Iron oxide colouring of highly-translucent 3Y-TZP ceramics for dental restorations

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Abstract

The influence of 0.01-2 mol% Fe₂O₃ powder addition on the microstructure, mechanical and optical properties, and hydrothermal stability of highly-translucent 3Y-TZP ceramics is assessed and compared with commercially available co-precipitated 0.18 mol% Fe₂O₃ doped ZrO₂ powder-based ceramics. Only those ceramics with up to 0.1 mol% Fe₂O₃ resulted in a proper shade for dental zirconia ceramics, with a typical composition of 87 vol% *t*-ZrO₂ and 13 vol% *c*-ZrO₂. The amount of cubic phase increased at higher Fe₂O₃ content. The hardness (~13 GPa) and fracture toughness (~3.6 MPa m^{1/2}) of the 0.01 mol% - 0.1 mol% Fe₂O₃ doped 3Y-TZP was comparable, whereas the hardness decreased above 0.5 mol% Fe₂O₃ and the fracture toughness decreased above 2 mol% Fe₂O₃. The hydrothermal ageing resistance slightly increased for Fe₂O₃ concentrations up to 1 mol%, whereas the translucency slightly decreased with increasing Fe₂O₃ content.

Keywords

zirconia, iron oxide, dental, restorative material, colouring

1. Introduction

Dental ceramics enable dentists to restore/replace teeth highly aesthetically [1]. Conventional porcelain-fused-to-metal (PFM) fixed dental prostheses (FDPs) do not provide a truly natural look, which requires metal-free full-ceramic FDPs [2]. Alternative conventional bi-layered zirconia crowns and bridges, consisting of a mechanically strong substructure veneered with aesthetic feldspathic porcelain however clinically often suffer from chipping defects of the veneering porcelain [2–4]. Therefore, highly translucent and colour-graded full-contour zirconia ceramics have been developed, but require further improvement of their mechanical properties and ageing resistance to fully replace PFM restorations [3].

3 mol% yttria stabilized zirconia (3Y-TZP) is highly favoured for dental restorations because of its good strength and fracture toughness [5]. The high fracture toughness is provided by the inherent stress-induced tetragonal-to-monoclinic (*t*→*m*) phase transformation characteristic for zirconia ceramics [6,7]. The translucency of 3Y-TZP

is on the other hand insufficient to match the translucency of natural teeth [8]. This is caused by porosities, birefringence and presence of scattering secondary phases [9]. Nowadays, the translucency of zirconia ceramics has been improved [9,10] and starting powders for highly translucent zirconia are commercially available. The Zpex zirconia powder grade (Tosoh, Tokyo, Japan) is a nanosized co-precipitated 3Y-TZP powder with 0.05 wt% alumina dopant, instead of the more common 0.25 wt% alumina [11]. The reduced Al_2O_3 content increases the translucency of the sintered 3Y-TZP [9].

Natural teeth are however not as white as pure 3Y-TZP ceramics, requiring dental zirconia ceramics to be slightly coloured. One option to obtain tooth-coloured zirconia ceramics is to simply apply a coloured veneering layer [5,12]. Veneering layers on ceramic crowns however often chip and are not reliable enough for dental restorations [5]. Colouring zirconia can be done by staining with a colouring liquid or by adding a colorant additive or dopant to the powder mixture [13]. Staining can be done by immersion of the zirconia green body or pre-sintered body into a colouring liquid for a given time or by painting with a brush prior to sintering [14]. Several brands of staining solutions exist, each with their own pigment choices and composition. The surface colour will however fade over time and might be inhomogeneous [15]. On top of that, although debated, it has been reported that staining can decrease the mechanical properties of ZrO_2 ceramics [16,17]. Hence, another option is to add dopants like iron and rare earth cations to colour the bulk ceramic [18]. Iron oxide doped 3Y-TZP starting powder is commercially available by from Tosoh (Grade Zpex Yellow) [11]. Coloured dental zirconia ceramics are also available on the market, such as Lava Esthetic (3M Oral Care, Seefeld, Germany), Vita YZ Ht^{Color} (Vita, Bad Säckingen, Switzerland) and Katana Zirconia (Kuraray Noritake, Tokyo, Japan).

This paper investigates the influence of iron oxide (Fe_2O_3) doping on the microstructural, mechanical and optical properties, as well as the ageing kinetics of sintered Zpex (Tosoh) powder-based zirconia ceramics. Iron oxide (Fe_2O_3) powder was added to the Zpex powder in different concentrations to achieve tooth-coloured zirconia ceramics and the results were compared using the commercially available co-precipitated Fe_2O_3 -coloured Zpex Yellow (Tosoh) powder as reference.

