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Investigation of a new 3Y-stabilized zirconia with an improved optical property for applications as a dental ceramic

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To study the mechanical and optical properties of a new nanocrystalline yttria-stabilized zirconia (PX242A Tosoh Japan). The influence of heating rates on its properties and its potential use as a dental ceramic were also evaluated. Samples of PX242A were divided into 4 groups according to heating rates : group H1 ($100^{o}Kh^{-1}$); group H2 ($200^{o}Kh^{-1}$); group H4 ($400^{o}Kh^{-1}$); group H6 ($600^{o}Kh^{-1}$). Group H0 (3Y-SBE Tosoh Japan) was made according to the manufacturer's recommendation as a control. The contrast ratio (CR), transparency parameter (TP) and total transmittance (TT) were measured by an Xrite spectrophotometer. The flexural strength and fracture toughness were also evaluated. The flexural strength and fracture toughness were found to be independent of the heating rate while the optical properties significantly increased when the heating rates were $600^{o}Kh^{-1}$, $200^{o}Kh^{-1}$ and $400^{o}Kh^{-1}$, but were not significantly different with $100^{o}Kh^{-1}$. A heating rate of $600^{o}Kh^{-1}$ is suggested as a time efficiency protocol, because it could provide desirable mechanical and optical properties, making zirconia suitable for clinical use.

Key words: Heating rate, Transparency, Ceramic, Mechanical property, Zirconia.

Introduction

All-ceramic restorations have become a trend in dentistry due to their excellent biocompatibility and superior optical properties. Adequate translucency plays an important role in optimal esthetics of all-ceramic restorations; however, 3Y-stabilized zirconia, which has been shown to possess excellent mechanical properties, may not meet the esthetics requirements because of its poor translucency. This material has traditionally been opaque with a white-to-grayish appearance in its polycrystalline form. Increasing requirements from both sophisticated industrial as well as consumer mass markets have asked for optically-transparent materials with extraordinary property combinations [1].

The 8 mol% yttria-stabilized zirconia (8YSZ) with a cubic structure possesses superior optical properties, but its low mechanical strength [2] hinders the fabrication of a ceramic for use in dental restorations. Optically-transparent polycrystalline YSZ has been produced using the spark plasma sintering (SPS) method. This method produced zirconia specimens with amber brown, dark orange and ruby-red colors, thus limiting this material's use in dental applications [3].

Translucency occurs when a light beam passing through a material is partly scattered, reflected, and transmitted through the object: the greater the quantity of light that passes through the object, the higher the translucency [4]. Scattering of light is generated by many factors, including different refractive indices, voids and porosities, a high crystalline content [5], and crystal number and size, especially when the crystal particles are slightly larger than the wavelength of the incident light [6].

The objective of the present work was to evaluate the traditional sintering technique with different heating rates for the preparation of dense bulk zirconia materials. Moreover, possible effects of the heating rates and grain size on the mechanical and optical properties of this material and its future application as a high load-bearing dental restoration material were also explored.

Materials and Methods

Materials

PX 242A (Tosoh, Tokyo, Japan) and a traditional commercially available 3 mol yttria-stabilized zirconia powder (3Y-SBE,Tosoh) were used to prepare the specimens. The powder (2.5 g) was pressed into pellets (20 mm in diameter and 1.5 mm thick) at a 2.5 MPa pressure and into blocks ($30 \times 35 \times 4.5$ mm^3) at a pressure of 10 MPa for 30 seconds, and then cold isostatically pressed at 100 MPa for 3 minutes. Subsequently, two-step sintering methods were adapted for these specimens. For the first step, all specimens were sintered at $50^{o}Kh^{-1}$ until they reached 900 ^{o}C. Specimens were then held for 2 hours, then naturally cooled in the furnace. For the second step, four different heating rates were used for four different groups of PX 242A. The first group of specimens were

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sintered at 100°Kh^{-1} until they reached 1450 °C. The second group of specimens were sintered at 200°Kh^{-1} until they reached 1450 °C. The third and fourth groups were also sintered until 1450 °C at 400°Kh^{-1} and 600°Kh^{-1}, respectively. After reaching 1450 °C, all specimens were held for 2 hours, then naturally cooled in the furnace. The 3Y-SEB specimens were sintered at 300°Kh^{-1} until they reached 1350 °C, held for 2 hours, then naturally cooled in the furnace. These four groups of PX 242A were grouped together for flexural strength and fracture toughness measurements, as well as all other measurements mentioned below. The sample discs of 3Y-SBE were used in the measurement of translucency only.

