Fluorescence of thulium-doped translucent zirconia

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The fluorescence and physical properties of thulium-doped zirconia were investigated. A standard grade of zirconia (TZ-3Y-E) and two translucent dental zirconia materials (Zpex and Zpex Smile) were examined. The specimens were prepared by addition of 0–1.5 wt% Tm_2O_3 and then sintering. When exposed to UV light, the Tm_2O_3 -doped zirconia exhibited blue fluorescence with a peak wavelength of 460 nm. The fluorescence intensity of Zpex and Zpex Smile was higher than that of TZ-3Y-E, with Zpex being more intense than Zpex Smile. Zpex exhibited maximum fluorescence intensity when doped with 0.8 wt% Tm_2O_3 . XRD analysis revealed that TZ-3Y-E and Zpex contained primarily tetragonal zirconia, while Zpex Smile contained largely cubic phase zirconia. There were no changes observed in the microstructure or physical properties of the zirconia specimens when doped with Tm_2O_3 .

Keywords: Zirconia, Fluorescence, Thulium, Monolithic fixed dental prosthesis, CAD/CAM

INTRODUCTION

With the growing demand for esthetic dental treatments, patients want prosthetics with whiter and brighter teeth. Generally, ceramics are used for the fabrication of tooth-colored fixed dental prostheses. Zirconia has the highest resistance to fracture among dental ceramics because of its great strength and fracture toughness¹. The difficulties associated with manually compensating for the shrinkage of zirconia that occurs during sintering have been overcome with the advent of CAD/CAM systems. This allows these materials to be processed with great accuracy, which has led to the popularity of zirconia in the clinical dental setting^{2,3}.

Zirconia has a crystalline structure that is stabilized in the tetragonal phase by the addition of yttria. This material was first used in dentistry to make the frames of fixed dental prostheses. While it was a strong material, it was not very translucent^{2,4} and so these zirconia frameworks needed to be veneered with porcelain. This leads to problems with the porcelain veneer on the framework chipping or fracturing^{5,7}. A new form of zirconia has been developed recently^{7,8} that is more translucent than the form traditionally used for frameworks. A monolithic, fixed dental prosthesis has been fabricated from this translucent zirconia, which reproduces the natural color of teeth and is highly resistant to fracture^{9,10}.

Natural teeth are fluorescent, which gives them a visual quality beyond the shades shown on the product shade guide^{11,12}. When exposed to UV light, the fluorescence of natural teeth makes them appear a bluish white and those in areas within the oral cavity that are poorly lit look whiter and brighter than non-

fluorescent materials¹³. Therefore, glass ceramics and resin composites that are used as tooth-colored materials often incorporate fluorescent materials^{14,15}.

Dental zirconia is not generally fluorescent¹⁶ and so when it is used as a framework for prosthesis it is commonly veneered with fluorescent porcelain. However, when making a monolithic prosthesis it is preferable that the zirconia itself fluoresces. The addition of small amounts of rare-earth elements¹⁷ used in inorganic fluorescent pigments would likely make zirconia fluorescent. To examine this proposal, zirconia specimens with trace amounts of added thulium were prepared and the fluorescence, translucency and physical properties of these materials were evaluated.

MATERIALS AND METHODS

Specimens

Three commercially available yttria-stabilized zirconia powders (TZ-3Y-E, Zpex, and Zpex Smile) were used as the starting materials for the samples (Tosoh, Tokyo, Japan). TZ-3Y-E is a standard grade of zirconia and both Zpex and Zpex Smile are translucent dental zirconia materials. TZ-3Y-E contains 0.25 wt% alumina, while Zpex and Zpex Smile contain almost no alumina. Zpex Smile contains more yttria than the other two types of zirconia that we used (Table 1).

The specimens were prepared using the following procedure: thulium (Tm_2O_3) powder was added at different concentrations (0, 0.5, 0.8, 1.0, 1.2, and 1.5 wt%) to each of the three zirconia powders. The mixtures were subjected to wet ball-milling for 24 h using ethanol and zirconia balls, followed by dry ball-milling for 24 h using zirconia balls. After milling, the powder mixtures were molded into pellets under cold isostatic pressure (CIP) at 200 MPa for 5 min and then sintered at 1,500°C

Color figures can be viewed in the online issue, which is available at J-STAGE.