2. Experimental procedures

2.1 Materials preparation

ZrO_2 powder (Zpex, 40 nm particle size, Tosoh) was doped with Fe_2O_3 (98% purity, 20-40 nm particle size, Alfa Aesar W, Ward Hill, MA, USA). Zpex powder is a commercially available co-precipitated 3 mol% yttria stabilized (3Y-TZP) zirconia powder with 0.05 wt% Al_2O_3 containing 3 wt% organic binder. Zpex Yellow powder (Tosoh) is a 3 wt% organic binder containing 3Y-TZP powder that was co-precipitated with 0.15 wt% (0.18 mol%) Fe_2O_3 and 0.05 wt% Al_2O_3 .

Various amounts of iron oxide in the 0.01-2 mol% range were added to the Zpex powder and mixed on a multidirectional mixer (Turbula type T2C, Basel, Switzerland) for 24 hours in ethanol using 5-mm Y-TZP milling balls (grade TZ-3Y; Tosoh). The Zpex powder was debinded at 400°C for 1 hour prior to mixing with Fe₂O₃, dried and then sieve granulated (315 µm). Green powder compacts (discs with a diameter of ~20 mm and thickness of ~4 mm) were obtained by cold isostatically pressing (EPSI, Temse, Belgium) ~3 g powder at 300 MPa and pressureless sintered in air at 1450°C for 2 h. The sintered zirconia ceramics are referred to as Zpex-xFe, with x indicating the mol% of Fe₂O₃ dopant. Zpex and Zpex Yellow powder-based reference ceramics were pressed from as-received binder-containing powder and sintered under the same conditions. The density of all sintered, unpolished ceramics was measured in ethanol at the same moment using the Archimedes principle. The density of ethanol was determined before measurement. A theoretical density of 6.08 g/cm³, the reported Tosoh value for Zpex, was used to calculate the residual porosity.

2.2 Characterisation

The fracture resistance (K_{IC}) and Vickers hardness (H_V) of the sintered and polished materials were obtained from indentation measurements using a Vickers diamond indenter (Model FV700, Future Tech, Tokyo, Japan), applied with a load of 98 N for 15 s. The Vickers indentation crack pattern was identified as a Palmqvist crack pattern, justifying the use of the formula of Niihara for the indentation fracture resistance measurement. The fracture resistance was also measured according to the formula of Anstis to allow a direct comparison with literature data. The reported values are the average and standard deviation of 10 indentations. The four-point bending strength of Zpex, Zpex-0.01Fe, Zpex-0.05Fe, Zpex-0.1Fe and Zpex Yellow ceramics was measured using ten bending bars of 45 x 4 x 3 mm³. These bars were prepared according to the ISO standards [19,20]. The strength was measured with an inner and outer span width of 20 and 40 mm, respectively, and a crosshead speed of 0.5 mm/min.

X-Ray Diffraction (3003 T/T, Seifert, Ahrensburg, Germany) was used to determine the phase composition of all zirconia ceramics using Cu-K_α radiation at a voltage of 40 kV and a current of 40 mA. Four discs of each composition were scanned over a range from 20° to 90° 2θ with a step width of 0.2° and a scan speed of 2 s/step. The obtained XRD patterns were quantitatively analysed by Rietveld refinements using the Chebyshev II Polynomial Function in TOPAS-Academic software (Bruker AXS, Karlsruhe, Germany). Cubic, tetragonal and monoclinic zirconia phases were assumed to be present. The unit cell parameters of each phase were determined. All analysed scans had an R-value below 10% to assure the quality of the Rietveld refinement.

The microstructure, porosity and grain size of the sintered, thermally etched (1250°C for 25 min in air at a heating rate of 20°C/min) and platinum coated ceramics were analysed by scanning electron microscopy (SEM; XL30-FEG, FEI, Eindhoven, The

Netherlands). The line intercept method was used to determine the grain size with the help of IMAGE-PRO software (Media Cybernetics, Rockville, MD USA). The average of at least 500 grains is reported with a correction factor of 1.56 [21].

