Effect of Fe_2O_3 on Optical Properties of Zirconia Dental Ceramic

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Objectives: *To evaluate the effect of Fe_2O_3 on the optical properties of yttria-stabilised tetragonal zirconia (Y-TZP) dental ceramic when added, and to determine the correct content required to mimic the natural dentin.*

Methods: *Disc-shaped Y-TZP specimens (0.50 ± 0.01 mm in thickness) containing various contents of Fe_2O_3 were fabricated by cold isostatic pressing and pressureless sintering, and then compared with human dentin slices (n = 40) under different moisture conditions. The visible light transmittance and colour parameters were recorded by a computer-controlled spectrocolourimeter. Sintered density and microstructure were investigated with the Archimedes' method and scanning electron microscopy (SEM), respectively.*

Results: *With the reduction of moisture in dentin slices, the direct transmittance dropped from 1.58% to 0.87%. The direct transmittance of coloured zirconia specimens, ranging from 1.22% to 1.40%, covered the range of dentin. With increasing Fe_2O_3 content, the L* value of the coloured specimens decreased from 88.95 to 84.18, while b* increased from 3.43 to 12.02. The relative densities of all groups were over 99% of the theoretical value. The SEM indicated that zirconia with various amounts of Fe_2O_3 retained the compact microcrystalline tetragonal structure.*

Conclusion: *Small amounts of colourant additions affected the colour and the transmittance slightly, but had no influence on the sintered density and microstructure. Y-TZP could be improved by the control of colourant additives of Fe_2O_3 in order to mimic the natural colour of dentin and to obtain a better aesthetical appearance of restorations, especially when the content was around 0.08 wt%.*

Key words: *colourant, Fe_2O_3, optical property, translucency, Y-TZP, zirconia*

In pursuit of mimicking the natural colour of teeth, all ceramic materials have been used in more and more clinical cases, in order to improve the aesthetic outcome of porcelain-fused-to-metal (PFM) restorations. The optical property of ceramic plays a leading role in affecting the final appearance of restorations[1,2].It was reported that effective translucency was one of the dominant factors in achieving aesthetical results and could influence the shade of the artificial restorations significantly[3]. Yttria-stabilised tetragonal zirconia (Y-TZP) has proved to be a promising ceramic material for its excellent mechanical property[2]. Yet the poor translucency and ivory-like colour have limited the use of Y-TZP[4]. In order to improve the optical property various methods have been proposed; and adding colourants would be a simple but effective one. In dentistry, coloured zirconia is prepared for simulating the natural dentition. If the substructure of restorations made of zirconia were already similar to the basic colour shade of the dentition, then thinner veneer ceramic would be required and it would be much easier to match the translucency and

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chroma of natural teeth[2,5]. Therefore, lesser amounts of dentin tissue would be cut and better aesthetic results would be achieved.

Zirconia mixed with colourants which have better consistency would be an ideal solution. Cales et al have determined that coloured zirconia could be obtained by small additions of various metal oxides to the starting powders[6]. Some colourants were reported to act as nucleating agents or co-nucleating agents in the glass-ceramic and can alter the grain size and volume fraction, therefore changing translucency as well as chroma[7]. Hence, the effect of colourant additions on the crystalline phases and the translucency should not be ignored. The previous study identified the influence of P_2O_5, $AgNO_3$ and $FeCl_3$ on colour and translucency of lithia-based glass-ceramics[8]. However, no studies have investigated the relationship between the amount of colourant additions of Fe_2O_3 and the optical properties of Y-TZP. In this study, the effect of different amounts of colourant additions of Fe_2O_3 were evaluated and compared with the natural colour of dentin in order to enhance the aesthetic appearance of Y-TZP for dental application.

Materials and methods

Dentin slice preparation

Forty non-carious human permanent teeth, including 14 incisors and 26 premolars which were vital, intact, non-stained or discoloured were used in the study. The teeth were collected once the patients' informed consent had been obtained, under a protocol approved by the Medicine Ethics Committee of West China College of Stomatology of Sichuan University. The teeth were stored in 0.5% chloramine, in water at 4°C and used within 1 month after extraction. First, the teeth were cleaned and the roots were removed by handpieces. The crowns of the teeth were embedded by self-curing resin and were then cut in parallel to the buccal surface of the teeth, from the buccal dentin-enamel junction inwards, using an Isomet diamond saw (Isomet 1000, Buehler, Illinois, USA), into slices, which were 0.5 mm in thickness. Forty slices were randomly divided into four groups: group A (wet by deionised water), group B (dried with compressed air for 20 s), group C (dehydrated by gradient ethanol solutions) and group D (immersed in saline for 48 h at 4°C after dehydration).