Characterization

After sintering, the specimens were characterized with respect to their optical properties, mechanical properties, and crystalline phases present.

Fracture toughness

The fracture toughness ($K_{Ic}10$) was determined based on radial crack length measurements according to the formula of Anstis *et al.* [7]. The reported data are the mean of ve indentations.

Flexural strength

Sintered blocks of PX242A were grouped into four groups with the aforementioned four heating rates for flexural strength measurements. Each group contained ten testable bars, each measuring 1.2 × 4 × 20 mm^3 per bar, according to ISO6872. All surfaces of the test bars were finely ground on an 800-grit diamond wheel, and the edges were beveled. The direction of both the diamond grinding and of the beveling was parallel to the bar lengths. Ten test bars from each heating rate were subjected to the three-point bending test using a universal testing machine (EASY TESTEZ20, Lloyd Instruments LTD, UK) with a crosshead speed of 0.5 mm/minute. The span length was 20 mm.

SEM examination

The microstructures of the densied PX242A specimens were studied by eld emission scanning electron microscopy (FE-SEM) (Hitachi S-4300SE) on polished and thermally etched surfaces. Thermal etching for 60 minutes at a temperature 100 °C below the sintering temperature was used. The average grain size was estimated from the FE-SEM micrographs by image analysis software (Carl Zeiss, Germany).

Measurement of translucency

A quantitative measurement of translucency was completed by comparing the reflectance of light [8] (ratio of the intensity of reflected radiant flux to that of the incident radiant flux) through a test specimen over a backing with a high reflectance to that of a low reflectance or high absorbance. This procedure produced a contrast ratio (CR) in which CR = Yb/Yw: the reflectance of light of the material on a black surface (Yb) to the reflectance on a white surface (Yw). This ratio tends towards unity for opaque materials and towards zero for transparent materials [9].

Five discs (18 mm in diameter and 0.50 ± 0.01 mm in thickness) of each group were finished flat on a grinder/polisher with wet 120-, 240-, and 400-grit silicone carbide paper. The specimens were ultrasonically cleaned in distilled water to be measured with a digital spectrometer (Color i7, XRite, USA). Each specimen was measured 3 times; the averages of the measurements were recorded. Data were measured with CIE illuminant D65 and the 2-degree observer function. Each specimen was placed at the reflectance specimen port, and 3 measurements were made with the white reference backing (Yw) and then the black backing (Yb), resulting in a total of 6 measurements per specimen. Mean contrast ratios were calculated as Yb/Yw.

The difference between a zirconia specimen on white and black reference backing was also calculated as the translucency parameter (TP), suggested for maxillofacial prostheses [10]:

$$TP = \{(L^*_B - L^*_W)^2 + (a^*_B - a^*_W)^2 + (b^*_B - b^*_W)^2\}^{1/2} \quad (1)$$

where the subscript B refers to the color parameter on the black backing and the subscript W on the white backing. The averages for the 3 readings of L*, a*, and b* values were calculated for each specimen and each background.

Total transmittance (TT) was also measured by Color i7 as the parameter to indicate the masking ability of the specimens over the background color [11]. The specimen is placed in front of the spherical entrance port of the equipment through which the light beam enters. The sphere collects all the light passing through the specimen. Measurements were made over the wavelength range 460 nm to 720 nm under the UV included condition. TT includes the parallel transmittance (PT) and diffuse transmittance (DT), which are useful in determining the degree of transparency of a material. The numerical value tends towards 0 for opaque materials and towards 1 for transparent materials. Each specimen was measured 3 times, and the averages of the measurements were recorded.

Results

Analysis of the data by ANOVA and the Sheffé post hoc test shows that PX242A has a higher bending strength when the heating rate was 100°Kh^{-1}(Table 1). Although the strength value of the 100°Kh^{-1} sample is greater than those of the others, there is no significant statistical difference in bending strength between these materials (P = 0.07).

Three point bending strengths and fracture toughnesses of different heating groups are reported in Table 1 along with the corresponding standard deviations. When the heating rate was 100°Kh^{-1}, the fracture toughness of PX242 was slightly lower than the other groups, but there is no significant statistical difference between these materials(P = 0.367).