The distribution of Fe³⁺, Y³⁺, Al³⁺ and Zr⁴⁺ cations at the grain boundaries of the Zpex-0.1Fe ceramic was analysed using transmission electron microscopy (TEM; JEOL ARM 200F, Jeol, Tokyo Japan). Electron transparent samples were prepared by ion-milling with an Ion Slicer (EM-09100IS, Jeol). TEM images were acquired by scanning transmission electron microscopy (STEM) operated at 200 kV. The distribution analysis of the cations was measured by energy dispersive spectroscopy (STEM-EDS) using the Analysis Station software (Jeol). Elemental distribution maps around triple points were acquired and line analysis across the grain boundaries was performed. The atomic percentage of each element referring to the overall composition of the ceramic is given.

Three as-sintered discs of each zirconia composition were aged by *in vitro* accelerated hydrothermal testing. The zirconia discs were submerged in a stainless steel autoclave, partially filled with demineralized water. The autoclave was submerged in an oil bath at 134°C. According to literature, "1 h of autoclave treatment in steam at 134°C is theoretically the same as 3-4 years *in vivo* at 37°C" [22]. The discs were removed from the autoclave at predefined times to measure the fraction of tetragonal phase that transformed to monoclinic phase using XRD (3003-TT, Seifert). Both sides of each disc were scanned so that a total of 6 surfaces of each composition were analysed. The volume fraction of formed monoclinic phase on the surface was calculated using the formula of Toraya *et al.* [23]. Before ageing, each side of the discs was scanned over the same range ($27.6^\circ \leq \theta \leq 31.7^\circ$) to check whether any monoclinic phase was already present. The obtained degradation curves were fitted by the Mehl-Avrami-Johnson (MAJ) model [24] :

$$\frac{V_m}{V_{ms}} = 1 - \exp(-(bt)^n)$$

with V_{ms} , the *m*-ZrO₂ saturation level reached during hydrothermal ageing; *b*, the constant that describes the *t*→*m* transformation and *n*, the constant that describes the mechanism of nucleation and growth of the monoclinic grains [22,25].

The CIELAB coordinate for lightness (L*) of the Zpex, Zpex Yellow, Zpex-0.01Fe, Zpex-0.05Fe and Zpex-0.1Fe ceramics was measured using a dental colorimeter (SpectroShade™ MICRO, MHT Optic Research, Niederhasli, Switzerland) with a calibration plate. Six discs of each composition were ground plan-parallel to a thickness of 0.5 ± 0.05 mm and polished on both sides using colloidal silica (OPS, Struers, Maassluis, The Netherlands). The contrast ratio (CR) was determined using the ratio of illuminance of the material on a black (*Y_b*) and white (*Y_w*) background. The disc was adhered to the background with vaseline to improve the optical contact. The following equation was used: [26]

$$CR = \frac{Y_b}{Y_w}$$

The illuminance factor (Y) for both is given by the following formula:

$$Y = \left(\frac{L^* + 16}{116} \right)^3 \times Y_n$$

in which Y_n is assumed to be equal to 100, implying the white colour in simulated object colours is a perfect reflecting diffuser. Transparent materials have a CR value of 0.0 and 1.0 for completely opaque materials [27].

3. Results and discussion

The iron oxide doping resulted in a clear colouring of the zirconia ceramics, showing that simple admixing of Fe_2O_3 is a successful way of producing homogeneously coloured zirconia ceramics. Fig. 1 shows the six different experimental compositions that were prepared, as compared to the Zpex (Tosoh; non-coloured) and Zpex Yellow (Tosoh; 0.18 mol% Fe_2O_3) reference formulations. The density is reported in Table 1. The Fe_2O_3 -free zirconia (Zpex, Tosoh), the three lowest iron oxide-containing experimental zirconia formulations and the Zpex Yellow were nearly fully dense. At Fe_2O_3 contents ≥ 0.5 mol%, the residual porosity after 2 hrs in air at 1450°C increases. Assuming a theoretical density of 6.08 g/cm³ for Zpex, as stated by Tosoh, the porosity for pure Zpex is 0.12 $\pm$ 0.05 vol%, 0.16 vol%, 0.29 vol% and 0.24 vol% for 0.01, 0.05 and 0.1Fe respectively and 0.30 $\pm$ 0.06 vol% for Zpex Yellow, whereas the ceramics with ≥ 0.5 mol% Fe_2O_3 contained some residual porosity (up to 1.73 vol %).

Figure 1: Fe_2O_3 -doped Zpex powder-based zirconia ceramics.