Received Oct 30, 2017; Accepted Mar 5, 2018

doi:10.4012/dmj.2017-384 JOI JST.JSTAGE/dmj/2017-384

Table 1 Compositions of materials

Material (Trade name)	Y ₂ O ₃ (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ , Fe ₂ O ₃ (wt%)
Conventional Y-TZP (TZ-3Y-E)	5.26	0.251	≅0.002
Translucent Y-TZP (Zpex)	5.35	0.048	≅0.002
Translucent Y-TZP (Zpex Smile)	9.42	0.049	≅0.002

for 2 h. The heating and cooling rates used for each specimen were 10°C/min. After sintering, each pellet was polished with a water resistant #1000 abrasive paper, which yielded the final disk-shaped zirconia specimens (diameter=12 mm, thickness=1.0 mm). Five disks were fabricated for each of the six doping concentrations for the three different zirconia samples, giving a total of 90 specimens.

Fluorescence and translucency

The fluorescence spectra of the specimens (excitation wavelength=365 nm, irradiance=743 μW/cm²) were recorded using a fluorescence spectrophotometer (FP-6500, JASCO, Tokyo, Japan). In addition, the intensity of the fluorescence produced at 460 nm was measured. The translucency of each specimen was evaluated using the translucency parameter (TP). The TP was obtained by measuring the CIE LAB coordinates placed on a standard white plate (L*: 98.21, a*: -0.29, b*: 4.41) and a black plate (L*: 7.39, a*: -0.13, b*: 2.55) using a spectrophotometer (CM-2600d, Konica Minolta, Tokyo, Japan). The measurements were repeated three times and the average values were calculated. After measurement, the TPs of each specimen were determined by the color difference on black (B) and white (W) backgrounds using the following formula:

$$TP = [(L_B^* - L_W^*)^2 + (a_B^* - a_W^*)^2 + (b_B^* - b_W^*)^2]^{1/2}$$

Crystalline structure and physical properties

The crystalline structures of the Tm₂O₃-free and Tm₂O₃-doped specimens were analyzed using X-ray diffraction (XRD; D8 Advance, Bruker AXS, Karlsruhe, Germany). The specimens were polished to a mirror finish (#10000 grit) using a diamond lapping film (3M Japan, Tokyo, Japan) and then some of the specimens thermally etched at 1,400°C for 30 min in the ambient atmosphere. The microstructure of the thermally etched specimens was observed using a scanning electron microscope (SEM; SU9000; Hitachi High-Technologies, Tokyo, Japan). Furthermore, the hardness of each specimen was measured in accordance with JIS R 1607¹⁸⁾ using a Vickers hardness meter (FV-310e, FUTURE-TECH, Kawasaki, Japan) by applying a 98 N (10 Kg) load to each specimen for 20 s using a diamond indenter. The fracture toughness was measured using the indentation fracture (IF) method by examining the indentation created by the Vickers indenter and any cracks that occurred in the specimen. The fracture toughness (K1c) of each specimen was calculated using the following formula¹⁹⁾:

$$K1c = 0.018(E/H)^{0.5}(P/c^{1.5}),$$

where E is the elastic modulus in GPa, H is the Vickers hardness (HV), P is the indentation load in N, and c is half of the crack length in m.

A statistical comparison of the fluorescence intensities, TP values, Vickers hardness and fracture toughness of the specimens was performed using one-way ANOVA and Tukey-Kramer's multiple comparisons test. SPSS Statistics 17.0 (IBM Japan, Tokyo, Japan) statistical software program was used for the statistical analysis. The level of significance was set at 5%.

RESULTS

Fluorescence and translucency

When exposed to UV light, the Tm₂O₃-free specimens did not fluoresce at all while those doped with Tm₂O₃ emitted a blue fluorescence (Fig.1). The fluorescence of the Zpex and Zpex Smile specimens that were doped with Tm₂O₃ was more intense than that of the TZ-3Y-E specimens doped with Tm₂O₃.

The fluorescence spectra of the specimens containing 0.8 wt% Tm₂O₃ are shown in Fig. 2. These samples emitted a blue fluorescence with a peak wavelength of 460 nm when exposed UV light (365 nm). The intensity of the fluorescence produced by the translucent Zpex samples with different doping concentrations was 1.8 to 2.7 times greater than that observed from the TZ-3Y-E samples, while that from the Zpex Smile samples was 1.4 to 2.1 times greater than the TZ-3Y-E samples (Fig. 3).

All three zirconia specimens that were free of Tm₂O₃ did not exhibit any significant fluorescence. The Zpex specimens that were doped with Tm₂O₃ exhibited the highest fluorescence intensity, followed by the Zpex Smile specimens and then the TZ-3Y-E specimens, regardless of the amount of Tm₂O₃ added. The Zpex and Zpex Smile specimens that were doped with 0.8 wt% of Tm₂O₃ exhibited the most intense fluorescence and the fluorescence intensity of all three zirconia specimens decreased when doped with 1.5 wt% Tm₂O₃.