Coloured Y-TZP preparation

The starting powders of Y-TZP were TZ-3YB-E (Tosoh Corporation, Tokyo, Japan) with a particle size of approximately 40 nm. The colouring zirconia powders containing Fe_2O_3 of 0.102 wt% were TZ-PX-154 (Tosoh Corporation, Tokyo, Japan) with the same particle size as the starting powders. The powders were mixed and divided into six groups based on the Fe_2O_3 content: 0 wt%, 0.02 wt%, 0.04 wt%, 0.06 wt%, 0.08 wt% and 0.10 wt%. Then the composites were compacted by cold isostatic pressing and sintered in a high-temperature furnace (Nabertherm, Lilienthal, Germany) with a final temperature of 1450°C. Five disc specimens (0.50 ± 0.01 mm in thickness, 17.00 ± 0.05 mm in diameter) and five cylindrical specimens (5.00 ± 0.01 mm in thickness, 17.00 ± 0.05 mm in diameter) were included in each group. All the disc specimens were polished by diamond polishing paste and washed in an ultrasonic bath for 3 min.

Measurement

The sintered density and relative density of specimens were determined by the Archimedes' method, with respect to the theoretical density of tetragonal zirconia ($6.10\ g/cm^3$).

The transmittance was investigated by the spectrocolourimeter (PR-650, Photo Research, California, USA). The spectrocolourimeter was preheated for 30 min. The specimens were fixed to guarantee light vertical incidence to the surface; and the light source, spectrocolourimeter and specimen were aligned. The measuring field was a black spot with a diameter of 1.5 mm. The working wavelength, ranging from 400 to 780 nm was scanned at 4 nm intervals. All measurements were conducted by the same operator in a dark room, with a room temperature between 18°C and 25°C and a relative humidity between 50% and 60%.

The colour of the specimen was measured against the black background according to the CIE *(*Commission Internationale de l'Eclairage*)* L*a*b* colour scale using the spectrocolourimeter (PR-650, Photo Research, California, USA). The values of L*, a*, b* and C^*_{ab} were analysed. C^*_{ab} represents the intensity and saturation of the colour, which is expressed as C^*_{ab} [$C^*_{ab} = (a^{*2}+b^{*2})^{1/2}$].

The microstructure of the specimens were analysed using a scanning electron microscopy (SEM; INSPECTF, FEI, Oregon, USA). The specimens of the different groups were fractured and etched in 5% hydrofluoric acid solution for 2 min before SEM examination.

Table 1 The optical properties of dentin slices under different moistures.

	Group A	Group B	Group C	Group D
Direct transmittance (T/%)	1.58 ± 0.41[a]	1.14 ± 0.43[b]	0.87 ± 0.22[b]	1.51 ± 0.33[a]
L*	67.28 ± 3.81[a]	73.36 ± 4.03[b]	76.35 ± 3.37[c]	69.32 ± 3.75[a]
a*	-1.84 ± 0.10[a]	-1.86 ± 0.55[a]	-1.74 ± 0.30[a]	-1.79 ± 0.37[a]
b*	9.46 ± 2.48[a]	9.33 ± 1.63[a]	9.51 ± 1.94[a]	9.23 ± 2.50[a]
C^*_{ab}	9.64 ± 1.45[a]	9.51 ± 1.83[a]	9.67 ± 2.04[a]	9.40 ± 2.12[a]

Values with different superscript letters are significantly different within a row according to Tukey's multiple-comparison test ($P < 0.05$)

All data were compared with one-way ANOVA followed by Tukey's multiple-comparison test. The alpha value (*P*) was set at 0.05.

Results

The optical property of dentin slices under different moistures

Macroscopically, the wet dentin slices showed a pale yellow appearance with certain translucency. The optical properties of dentin are shown in Table 1. Under different moistures, the direct transmittance ranged from 0.87% to 1.58% with the L* value from 67.28 to 76.35. The results of one-way ANOVA indicated that with the reduction of moisture, the translucency dropped slightly, the value of L* increased, while the value of a* and b* didn't change. However, the optical parameters recovered after rewetting.