Table 1. Average and standard deviation of flexural strength and fracture toughness

Heating Rate	Flexural strength (MPa)	Fracture toughness (MPa $m^{1/2}$)
100°Kh^{-1}	1487(168)[1]	4.34(0.12)[1]
200°Kh^{-1}	1281(153)[1]	4.46(0.14)[1]
400°Kh^{-1}	1396(126)[1]	4.44(010)[1]
600°Kh^{-1}	1449(176)[1]	4.44(0.11)[1]

There is no significant statistical difference between materials with the same superscript number.

SEM micrographs of a selection of sintered PX242A specimens with different heating rates are shown in Fig. 1. Image analysis on many such micrographs showed that the specimens had average grain sizes of 250 nm, 237 nm, 243 nm, and 230 nm when the heating rates were 100°Kh^{-1}, 200°Kh^{-1}, 400°Kh^{-1}, and 600°Kh^{-1}, respectively. The average grains size is quite similar for the four specimens, although the grain size distribution appears to be a little different (Fig. 2). Slightly smaller grains (below 200 nm) can be observed in the 600°Kh^{-1} sintered specimen. The average and standard deviations of total transmission, transparency parameter and contrast ratio of PX242A and 3Y-TZP are shown in Table 2.

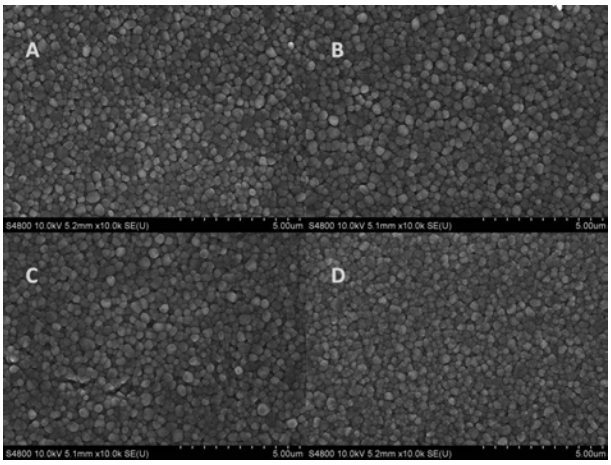

Fig. 1. SEM micrographs of sintered PX242A specimens of different heating rates : (A) 100°Kh^{-1}, (B) 200°Kh^{-1}, (C) 400°Kh^{-1} and (D) 600°Kh^{-1}.

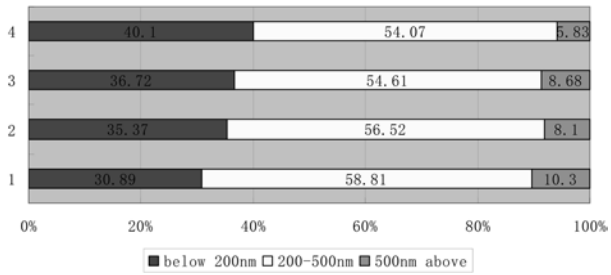

Fig. 2. Grain size distributions of sintered PX242A specimens with different heating rates : (1) 100°Kh^{-1}, (2) 200°Kh^{-1}, (3) 400°Kh^{-1} and (4) 600°Kh^{-1}.

Table 2. Average and standard deviation of total transmission, transparency parameter and contrast ratio

Heating Rate	Total transmission (TT)	Transparency Parameter (TP)	Contrast Ratio (CR)
100°Kh^{-1}	35.19(0.39)[1]	12.72(0.22)[1]	0.69(0.004)[1]
200°Kh^{-1}	32.79(0.89)[2]	11.66(0.48)[2]	0.71(0.009)[2]
400°Kh^{-1}	33.27(0.89)[2]	11.93(0.56)[2]	0.70(0.012)[2]
600°Kh^{-1}	35.29(0.21)[1]	12.85(0.64)[1]	0.68(0.001)[1]
3Y-SBE	28.44(1.88)[3]	9.88(0.12)[3]	0.77(0.002)[3]

There is no significant statistical difference between materials with the same superscript number.

