O U R N A L O F

Ceramic Processing Research

Sintering behavior of Y-doped ZrO₂ ceramics: the effect of additive rare earth oxides

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Rare earth element as colorants have been used in industry for many years. In this study, tooth-like dental ceramic has been prepared by adding rare earth oxides as colorants to nano 3Y-TZP. And the effect of Pr_6O_{11} and CeO_2 additions as dopants in yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) on the sintering densification, microstructure and transformation behavior of the composites was examined. The experimental results are discussed in terms of defect chemistry by aliovalent cation substitutions. It is found that a small amount of Pr_6O_{11} and CeO_2 additions has no significant effects on the material sintering properties, and by this means it is possible that bioceramics with a color similar to natural dentine could be developed.

Key words: Y-TZP, Rare earth, Ceramic, Sintering.

Introduction

The debate about the side effects of dental materials on patients, dental staff and the environment and the increased popularity of tooth-colored materials have focused on the search for strong, esthetic and chemicallystable restorative materials. Dense sintered ceramics fulfill those desires to a high degree. One dense sintered ceramic used as a biomaterial is polycrystalline yttriatetragonal zirconia (Y-TZP). As promising structural materials due to their excellent fracture strength and toughness, yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) have attracted a great deal of attentions [1]. Y-TZP is known to poses superior fracture toughness (2-20 MPa/m^{1/2}) incombination with excellent bend strength (700-1200 MPa) [1]. The high toughness of monolithic Y-TZP arises from the volume expansion (4-5%) due to stress-induced transformation of the metastable tetragonal (t) phase to the room temperature stable monoclinic (m) phase, in the stress field of propagating cracks, thus resulting in a net compressive stress in the process zone around the crack tip-a phenomenon known as 'transformation toughening' [2]. It has also been reported that fine-grained Y-TZP ceramics exhibit a superplastic deformation property, which has opened up the possibility of using ceramics in ductile near net shape forming operations [3].

At present, zirconia-based ceramics are gaining popularity in dentistry, particularly in fixed prosthodontics. Clinically, it is important that ceramic restorations reproduce the translucency and color of natural teeth [4]. But the basic color of zirconium oxide is white to ivory. As for all-ceramic dental the restorations, they should reproduce as accurately as possible the color of natural teeth to create a restoration in accordance with the esthetic wishes and ideas of the patient.

Rare earth elements as colorants have been used in industry for many years. Color formation correlates strongly with the processing temperature, mineralizer content, and, to a lesser extent, particle size of the zirconia raw material. Also through the additive of minor amount of rare earth oxides Pr₆O₁₁ and CeO₂, tooth-like dental ceramics have been acquired. Numerous studies have been focused on the effect of small amounts of additives. dopants or impurities on the sintering behaviour of zirconia. Such studies have allowed a better comprehension of the densification process and microstructural evolution in commercial zirconia powders which typically contain several thousands parts per million (ppm) of impurities such as magnesium, calcium and silicon or trace amounts (< 1000 ppm) of zirconium or rare earth dopants such as yttrium, lanthanum and neodymium [5,6]. To the knowledge of the authors, a quantitative description of the effects of the processing parameters does not exist in the literature. Also much effort has been addressed on enhancing the sinterability of zirconia-based ceramics because this is important not only in terms of production costs, but also for the development of multi-component devices. One approach to improve the sinterability of ceramics is to increase the powder reactivity via a reduction in particle size. It has been reported in many studies that nano-sized Y-TZP powders with weak agglomerates exhibit greatly enhanced sintering activity and thus sintering proceeds rapidly at relative low temperatures (< 1100) [7-9]. However, understanding the exact role of Pr₆O₁₁ and CeO₂ in nano-sized tooth-

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like Y-TZP and a systematic study of the sintering mechanism are incomplete. In this paper, a mechanical mixture process, with the advantages of a simple process, lower cost and suitability for industry, was applied to prepare composite powder which used a more conventional, economical and widely available sintering technique, i.e. pressureless two-stage sintering (grain growth is a major problem for nano-sized powder. Initial research proposed that a high green density and a minimum sintering temperature are beneficial in controlling the grain growth of nano-sized powder. Two-stage sintering(2SS) is reported to be able to refine the microstructure and enhance the material properties.). The sintering behavior of minor additions of Pr_6O_{11} and CeO_2 added to nano-sized 3Y-TZP was examined.

Hence, the aim of the present study was to assess the influence of minor additions of Pr_6O_{11} and CeO_2 on the densification behavior and microstructure of nano-sized Y-TZP.

