an esthetic zirconia implant material for use in dental applications. In this experiment, the supplied Prettau zirconia block was finally sintered at 1600°C for 2 h. The Prettau block was used as a reference sample for the CaP-doped zirconia in the SEM microstructure and EDS analysis.

The CaP-precipitated YSZ powders were calcined at 675°C, 750°C and 800°C for 2 h and were then cooled. The powders were uniaxially shaped under 5 tons of pressing. The samples were then sintered at 1600°C for 2 h.

2.2. Characterization

The crystal phase was confirmed using X-Ray diffraction [Bruker, M18XCE] of the crushed powders. The microstructure of the CaP-doped YSZ ceramics was observed by means of FE-SEM [Hitachi, S-4800].

3. Results and Discussion

In the preparation of the CaP-doped 3YSZ powders and ceramics, the major crystals are tetragonal, and the monoclinic phase was partially developed for the YSZ samples calcined at 675 -800 °C. In Fig. 2, the XRD intensity of the monoclinic phase is shown to decrease with an increase in the calcining temperature.

In Fig. 3(a), the grain sizes of the TZ-3Y are 200-600 nm and 400-1200 nm for the samples sintered at 1550°C and 1600°C, respectively. Figure 3(b) shows the grain microstructure of the commercial dental block, Prettau, sintered at 1600 °C. The microstructure in Fig. 3(b) is similar with that shown in Fig. 3(a), but it was noted that the dental block shows unique micro-grain growth during full densification at 1600°C. The circled region in the expanded image in Fig. 3(b) shows the individual micro-grain growth in a grain. The arrows indicate the micro-grain boundary region, which moves with the micro-grain growth in the grain. It is noted in Table 1 that the Prettau sample, a typical esthetic zirconia block, has a considerable amount of CaP composition along the grain boundary region. In Table 1, the compo-

sition was obtained by an EDS analysis of the sintered body. It is assumed that CaP-doped YSZ powders were used in the Prettau block and that the final grain growth was enhanced by the micro-grain growth, which arose from the powder granules during the sintering densification process. The CaP incorporation into the YSZ matrix may contribute to enhancing the grain boundary migration. From the internal microstructure morphology of a grain, it appears that the CaP phase was homogeneously coated on the YSZ matrix. In Fig. 3(b), the circled region shows the internal grain growth in a grain, in which a smaller grain boundary migrated to form a larger grain during the sintering process at 1600°C. In fact, for a dental laminate application, the pre-sintered block at 1100°C is machined using CAD and finally sintered at 1600 °C. The requirements for the fired laminate sample are translucency and color to match those of the patient's teeth. From the above-mentioned results pertaining to TZ-3Y and Prettau samples, it is assumed that the commercial dental product Prettau was composed of CaP-doped 3YSZ powders, which induces bone-like behavior in terms of translucency and color.