The appearance and characteristics of the coloured Y-TZP specimens

As shown in Fig 1, the surfaces of the specimens were relatively smooth and glassy. With the addition of Fe_2O_3, the degree of translucency tended to decrease; and the colour changed from ivory to pale yellow.

Effect of Fe_2O_3 addition on the sintering density, relative density and the transmittance of coloured Y-TZP specimens

As shown in Table 2, the sintering density with different amounts of colourants ranged from 6.0585 to 6.0640 g/cm^3, while the relative density varied from 99.30% to 99.41%. The results of one-way ANOVA indicated that the content of Fe_2O_3 had no significant effect on the sintered density ($P > 0.05$). The relative density of all groups was over 99% of the theoretical value.

The direct transmittance of zirconia specimens ranged from 1.22% to 1.40%. The statistical analysis indicated that a small amount of colourant additions affected the transmittance slightly ($P < 0.01$). Comparison between groups showed that the transmittance of 0.06 wt%, 0.08 wt% and 0.10 wt% groups had no difference ($P > 0.05$); and with increasing Fe_2O_3 content the direct transmittance decreased slightly. While the amount of Fe_2O_3 additions was less than 0.10 wt%, the translucency of coloured zirconia changed a little.

Effect of Fe_2O_3 addition on the colour of Y-TZP specimens

As shown in Table 3, the L* value of coloured specimens ranged from 84.18 to 88.95; b* varied from 3.43 to 12.02 and C^*_{ab} from 3.60 to 12.11. The results of one-way

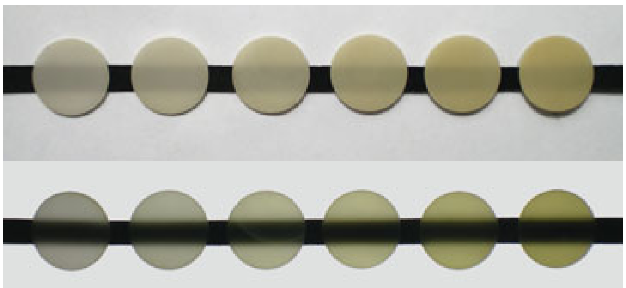

Fig 1 Glazed specimens with different amounts of Fe_2O_3 on a black and white background with reflected and transmitted light. From left to right: 0 wt%, 0.02 wt%, 0.04 wt%, 0.06 wt%, 0.08 wt% and 0.10 wt%.

Table 2 The sintering density, relative density and direct transmittance of specimens with different amounts of Fe_2O_3.

Content	Sintering density (g/cm^3)	Relative density (%)	Direct transmittance (%)
0 wt%	6.0627 ± 0.0074	99.39	1.4012 ± 0.0253
0.02 wt%	6.0616 ± 0.0126	99.37	1.3883 ± 0.0353
0.04 wt%	6.0640 ± 0.0131	99.41	1.3703 ± 0.0107
0.06 wt%	6.0604 ± 0.0104	99.35	1.3337 ± 0.0111
0.08 wt%	6.0573 ± 0.0153	99.30	1.2477 ± 0.0179
0.10 wt%	6.0585 ± 0.0122	99.32	1.2275 ± 0.0280

Table 3 The colour of Y-TZP specimens containing different amounts of Fe_2O_3.

Content	L*	a*	b*	C^*_{ab}
0 wt%	88.95 ± 0.67	-1.06 ± 0.22	3.43 ± 0.36	3.60 ± 0.40
0.02 wt%	87.37 ± 0.50	-1.08 ± 0.03	4.15 ± 0.27	4.53 ± 0.28
0.04 wt%	87.23 ± 0.53	-1.97 ± 0.12	5.65 ± 0.27	5.98 ± 0.29
0.06 wt%	86.84 ± 0.28	-1.93 ± 0.04	7.58 ± 0.18	7.82 ± 0.17
0.08 wt%	86.43 ± 0.31	-1.72 ± 0.08	8.92 ± 0.28	9.08 ± 0.29
0.10 wt%	84.18 ± 0.49	-1.48 ± 0.05	12.02 ± 0.48	12.11 ± 0.48

ANOVA indicated that the Fe_2O_3 addition had a significant effect on the value of L*, b*and C^*_{ab} ($P < 0.05$), but had no significant effect on the value of a*($P > 0.05$). Comparison between the groups showed that the L* value of 0.02 wt%, 0.04 wt%, 0.06 wt% and 0.08 wt% groups had no statistically significant difference, while the L* value of other groups and the b* and C^*_{ab} values of all groups had a significant difference ($P < 0.05$). With increasing Fe_2O_3 content the value of L* changed a little, while b* and C^*_{ab} increased greatly.