Experimental Procedure

Commercially available 3 mol%-yttria-stabilized tetragonal zirconia (3Y-TZP) nano-sized powders: a low calcined TZ-3Y-BE grade (Lot No. Z 305181P, Tosoh, Tokyo, Japan) were used in preparing the samples. Additives of Pr₆O₁₁ (99.9%, Shanghai regeant Co., Shanghai, China) and CeO₂ (99.9%, Shanghai regeant Co., Shanghai, China) were added to 3Y-TZP individually and incombination. In the case of an individual addition, 0.005, 0.01, 0.02 wt% of Pr₆O₁₁ or 0.2, 0.4, 0.8 wt% of CeO₂ were added. In the case of a combined addition, the amount of CeO₂ was varied from 0.2, 0.4, 0.8 wt% individually and the amount of Pr₆O₁₁ was fixed at 0.02 wt%. The weighed powders were wet mixed for 24 h in a plastic jar with zirconia balls and ethanol, then dried in an oven at 100 °C. Samples were pressed under a low pressure, 5 Mpa, into pellets (20 mm in diameter and 2 mm thick) and 15 MPa into bars (30 mm*35 mm) for 1 minute, and then cold isostatic pressed at 300 MPa for 3 minutes. The green densities (measured by the Achimedes' technique in mercury) of the compacts were 44-46% of the theoretical density of tetragonal zirconia. Subsequently two-step sintering methods were adapted for the samples. In the first step, a slow thermal debinding profile with a very slow heating rate (1 Kminute⁻¹ to 600 °C held for 2 hours; and 5 Kminute⁻¹ to 1100 °C held for 2 hours and 5 Kminute⁻¹ to room temperature) was carried out in Nabertherm Furnace in an atmosphere environment. The slow heating rate can prevent defects such as microcracks that are induced during the binder extraction process; while pre-sintering to 900 °C provided strength to the debound sample for easy handling. In the second step, the samples were sintered in air at 1350 °C for 2 hours, followed by 5 Kminute⁻¹ cooling down to room temperature.

There are many parameters that can be used to assess the sintering process, such as microstructural measurements, material properties and dimensional changes [10]. Despite a wide range of measurements, weight loss, shrinkage, density, hardness and microstructure in particular are recorded in the experiments.

Sinterability was evaluated through the shrinkage, density value. The percent shrinkage measures the dimensional change of a sintered body from a green body, as indicated by the fractional shrinkage, $\Delta L/L0$ in length. The relative density of sintered specimens was determined by the Archimedes method using distilled water as the immersion liquid and the relative density were calculated based on assuming the theoretical densities of 6.10 g/cm³, 6.88 g/cm³, 6.576 g/cm³ for tetragonal zirconia, Pr₆O₁₁ and CeO₂ respectively. The SEM used in this study was a JEOLJSM-6700F analytical scanning electron microscope fitted with a 10/85-Link microanalysis system manufactured by Oxford Instrument. The SEM was used to examine the fracture surface morphology, and in grain size determinations. The phase identification of sintered samples was carried out by an X-ray diffractometer (XRD, Rigaka, D/max 2550 V) with the XRD patterns being collected at a rate of 3 Kminute⁻¹ with a fixed counting time of 3 s. The hardness of the samples was determined from Vickers indentations obtained with a load of 10 kg for 10 seconds. Vickers hardness HV 10 was computed from Equation1:

$$HV10 = \frac{1.8544.P}{d^2}$$
(1)

where HV is the Vickers hardness, P is the applied indenter load and d is the average diagonal length for an individual indentation. The cracks that originated from the Vickers indentations were also used to compute the fracture toughness by the indentation fracture method, using Equation 2 proposed by Niihara et al. [11].

$$K_{lc} = 0.018.H.a^{1/2} \left(\frac{E}{H}\right)^{0.4} \cdot \left(\frac{a}{c} - 1\right)^{-1/2}$$
(2)

where K_{Ic} is fracturer toughness, H is the Vickers hardness, a is the half diagonal of the indentation, E is the elastic modulus, c is the crack length (measured from the center of indentation).

Results and Discussion

Sintering behavior

After the samples with additions of Pr_6O_{11} and CeO_2 individually and incombination were sintered at 1350/ 1100 °C, the relationships between content and relative density and linear shrinkage are illustrated in Fig. 1 and Fig. 2.