Figure 4 shows the CaP-doped YSZ samples, specifically the 1.25 CaP TZ3Y and 1.0 CaP KZF-3Y samples, compared
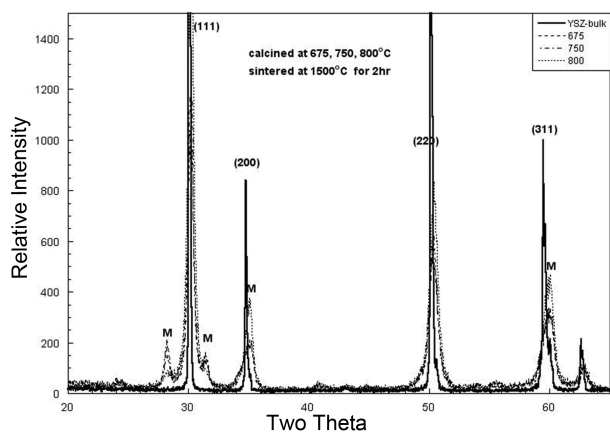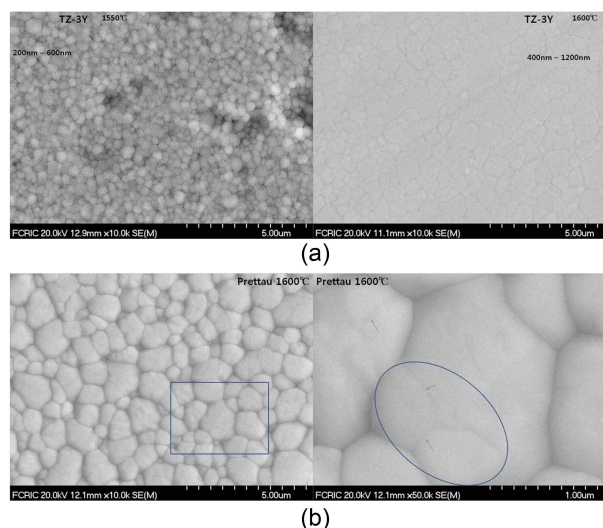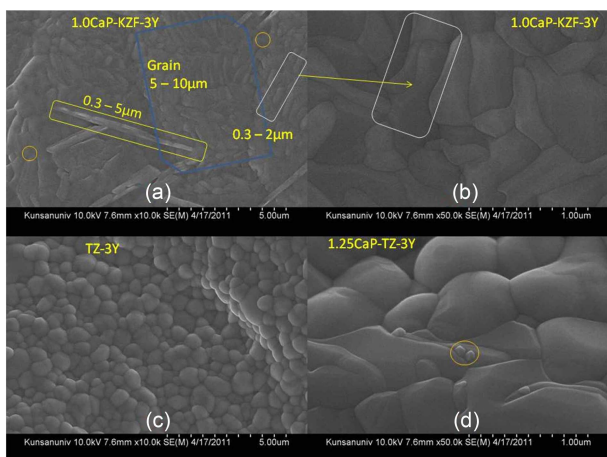
Fig. 3. FE-SEM photographs of YSZ ceramics: (a) TZ-3Y ceramics fired at 1550°C and 1600°C, (b) Prettau ceramics fired at 1600°C showing internal grain growth.

Table 1. Compositions (wt%), BET, and Translucency for the Samples of TZ-3Y, KZF-3Y-0, and Prettau.

	TZ-3Y	KZF-3Y-0	Prettau
ZrO_2	94.21	94.53	93.90
Y_2O_3	5.21	5.47	5.423
Al_2O_3	0.005	0.216	0.004
Ca, P			Ca 0.374 P 0.393
Mg			Mg 0.015
BET(m2/g)	14.8	12.9	
translucency	7	7	10

Fig. 2. X-ray diffraction patterns of the CaP-doped YSZ powders fired at 675, 750, 800, and 1500°C.

Fig. 4. FE-SEM microstructure for CaP-doped YSZ ceramics: (a) KZF-3Y_1.0 CaP/Mg, (b) KZF-3Y_1.0 CaP/Mg, (c) TZ-3Y, and (d) TZ-3Y_1.25 CaP/Mg.

with the Prettau sample, in Fig. 3. The CaP-coated samples were sintered at 1600 °C for 2 h. In Fig. 4(a) there are three types of morphology: long rectangles at 0.3 μm W × 5 μm L, small spheres with a 0.3 μm diameter, and largely distorted rectangle shapes 0.3 μm W × 2 μm L in size. The grain has the hexagonal shape, which is a combination of rectangular micro-grains. In Fig. 4(b), each grain is composed of an alignment of distorted rectangular micro-grains. Figure 4(c) shows a normal microstructure with sphere-like grains, as in TZ-3Y. In the 1.25 CaP-doped TZ-3Y ceramics in Fig. 4(d), the circled region shows small spheres in which the incorporation limit may lead to the formation of the CaP phase around the grain boundary. The grains show rounded rectangle-shaped grains and a few spheres. From the EDS analysis and the sintering densification process, the solid-state interaction between the zirconia matrix and the formed CaP was less effective in the TZ-3Y series, though it was very effective in KZF-3Y. As shown in Fig. 4, it was not easy to obtain a uniform grain morphology composed of rectangular micro-grains of the types which may be formed through the incorporation of CaP into the zirconia matrix region. In the 0.75 CaP-TZ-3Y samples, obtaining a uniform grain morphology composed of rectangular micro-grains was more difficult despite the fact that the amount of CaP added was considerably reduced. On the other hand, in the 1.0 CaP doped KZF-3Y, the grain growth was uniformly distributed through a combination of internal, rectangular micro-grains.