The microstructure of coloured Y-TZP specimens

From the SEM images of the fracture surfaces (Fig 2), the zirconia retained the compact microcrystalline tetragonal structure with varying amounts of Fe_2O_3. A small amount of intergranular pores were observed. The grain size, grain shape and microstructure uniformity did not appear to vary greatly compared to the non-coloured zirconia at the same sintering temperature.

Discussion

In order to achieve natural looking restorations, all-ceramic based materials have been widely used because of their excellent optical characteristics. Better aesthetic outcomes would be achieved if there was better shade matching between the dental restorations and the natural dentition. Therefore, when used as a base material, Y-TZP should possess the same optical properties as dentin. However, the optical properties of dentin may be affected by the dynamic oral environment, especially the changes in moisture[9]. In the present study, four groups of dentin slices under different moistures were set to simulate changes in the complex oral environment. Disc specimens with the same thickness as dentin slices were then fabricated and compared with them. Results showed that decreases in moisture only caused slight changes in the optical properties of dentin. Also they recovered after dentin slices were immersed in saline for 48 h. The colour range of wet and dehydrated dentin was in line with data previously published[8]. It indicates that the reduction of moisture does not affect the optical properties of dentin greatly. Uneven mineralisation and a rich amount of organic matter may be the possible reasons for this phenomenon[10].

When the Fe_2O_3 content increased, the opacity of specimens became greater. But while the amount of Fe_2O_3 additions was less than 0.10 wt%, the translucency of coloured zirconia changed a little. Furthermore the translucency of all groups lay within the range of dentin from 0.87% to 1.58% (Fig 3). The Kubelka-Munk reflectance theory describes the relationship between the optical absorption, the scattering coefficient and the concentration of colourant[11]. From this theory, the concentration of colourants may influence the absorption coefficients and directly determine the degree of translucency. With an increase in colourant additions, the colourant particles may cause greater absorption and scattering between different crystals. Thus adequate translucency can be achieved by limiting the amount of colourant additions. Moreover, gaining theoretical density can greatly diminish the porosity that contributes to opacity[12]. It is reported that pores played an important role in affecting the optical property[13], as they functioned as highly efficient light scatters[14,15]. In the present study, the nanoscale particle of Y-TZP powders and the complete combustion of organic matters in the sintering process were helpful in improving the final density. As shown in Fig 2, the compact crystal structure and the porosity were not affected by changes in Fe_2O_3 content. Although many colourant additions may have a synergistic effect on the crystallisation process; and iron oxides have been distinguished as nucleating agents in some systems, the effect in the zirconia system has not been confirmed[7,8,16]. In this study, the amount of Fe_2O_3 additions, in some cases as low as 0.10 wt % was sufficient to produce a satisfactory translucency similar to dentin, without affecting the microstructure such as the grain size or crystal structure. Also an increase in the Fe_2O_3 concentration resulted in a significant increase in the optical absorption and scattering coefficients, but a decrease in the reflected light intensity of the zirconia surface against the black and white background.

Iron compounds are the most common colouring agent in ceramics. Also Fe_2O_3 has been proven to be a better ceramic pigment for the dental zirconia[17]. The Fe_2O_3 can give zirconia a yellow colour at different magnitudes. By increasing Fe_2O_3 content, the saturation of yellow colour became greater. By mixing colourless zirconia powders with Fe_2O_3 of different weight percentages, zirconia with colour gradients which are similar to dentin can be acquired. The results showed