Figure 1 shows the relative density (corrected for weight loss) with additions of Pr_6O_{11} and /or CeO₂, during heating in an oxygen flow. The data of undoped 3Y-TZP are also shown in the figure for comparison. Sintering of the composites at 1350 °C resulted in greater than 98% densification, and as can be seen in Fig. 1, compared with undoped 3Y-TZP, in the case of Pr_6O_{11} additions,



Fig. 1. Bulk relative density of samples with additions of Pr_6O_{11} and CeO_2 individually and incombination.

the relative densification was continuously promoted and showed a maximum relative density at 0.02 wt% of Pr_6O_{11} . In the case of CeO₂ additions, however, a continuous decrease in density was observed as the content of CeO₂ increased, and in the case of Pr_6O_{11} and CeO₂ additions incombination, a continuous increase in density was observed as the content of CeO₂ decreased, and the relative density was higher than the case of an individual addition of CeO₂.

Considering the changes in the sintered relative density of the 3Y-TZP samples with 0.02 wt% of Pr_6O_{11} and differing amounts of CeO_2 0.2, 0.4, and 0.8 wt%, it was found that a sintered relative density near to the full theoretical density decreased from 99.82% to 99.26% with an increasing CeO_2 content. The increase of the sintered density of samples can be attributed to the decrease of CeO_2 existing as the second phase. According to the solid forming condition and sintering dynamic theory, the substitutions of Ce and Pr resulted in the formation of anion and cation vacancies, respectively for the compensation of effective charges, which enhances the sintering activity.

Figure 2 shows the linear shrinkage rate ($\Delta L/L0$) with additions of Pr₆O₁₁ or CeO₂ content, during heating in an oxygen flow. The data for undoped 3Y-TZP are also shown in the figure for comparison. As can be seen in Fig. 2, in the case of Pr_6O_{11} or CeO_2 additions, the linear shrinkage rate was lower compared with undoped 3Y-TZP, however, in the case of Pr_6O_{11} additions, the linear shrinkage rate was continuously promoted as the content of Pr_6O_{11} increased. In the case of CeO_2 additions, however, a continuous decrease in linear shrinkage rate was observed as the content of CeO_2 increased, and in the case of Pr_6O_{11} and CeO₂ addition incombination, a continuous decrease in linear shrinkage rate was observed as the content of CeO₂ increased. Furthermore, the linear shrinkage rate is lower than the case of individual CeO₂ additions. The sintering shrinkage has two contributions: loss of polymer in the early stages and loss of porosity at the sintering temperature.

With a decreasing content of CeO₂ under 0.8 wt%, the



Fig. 2. Linear shrinkage rate of samples with additions of Pr_6O_{11} and CeO_2 individually and incombination.

increase of porosity may have caused the decrease in shrinkage while with increasing content of Pr_6O_{11} up to 0.005 wt%, a lower porosity may have caused the increase in shrinkage. While the percentage linear shrinkage of all samples did not vary to a great extent, this may due to the fact that all samples were densified near to theoretical density.

Figure 3 shows SEM images of the cross-sectional surfaces of the pure 3Y-TZP and Pr_6O_{11}/CeO_2 added samples. Compared with the 3Y-TZP sample with 0.02 wt% of Pr_6O_{11} and differing amount of CeO₂ such as 0.2, 0.4, and 0.8 wt%, a similar grain size to that of the pure 3Y-TZP was observed and the grain size varies in a wide range from 100 nm to 300 nm, indicating that normal grain growth occurred during sintering at 1350 °C. More porosity can be detected in the grain boundaries of the undoped sample, however, the sintered composite with additions exhibits a relatively dense structure. This is caused by the accelerated diffusion due to oxygen vacancies, which were generated during the formation



Fig. 3. Cross-section SEM images of (a) $0.02 \text{ wt\% Pr}_6O_{11}$ and 0.2 wt% CeO₂, (b) $0.02 \text{ wt\% Pr}_6O_{11}$ and 0.4 wt% CeO₂, (c) 0.02 wt% Pr $_6O_{11}$ and 0.8 wt% CeO₂ added into 3Y-TZP samples, and (d) pure 3Y-TZP.



Fig. 4. X-ray diffraction profiles of pure (a) and (b) 0.2, (c) 0.4, (d) 0.8 wt% CeO₂ with Pr_6O_{11} fixed at 0.02 wt% added 3Y-TZP samples.

of a solid solution of Pr and Ce in Y-TZP. A limited grain growth was observed, probably because nanocrystallites are agglomerated in a crystallized envelope.