Ceramic	Theoretical density (g/cm ³)	Density (g/cm ³)	<i>t</i> -ZrO ₂ (vol%)	<i>c</i> -ZrO ₂ (vol%)	<i>m</i> -ZrO ₂ (vol%)	Porosity (vol%)
Zpex	6.08	6.07 $\pm$ 0.01	86.9 $\pm$ 0.5	13.1 $\pm$ 0.5	0.0 $\pm$ 0.0	0.12 $\pm$ 0.05
Zpex-0.01Fe	6.08	6.07 $\pm$ 0.00	87.3 $\pm$ 0.4	12.7 $\pm$ 0.4	0.0 $\pm$ 0.0	0.16 $\pm$ 0.05
Zpex-0.05Fe	6.08	6.07 $\pm$ 0.01	87.0 $\pm$ 0.5	13.0 $\pm$ 0.5	0.0 $\pm$ 0.0	0.29 $\pm$ 0.04
Zpex-0.1Fe	6.08	6.07 $\pm$ 0.01	86.0 $\pm$ 0.6	14.0 $\pm$ 0.6	0.0 $\pm$ 0.0	0.24 $\pm$ 0.17
Zpex Yellow	6.08	6.06 $\pm$ 0.01	86.1 $\pm$ 0.5	13.9 $\pm$ 0.5	0.0 $\pm$ 0.0	0.30 $\pm$ 0.06
Zpex-0.5Fe	6.08	6.04 $\pm$ 0.02	81.9 $\pm$ 0.7	18.1 $\pm$ 0.7	0.0 $\pm$ 0.0	0.63 $\pm$ 0.09
Zpex-1Fe	6.08	6.04 $\pm$ 0.01	76.2 $\pm$ 0.8	23.8 $\pm$ 0.8	0.0 $\pm$ 0.0	0.62 $\pm$ 0.13
Zpex-2Fe	6.08	5.99 $\pm$ 0.01	64.0 $\pm$ 1.0	33.1 $\pm$ 2.3	2.9 $\pm$ 2.8	1.73 $\pm$ 0.42

t-ZrO₂: tetragonal zirconia; *c*-ZrO₂: cubic zirconia; *m*-ZrO₂: monoclinic zirconia

Table 1: Density and phase composition, as obtained by XRD Rietveld analysis, of the zirconia ceramics as a function of the Fe₂O₃ concentration

3.1 Fe₂O₃-doping promotes the formation of cubic ZrO₂ phase

The XRD patterns of the sintered zirconia ceramics are compared in Fig. 2, indicating similar patterns except for the 2 mol% Fe₂O₃-doped ceramic that contains about 3 vol% monoclinic ZrO₂. A detailed analysis of the 72-76° 2 θ range, presented in Fig. 2, revealed that Fe₂O₃-doping favours the formation of the cubic ZrO₂ phase which peaks can clearly be observed at around 74° 2 θ . The quantitative results of the Rietveld analysis are presented in Table 1. The up to 0.1 mol% Fe₂O₃-doped Zpex zirconia ceramics contain 13-14 vol% cubic phase, which is comparable to the typical 15 vol% cubic phase in 3 mol% yttria stabilized zirconia (3Y-TZP) sintered at the same temperature [28,29]. With increasing Fe₂O₃ content, the amount of cubic phase content increased (Table 1). 0.5-2 mol% Fe₂O₃ doping in 3Y-TZP was reported to induce cubic phase formation in Y-TZP next to the tetragonal phase [30]. Fe₂O₃ can hence be used as a sintering aid for cubic phase formation [31]. The lower density of the 0.5-2 mol% Fe₂O₃-doped zirconia ceramics is explained by the formation of cubic ZrO₂ phase, which has a lower theoretical density (5.99 g/cm³) [32], and by the presence of residual porosity (Table 1). 2 mol% Fe₂O₃ addition resulted in *m*-ZrO₂ phase formation, which may cause micro-cracks that lower the density even more. The high amount of cubic phase in the 2 mol% Fe₂O₃-doped Zpex zirconia ceramics can cause a depletion of Y₂O₃ in the tetragonal phase [33]. When a fraction of the tetragonal phase around the cubic grains does not contain enough stabilizer, it will spontaneously transform during cooling from the sintering temperature, leading to the formation of *m*-ZrO₂ phase and possible concomitant micro-cracks [34]. The tetragonality (*c/a*) of the *t*-ZrO₂ phase increased with increasing Fe₂O₃ presence as well (Fig. 3d), which implies a higher phase transformability of the *t*-ZrO₂ phase present [35]. This could as well explain the *m*-ZrO₂ present in Zpex-2Fe. The commercial coprecipitated 0.18 mol% Fe₂O₃ Zpex Yellow powder-based ceramic was fully dense and had the same amount of *t*-ZrO₂ and *c*-ZrO₂ phase as the pure Fe₂O₃-free Zpex powder-based ceramic. There is no difference in the phase composition of the sintered ZrO₂ ceramics when doping with low amounts of Fe₂O₃ (≤ 0.18 mol%) by admixing or coprecipitation. The obtained density values allow to conclude that sintered pure Fe₂O₃-free Zpex (Tosoh), the 0.01-0.1 mol% Fe₂O₃-doped zirconia ceramics and Zpex Yellow (Tosoh) can clinically be used for load bearing dental applications, since their density is over 6.00 g/cm³ [19]. These ceramics also have less than 1 vol% calculated porosity (Table 1) and can be considered fully dense. These zirconia ceramics have the right colour for dental applications, as shown in Fig. 1, whereas Fe₂O₃ levels ≥ 0.5 mol% are too dark.