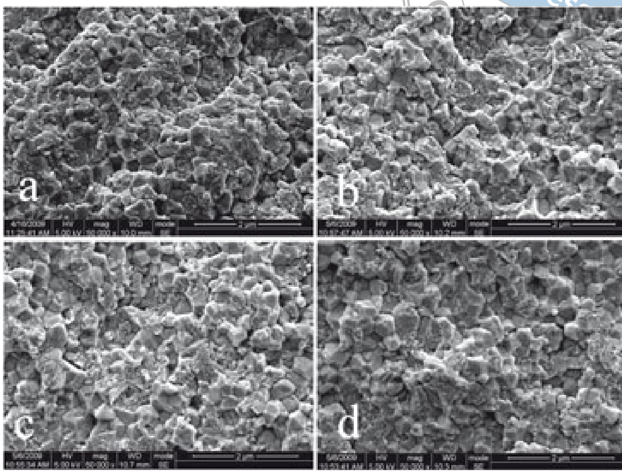

Fig 2 SEM of the specimen with different amounts of Fe_2O_3: a) 0 wt%*b) 0.04 wt%*c) 0.08 wt%*d) 0.10 wt%.

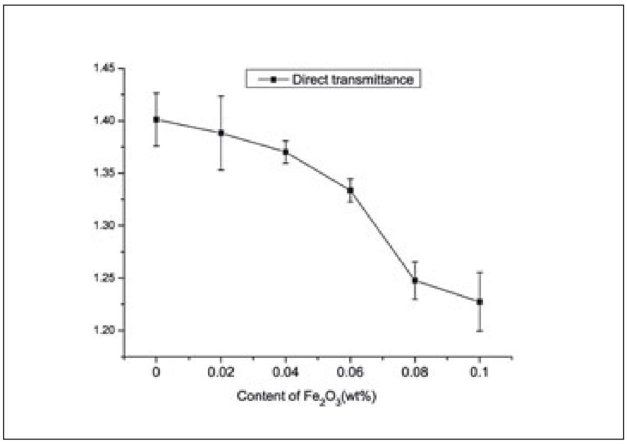

Fig 3 The direct transmittance of specimens with different amounts of Fe_2O_3.

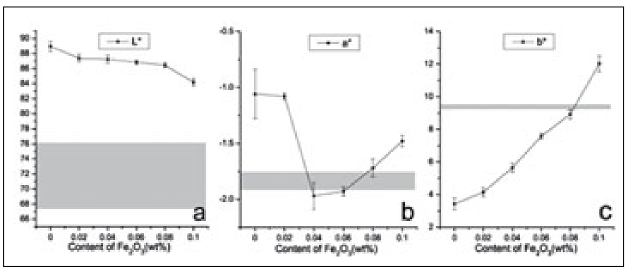

Fig 4 The L*, a* and b* values of specimens with different amounts of colourants. The coloured area represents the value of dentin slices.

that with the increase of Fe_2O_3 content, the value of L* dropped slightly and the value of b* and C^*_{ab} increased significantly. It means the decrease in zirconia's brightness, the increase in the saturation of yellow and the tendency of the hue to change from yellow-green to yellow-red, respectively. These results were consistent with previous reports[18,19]. As illustrated in Fig 4, the value of a* lay within the range of dentin; and the value of b* matched that of dentin when the content of Fe_2O_3 was close to 0.08 wt%. Additionally the value of L* of coloured zirconia within all groups was slightly higher than natural dentin with different moistures (Fig 4). However, this flaw can be compensated by covering it with veneer shade sintered on coloured zirconia, which is used as the substructure material of restoration. The brightness of restoration with overlying veneer generally shows a decreasing tendency[20]. Furthermore, the amount of light reflected is decreased with the addition of different colourants. In summary, it is acceptable that as substructure materials the coloured zirconia possesses adequately higher brightness than dentin. Previous studies suggested the different colourants differed substantially in their colouration ability[21]. The concentration of different colourants may strongly influence the final shade and transmittance of zirconia[22]. Therefore the amount of various colourants may be different and should be studied further.

Conclusion

The results of this study showed that small amounts of colourant additions had no influence on the sintered density, but affected the colour and transmittance slightly. A satisfactory colour and translucency control of zirconia was achieved by adding less than 0.10 wt% Fe_2O_3 to the starting nanopowders. Therefore, the optical properties of Y-TZP could be enhanced by adding Fe_3O_2 to mimic the natural colour of dentin ensuring a better aesthetic appearance for dental usage, especially when the concentration was close to 0.08 wt%.

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