Figure 4 shows the X-ray diffraction profiles of the pure 3Y-TZP and samples 3Y-TZP with 0.02 wt% of Pr_6O_{11} and differing amounts of CeO₂ such as 0.2, 0.4, and 0.8 wt%. The structure of the pure 3Y-TZP was identified as the tetragonal ZrO₂ phase (ICDD No. 42-1164). When 0.2, 0.4, 0.8 wt% of CeO₂ was added, the structure was found to be tetragonal (ICDD No. 42-1164) and the sample contained CeO₂ as a second phase, diffraction peaks from the second phase were observed. It was discovered that the peak intensity of the CeO₂ second phase increased as more CeO₂ was added, as expected.

The lattice constants of the fresh and aged CZ, a and c, are both larger than those of tetragonal ZrO_2 (a = 3.596 Å, c = 5.184 Å), which implies the insertion of Ce cations into the tetragonal lattice since the radius of Ce^{4+} (0.97 Å) is larger than that of Zr^{4+} (0.87 Å). The ionic radius of Pr and Ce is larger than that of Zr (0.87 Å) and the lattice constant of 3Y-TZP expanded. When larger Pr and Ce ions substitutes for Zr ions, the position of the surrounding oxygen anions is closer, which results in an increased repulsive force among anions. In this case, the repulsive force could contribute to the expansion of the lattice constants as observed in SnO₂ doped In₂O₃ reported by Nadaud et al. [12]. Otherwise, when the amount of solid solution is very small, it is commonly observed that there is no appreciable change in the lattice constant of the host crystal.

The lattice parameters were derived from a Rietveld refinement of XRD results and the crystal size calculated according to Scherrer's equation. The theoretical lattice constants were calculated according to Vegard's law [13] in Equation 3, where the ionic radius difference is obtained from $\Delta rk = rk$ -rCe, the valence difference is derived from $\Delta zk = zk$ -zCe, the mk stands for the molar percentage of the dopant k and 5.411 Å is the

lattice constant of cubic CeO₂.The ionic radii (Pauling) taken for the calculations were as follows: 0.87 Å for Zr^{4+} , 0.96 Å for Pr^{4+} and 1.126 Å for Pr^{3+} . It is assumed that all Ce existed in Ce⁴⁺ (0.97 Å).

$$a5:411 + \Sigma(0:0220\Delta rk - 0:0015\Delta zk)mk$$
(3)

With a combined addition of Pr_6O_{11} and CeO_2 , diffraction peaks from the second phase were observed. The peak intensity from the second phase of CeO_2 was stronger. Since there is no phase diagram of 3Y-TZP and CeO_2 available, the solid solution of CeO_2 could not be proved. Based on Fig. 4, it was presumed in this experiment that CeO_2 was soluble up to 0.2 wt.% in 3Y-TZP at 1350 °C for 2 h. The decrease of the CeO_2 second phase could be due to the increased solubility limit of CeO_2 by the effective charge compensation through co-doping, however, the second phase, which was identified as CeO_2 , appeared with a combined addition (the amount of CeO_2 was varied with 0.2, 0.4, 0.8 wt% individually and the amount of Pr_6O_{11} was fixed at 0.02 wt%) samples are shown in Fig. 4.

The substitutions of Ce and Pr resulted in the formation of anion and cation vacancies, respectively for the compensation of effective charges. From this pointof-view, when Pr_6O_{11} and CeO_2 are co-doped, the charge compensation would be achieved without the formation of defects. So the solubility limit of co-dopants can be increased more than in the case where only a single type of dopant is added. Moreover, the energy required for charge compensation by co-doping is lower than that for charge compensation by defect generation. This can also be inferred from the case in which MgO and TiO₂ were co-doped to Al_2O_3 by Roy et al. [14] and from the case in which Nb₂O₅ and CoO were co-doped to SnO₂ by Chang et al. [15] .On the basis of this background, various amounts of CeO₂ was added to 3Y-TZP with $0.02 \text{ wt\% of } Pr_6O_{11}$, which revealed the lowest density with the precipitated second phase of CeO_2 .

Mechanical behavior

Material properties determine the applications of a material. Hardness is a material property that can be measured on a polished surface with no stringent requirements on specimen dimensions. A Vickers hardness value (Hv) also relates to other material properties such as the strength and toughness. Toughness in particular can be calculated from a Vickers hardness test, with the measurement of crack lengths [16, 17]. If the surface underneath the indentation contains porosity that weakens the test surface, the indentation mark becomes bigger and will cause a low hardness reading. Hardness can also directly manifest whether the material is useable with acceptable strength. Thus, in the later discussions, Vickers hardness will be used as the sintering indicator, with the support of SEM micrographs to assess the microstructural properties, especially grain size distribution.