Figure 5 shows the EDS analysis results of three particular shapes in terms of their SEM microstructures. The EDS analysis in Fig. 5(b) for the parts labeled as 1, 2, and 3 shows the possible formation of the CaP phase. The 1.0 CaP doped KZF-3Y zirconia was sintered at 1600°C for 2 h. In general, 3YSZ ceramic materials show uniformly developed spherical grain growth. CaP-doped KZF-3Y zirconia ceramics show versatile microstructures such as rectangular modified spheres (1), broad rectangles (2), and spheres (3). In

(a)

Spectrum	O	Mg	P	Ca	Y	Zr	phase	Ca/P
1	53.53	0.37	12.03	12.97	9.99	11.11	TCP	1.396
2	52.98	0.32	11.55	6.77	22.57	5.81	DCPA/MCPA	0.759
3	55.74	0.40	3.27	3.90	4.39	32.31	TCP/OCP	1.545

(b)
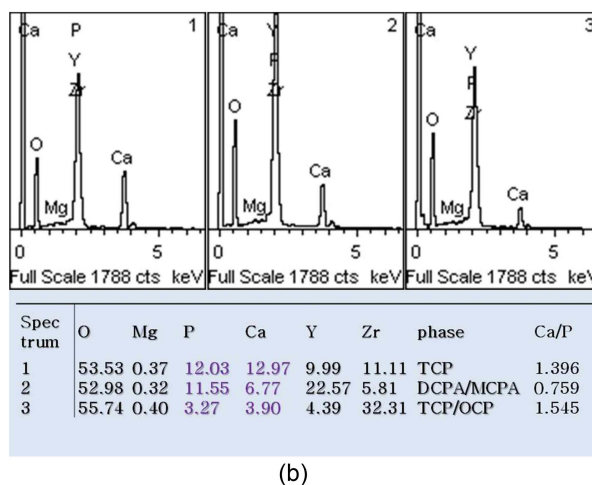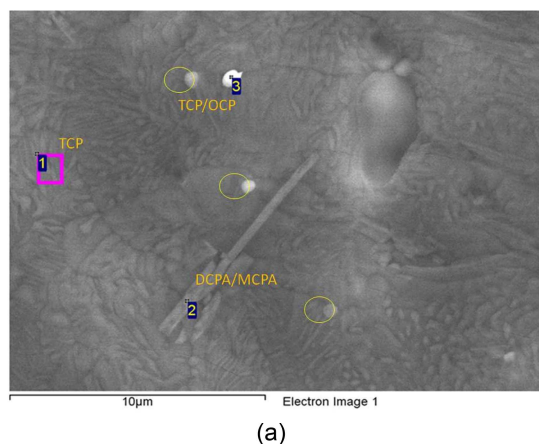
Fig. 5. EDS analysis of CaP-doped YSZ ceramics of KZF-3Y_1.0 OCP/Mg.

sphere region 3, the amount of CaP in the 3YSZ matrix is relatively low. With an increase of the incorporated CaP amount, the grain shape became broadly rectangular, as shown in region 2. From the EDS analysis, each region of differently shaped domains or grains is related to the degree of CaP incorporation into the YSZ particles. If an appropriate amount of CaP is chemically incorporated into the YSZ particles, the sintered body will show an entirely uniform microstructure.

TZ3Y is effective for the densification of zirconia ceramics and is feasible for use when shaping and sintering are required. The powder distribution quality is based on control of the particle size and granule formulation as prepared using a spray drier. Normally, the specified binder is left after spray drying, and this process is effective as a forming process using a hydrostatic press. However, for slip casting, the powders have to be uniformly distributed using a binder and a deflocculant for the dispersion of the zirconia suspension. In this research, we attempted to coat the surface of zirconia powders chemically. In the experiments, the CaP phase was formed on the as-received zirconia powders by a wet precipitation process. The sintering behavior was different in the TZ-3Yand KZF-3Y samples. The BET values (m²/g)
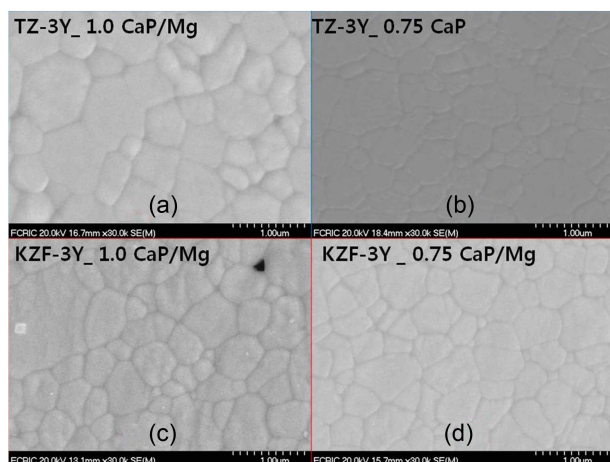
Fig. 6. FE-SEM microstructure for CaP-doped YSZ ceramics: (a) TZ-3Y_1.0 CaP/Mg (b) TZ-3Y_0.75 CaP/Mg (c) KZF-3Y_1.0 CaP/Mg, and (d) KZF-3Y_0.75 CaP/Mg.