TZ-3Y-E was less translucent than the other zirconia specimens, regardless of the amount of Tm₂O₃ added (Fig. 4). Zpex Smile was more translucent than Zpex at most doping concentrations examined. In addition, there was no difference in the translucency of Zpex or Zpex Smile when doped with 0.5 or 0.8 wt% Tm₂O₃.

Crystalline structures and physical properties

XRD analysis showed peaks that were characteristic

Fig. 1 Images of zirconia specimens exposed to UV light.

Fig. 2 Photoluminescence spectrum of 0.8 wt% Tm_2O_3 doped zirconia specimens under UV irradiation.

Fig. 3 Relative excitation intensity of zirconia specimens at a wavelength 460 nm with different additive amount of Tm_2O_3 under UV irradiation. The same superscript letters were not significantly different ($p < 0.05$).

Fig. 4 Translucent parameter of zirconia specimens with different additive amount of Tm_2O_3 . The same superscript letters were not significantly different ($p < 0.05$).

of the tetragonal phase for both TZ-3Y-E and Zpex, while Zpex Smile exhibited peaks characteristic of the cubic phase. For example, near 35° TZ-3Y-E and Zpex exhibited two peaks at 34.6° and 35.2° , while Zpex Smile

had one peak at 35.0° (Fig. 5).

SEM pictures revealed that the Zpex Smile specimens had a larger crystal grain size than the other two zirconia specimens (Fig. 6). There were no

Fig. 5 XRD patterns of zirconia specimens with or without Tm_2O_3 (0.8 wt%) addition.

Fig. 6 SEM images of zirconia specimens with or without Tm_2O_3 (0.8 wt%) addition.

Fig. 7 Vickers hardness of zirconia specimens with different additive amount of Tm_2O_3 . The same superscript letters were not significantly different ($p < 0.05$).

Fig. 8 Fracture toughness (K1c) of zirconia specimens with different additive amount of Tm₂O₃.
The same superscript letters were not significantly different ($p < 0.05$).

obvious differences in the crystalline structures of any of the zirconia specimens that were Tm₂O₃-free or doped with 0.8 wt% Tm₂O₃. The three zirconia specimens had Vickers hardness values ranging from 1,194 to 1,239, and these values were almost identical at all Tm₂O₃ doping concentrations (Fig. 7). The fracture toughness values (K1c) for TZ-3Y-E were 4.54–4.90, 4.42–4.84 for Zpex, and 2.89–3.10 for Zpex Smile. That is, those of Zpex Smile were lower than those of the other two zirconia specimens (Fig. 8).

DISCUSSION

Tooth-colored porcelains that are used to make fixed dental prostheses are fluorescent when rare-earth elements are added to the glass matrix in trace amounts^{20,21}. Rare-earth elements used for this purpose include the oxides of cerium, europium, terbium, dysprosium, and samarium²².

Zirconia is a polycrystalline material that, unlike porcelain, does not have a glass matrix. However, the addition of trace amounts of a rare-earth element, such as neodymium, europium or erbium, will cause the alumina present in the material to fluoresce²³.

Zirconia nanocrystals that contain the rare earth element thulium emit blue fluorescence when exposed to UV light²⁴. There are reports of fluorescence from pure zirconia (monoclinic phase) that has been doped with Tm³⁺ ions or yttria-rich tetragonal phase-stabilized zirconia^{25,26}. However, there are no reports that examine the fluorescence caused by the presence of Tm³⁺ ions in dental zirconia that is stabilized in the tetragonal phase by the addition of yttria. The dentin present in natural teeth emit blue fluorescence²⁷ when exposed to UV light (365 nm). Therefore, we have examined the fluorescence from dental zirconia containing various amounts of Tm₂O₃. Incidentally, euro banknotes make use of the fact that thulium (Tm³⁺) fluoresces blue when exposed to UV light²⁸.

In preliminary experiments, we observed that the fluorescence of TZ-3Y-E specimens doped with Tm₂O₃

decreased substantially when the doping concentration was increased from 1.0 wt% to 3.0 or 5.0 wt%. Therefore, the maximum amount of Tm₂O₃ added was limited to 1.5 wt%.

Zirconia that is stabilized with the rare-earth element yttria is used to make fixed dental prostheses. The addition of yttria without a lanthanoid does not make zirconia fluoresce¹⁶ and this is probably because lanthanoids contain electrons in their f orbital²⁹ that are necessary for fluorescence to occur, but yttria does not.