After the samples with additions of Pr_6O_{11} and CeO_2



Fig. 5. The hardness of samples with additions of Pr_6O_{11} and CeO_2 individually and incombination.

Table 1. The relationship between Pr_6O_{11} and CeO_2 content and the fracture toughness

Colorants	Content (%)	Fracture toughness K_{Ic} (Mpam ^{-1/2})
pure 3Y-TZP	0	5.84
Pr_6O_{11}	0.005	5.11
	0.01	5.07
	0.02	4.99
CeO_2	0.2	5.95
	0.4	6.03
	0.8	6.18
Pr_6O_{11}/CeO_2	0.02/0.2	5.88
	0.02/0.4	5.96
	0.02/0.8	6.12

individually and incombination were sintered at 1350/ 1100 °C, the relationships between content and Vickers hardness and fracture toughness are showed in Fig. 5 and Table 1. From Fig. 5, it is observed that the hardness increases with additions of Pr_6O_{11} and/or CeO_2 content, during heating in an oxygen flow. The data of undoped 3Y-TZP are also shown in the figure for comparison. Sintering of the composites at 1350 °C resulted in hardness values varying from 1208-1443 MPa which more appropriately reflects the degree of sintering when compared to shrinkage, and as can be seen in Fig. 5, compared with undoped 3Y-TZP, in the case of Pr_6O_{11} additions, the hardness was continuously promoted and showed a maximum relative density at 0.02 wt% of Pr₆O₁₁. In the case of CeO₂ additions, however, a continuous decrease in hardness was observed as the content of CeO_2 increased, and in the case of combined Pr_6O_{11} and CeO₂ additions, a continuous increase in hardness was observed as the content of CeO₂ decreased, and the hardness was higher than the case of an individual CeO_2 addition.

Table 1 shows the relationship between Pr_6O_{11} and CeO_2 contents and the fracture toughness. As can be seen in Table 1, for the case of Pr_6O_{11} additions, a continuous decrease in fracture toughness was observed and values lower than that of undoped 3Y-TZP, while, in the case of CeO₂ additions individually and incombination, the

fracture toughness were higher compared with undoped 3Y-TZP. The fracture toughness increase of composite materials may be attributed to the superposition of many toughening mechanisms. There are two main toughening mechanisms (a toughening mechanism by microcracks and stress-induced phase transformation toughening) in zirconia toughened ceramics, which is influential by the effect of grain size. The mechanism by which the creep resistance is enhanced by doping has been postulated to be a reduction of grain-boundary diffusivity. Also the increase of the fracture toughness of samples can be attributed to the decrease of CeO_2 existing as the second phase.

Conclusions

Based on the experiments conducted and the results obtained, the following conclusions can be drawn:

The addition of small quantities of Pr_6O_{11} and CeO_2 to a commercial zirconia powder has no significant effect on its densification and microstructural evolution.

2SS-1350/900 °C is found to be the optimum 2SS sintering condition. Sintering of the composites at 1350 °C resulted in greater than 98% densification and the percentage linear shrinkage of all samples did not vary to a great extent.

Within the solubility limit, the densification and linear shrinkage rate increased as the amount of Pr_6O_{11} increased under 0.02 wt%, while the densification and linear shrinkage rate decreased as the amount of CeO_2 increased above 0.2 wt%. Furthermore, the densification and linear shrinkage rate with co-dopants can be increased more than in the case where only a single kind of dopant (CeO₂) is added. This is caused by the accelerated diffusion due to oxygen vacancies, which were generated during the solid solution of Pr and Ce in 3Y-TZP.

A limited grain growth was observed, probably because nanocrystallites are agglomerated in a crystallized envelope. Within the solubility limit of CeO₂, the sintered density of 3Y-TZP improved due to accelerated materials transport. Since the cation vacancy of VZr by Ce substitution extinguishes Vö in 3Y-TZP, CeO₂ additions showed a decrease in density. When Pr_6O_{11} and CeO₂ were co-doped, the densification increased as the content of CeO₂ decreased, which signifies the solubility limit of CeO₂ is extended by co-doping.

By this way it is possible that bioceramics with a color similar to natural dentine could be developed.

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