of the primary particles in TZ-3Y and KZG-3Y were 14.8 and 12.9, respectively.

The FE-SEM and EDS results may explain the solid-state reaction between the CaP and YSZ powders. The purpose of CaP coating onto the zirconia powders was to obtain highly dense zirconia ceramics without losing translucency while retaining a CaP layer, which would show good biocompatibility as a dental implant. From the EDS analysis results in Fig. 5, KZF-3Y showed good solid-state interaction with CaP at above 1550°C compared to that of TZ-3Y.

The sintered body of the CaP-doped TZ-3Y showed a decrease in the sintering density and a loss of translucency. KZF-3Y retained its good sintering density in this experimental CaP composition range. TZ-3Y was developed as an engineering zirconia ceramic having a good sintering ability; therefore, the powder granules are useful in a dry pressing process to make sample bodies. Normally in the sintering process, the sample body was formed by dry pressing using spray-dried powders. The firing process of the shaped body is controlled to burn off the remaining binder in the spray dry powders, with final sintering at 1150°C for several hours to make a zirconia block for CAD/ACM machining. The machined body is finally sintered at above 1550°C for several hours.

From the EDS analysis, the CaP doping in KZF-3Y matrix was very effective to show an esthetic color change and retain a feasible level of translucency. That is, as a zirconia matrix showing good solid-state interaction with CaP, KZF-3Y powder was more effective. We could control the amounts of CaP, the CaP precursors, and other factors such as the MgO buffer layer. Fig. 5(b) shows the existence of the Mg composition excluding the CaP phase, indicating the MgO buffer layer. In TZ-3Y, CaP doping using the wet chemical process was less effective to show an esthetic color change and to retain the translucency. The Prettau sample shows the existence of the CaP composition from EDS data

in Table 1, which corresponds to the OCP phase. In this research, the KZF-3Y is appropriate for the modification of zirconia powders using CaP precursors.

For the CaP-doped samples sintered at 1600°C for 2 h, Fig. 6 it shows the microstructural change with the incorporation of CaP into the core grain around the grain boundary region. In Fig. 6(b) (d), the addition of 0.75 CaP into the KZF-3Y and TZ-3Y samples resulted in a similar microstructure. In Fig. 6(a) (b), showing CaP-doped TZ-3Y, the grain size was increased considerably with the addition of CaP. However, in Fig. 6(c) (d), showing CaP-doped KZF-3Y, the microstructure was less changed in the 1.0 CaP/Mg samples. The microstructural homogeneity was investigated with the amount of CaP/Mg ranging from 0.7 to 1.2. Above 1.0, the sintering was not homogeneous and the density decreased. It is known[7] that the existence of magnesium metaphosphate as an interlayer is very effective for the coating of β-tricalcium phosphate on yttria-stabilized zirconia. In the wet chemical process shown in Fig. 1, $Mg(OH)_2$ and/or Mg phosphate buffer layers were formed on YSZ powders. The precursors of the Ca^{2+} and PO_4 ions were mixed to make TCP and finally form the OCP phase on the YSZ powders. From this experiment, it is considered that $Mg(OH)_2$ buffer layers exist on the YSZ powders and that some of the $Mg(OH)_2$ buffer layers may react with Ca and phosphate ions. During the calcination and sintering process, the solid-state reaction may be affected by the Mg compound buffer layers.

4. Conclusions

The solid-state interaction between CaP and a zirconia matrix in 3YSZ ceramics was investigated. A CaP layer was chemically precipitated on nano-crystalline powders of 3YSZ. The solid-state interaction between the YSZ matrix powders and the CaP doping layer was different depending on the supplied commercial powder.

Acknowledgment

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