The Tm₂O₃-free zirconia specimens did not fluoresce when exposed to UV light. However, all specimens doped with Tm₂O₃ emitted blue fluorescence, which indicated that the addition of Tm₂O₃ was an effective method to cause these materials to fluoresce. The fact that the fluorescence of Zpex and Zpex Smile was more intense than that of TZ-3Y-E was likely caused by the difference in the translucency of the materials.

A silica-on-silicon waveguide that was doped with thulium displayed blue fluorescence with peaks at 455 and 475 nm when exposed to UV light³⁰. The Tm₂O₃-doped specimens examined in this study exhibited blue fluorescence with a peak wavelength of 460 nm, which was close to the values from the thulium-doped waveguide.

The peak fluorescent intensity varied with the amount of Tm₂O₃ that was added. The fluorescence from TZ-3Y-E was most intense when 1.0 wt% of Tm₂O₃ was added while that of Zpex and Zpex Smile most intense when 0.8 wt% of Tm₂O₃ was added. The fluorescence intensity from the three zirconia specimens did not increase any further when more Tm₂O₃ was added beyond 0.8 wt% (Zpex and Zpex Smile) or 1.0 wt% (TZ-3Y-E). This may have been caused by concentration quenching^{31,32}, which has been reported to occur in a glass that had erbium added to it.

Although Zpex Smile was slightly more translucent than Zpex, its fluorescence was less than that of Zpex regardless of how much Tm₂O₃ was added. Energy transfer in the form of UV radiation is known to affect the fluorescence of glass³³. We can assume that more UV

energy was transferred to the yttria in the Zpex Smile as it contained higher levels of yttria than Zpex, and this may have caused the lower fluorescence intensity.

The translucency of the zirconia specimens reported previously^{34,35} was higher in the monolithic translucent zirconia Zpex and Zpex Smile than in TZ-3Y-E. TZ-3Y-E contains alumina as an aid for sintering³⁶, but the other zirconia samples do not contain any significant amounts of alumina. The refractive index of alumina (1.76) is slightly lower than that of zirconia (2.15). Therefore, the presence of alumina appears to increase light scattering^{35,37}, which resulted in TZ-3Y-E being less translucent than Zpex and Zpex Smile. In addition, none of the zirconia specimens exhibited a reduction in their TPs when Tm_2O_3 was added to them, which showed that the addition of Tm_2O_3 in concentrations from 0.5 to 1.5 wt% did not affect the translucency of the zirconia.

Our XRD analysis showed that TZ-3Y-E and Zpex consisted mainly of tetragonal phase zirconia, while the Zpex Smile consisted primarily of cubic phase zirconia. These results were consistent with the literature³⁵. SEM revealed that the Zpex Smile contained larger crystals than the other two types of zirconia powder and that they appeared to be largely cubic phase zirconia. Again, these results were consistent with the literature^{10,35}.

It is likely that Zpex Smile was more translucent than Zpex because of reduced light scattering at the grain boundaries, as it contains more of the optically isotropic cubic zirconia³⁸. The addition of Tm_2O_3 to the zirconia did not change the XRD results, which indicated that the presence of Tm_2O_3 did not affect the crystalline structure of the zirconia within the doping concentration range examined in this study.

Highly translucent dental zirconia, which contains a high percentage of cubic phase zirconia, has less strength and fracture toughness than materials containing mainly tetragonal phase zirconia^{10,35}. We found that Zpex Smile, which contained a large amount of cubic phase zirconia, had lower fracture toughness than the other zirconia samples. This may have been because stress-induced transformation³⁹, the reason that tetragonal phase zirconia is quite strong, does not take place in Zpex Smile, in which cubic phase zirconia predominates.

CONCLUSIONS

When Tm_2O_3 was added to yttria-stabilized zirconia, the resulting materials emitted blue fluorescence with a peak wavelength that was close to that of natural teeth when irradiated with UV light. Notably, the translucent dental zirconia that consisted primarily of the tetragonal phase exhibited its highest fluorescent intensity when 0.8 wt% Tm_2O_3 was added to the material. This study suggested that if the addition of Tm_2O_3 to yttria-stabilized zirconia is limited to the concentration range examined, the microstructure and fracture toughness of either form of zirconia are not affected. Therefore, this work gives a simple and effective method for making fluorescent dental zirconia.

ACKNOWLEDGMENTS

This study was supported in part by a Grant-in Aid for Scientific Research (17K11745) from the Ministry of Education, Culture, Sports, Science and Technology in Japan.

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