Discussion

The main goal of this study was a comparison of the use of different heating rates with conventional sintering for a new nanometric zirconia powder in terms of mechanical and optical property changes. The application of this material as a future high load-bearing dental restoration was also explored. For these purposes, four different heating rates that could be easily replicated were chosen.

Microstructure and mechanical property

The conventional sintering experiments showed that the heating rate had an effect on densication behavior: a slower heating rate resulted in a higher nal density [12]. The absolute density was measured by the Archimedes method, and was above 99.3% for all four heating groups. This method is insensitive to extremely low porosity, making it difficult to compare with previously published work.

The mean values of flexural strength and fracture toughness are reported in Table 1. As far as strength is concerned, different heating rates did not show any statistical difference. The average flexural strength of each group was above 1250 MPa. The fine nanostructure can provide significant improvement in mechanical properties. The flexural strength is also higher than some of the most representative zirconia-based dental ceramics, i.e., In-Ceram Zirconia (IZ) (Vita Zahnfabrik, Bad Sackingen, Germany) and DC-Zirkon (DZ) (DCS Dental AG, Allschwil, Switzerland) [13]. The present study demonstrated that the fracture toughness of PX 242A was about 4.42 MPa $m^{1/2}$, lower than traditional Y-TZP as reported by Yan *et al*. [14].

SEM photomicrographs showed more smaller grains (below 200 nm) in the 600°Kh^{-1} sintered specimen. The results indicate that a higher heating rate can suppress grain growth.

Transparency

Translucency of esthetic dental materials is usually evaluated by the contrast ratio (CR) and the translucency parameter (TP). Total transmittance (TT) as a direct measurement of light transmittance and was used to evaluate translucency in the present study.

CR is one of the most widely used parameters to compare

relative translucency, and TP is the color difference between a uniform thickness of material and corresponds directly to a common visual assessment of translucency [15].

Light incident upon the nanocrystalline specimens can be reflected, scattered, or absorbed in the bulk. Previous work on ceramics densified from powder has confirmed that scattering is the primary reason for the opacity of most ceramics. In turn it has been found that light scattering is largely a function of the porosity of a material. The scattering efficiency for spherical pores, however, decreases dramatically when the size is reduced to the nanometric range [16]. For this reason it is believed that nanostructured polycrystalline materials would provide better transparency than materials with a grain size in the micrometric range.

Anselmi-Tamburini *et al*. found that porosity plays a large role in the transparency of YSZ, and only pores larger than ~50 nm cause significant scattering and thus reduction of transmission [17]. In the present study, such large pores were seldom found in the SEM for all four heating groups. Particles similar in size than the light wavelength have the greatest scattering effect [18]. Small particles (approximately 200 nm in diameter) could be less opaque because of less refraction and absorption. The percentage of particles below 200 nm in the $600^{o}Kh^{-1}$ group is higher than in the other groups. Therefore, its improvement in light transmittance might be attributable to the smaller grain size.

Kim *et al*. found that slow heating allows the powder to stay in the open porosity state longer and results in a low defect concentration in the specimen [19]. The improved optical property might also be a result of the low defect concentration of the $100^{o}Kh^{-1}$ group.

All samples' thicknesses were measured before the spectrophotometer reading to ensure similar thickness. This ratio tends towards unity for opaque materials and towards zero for transparent materials. Heffernan *et al*. reported that In-Ceram Zirconia was opaque, with values equal to those of metal ceramics (contrast ratio = 1.0) [5 6]. Thickness is a covariable relative to opacity, with thicker materials having greater opacity. The thickness of the flat specimens in that experiment was also 0.5 mm. So the transparency property of the PX242A in the present study was better than with the previous generation of zirconia. In the present study, the transparency property of PX-242A was significantly higher than 3Y-TZP ($P < 0.05$).

When an all-ceramic restoration is chosen as a dental material, the amount of force that the restoration must withstand should be evaluated, not just the esthetic qualities [20]; however, no significant strength difference was found with the four heating rates in the present study. Therfore, it is believed that a higher heating rate will improve the efficiency in clinical practice.

Conclusions

Within the limitations of this study, the following conclusions were drawn :

1. Using the traditional sintering technique, different heating rates do not significantly influence PX 242A zirconia's mechanical properties.
2. A higher heating rate was suggested to choose as a time efficiency protocol because it could obtain desirable mechanical and optical properties for clinical use of PX 242A zirconia.

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