Figure 2: XRD patterns of the sintered zirconia ceramics as a function of the mol% Fe_2O_3 dopant content.

Residual porosity and a decrease in density was observed at Fe_2O_3 contents above 0.5 mol% (Table 1). A decrease of both tetragonal and cubic unit-cell parameters was measured as function of an increasing Fe_2O_3 content, as respectively shown in Fig. 3(a,b) and (e). The decrease in cubic unit-cell parameter with increasing amount of Fe_2O_3 dopant was also reported in literature up to 0.5 mol% [30]. Fe^{3+} cations substitute the larger Zr^{4+} cations, generating oxygen vacancies for charge neutralization, which reduces the dimensions of the cubic unit cell [31,36]. The decrease in cubic unit cell volume was more than 7 times larger than for the tetragonal phase, indicating that the Fe^{3+} cations mainly dissolved in the cubic phase. Despite the higher Fe_2O_3 -doping of the cubic phase, it still has a lower density than the tetragonal phase, causing a decrease in the overall density with increasing amount of cubic phase present in the zirconia ceramic. Although enhanced densification with increasing Fe_2O_3 content was expected for admixed starting powders, as indicated in literature [30,31,37].

No secondary phase particles were observed by XRD measurements (Fig. 2), Rietveld analysis (Table 1) or SEM (Fig. 4) in any of the ceramics, which means that the solubility limit of neither Fe_2O_3 nor Al_2O_3 was reached [30]. There is still a lot of uncertainty about the solubility limit of Fe_2O_3 in zirconia. In fact, a high range of solubility limits have been reported for Fe_2O_3 in zirconia [31,38]. The solubility limit of 2-3 mol% Fe_2O_3 in $c\text{-ZrO}_2$ was reported by Verkerk *et al.* [31]. Štefanic *et al.* reported a solubility limit of 2 mol% in sintered ZrO_2 and observed the formation of monoclinic phase when the solubility limit was exceeded [38]. The latter finding could be another explanation for the formation of $m\text{-ZrO}_2$ phase in 2 mol% Fe_2O_3 -doped Zpex zirconia

ceramics. Our research shows that up to 2 mol% of Fe_2O_3 can be dissolved in 3Y-TZP when sintering at 1450°C for 2 hours. The Fe^{3+} cations will diffuse easily into the lattice during sintering.

Figure 3: Unit cell dimensions of the t - and c - ZrO_2 phases in Zpex, Zpex Yellow and Fe_2O_3 doped Zpex zirconia ceramics.

Ceramic	Grain size (nm)	H _v (GPa)	K _{IC} (Niihara) (MPa m ^{1/2})	K _{IC} (Anstis) (MPa m ^{1/2})	σ _b (MPa)	CR
Zpex	437 ± 174	13.3 ± 0.2	4.9 ± 0.1	3.6 ± 0.2	883 ± 102	0.44 ± 0.01
Zpex-0.01Fe	426 ± 176	13.2 ± 0.1	4.8 ± 0.1	3.6 ± 0.1	550 ± 85	0.45 ± 0.02
Zpex-0.05Fe	440 ± 185	13.1 ± 0.1	4.8 ± 0.1	3.6 ± 0.2	516 ± 46	0.47 ± 0.01
Zpex-0.1Fe	437 ± 182	13.1 ± 0.1	4.8 ± 0.1	3.7 ± 0.1	446 ± 36	0.52 ± 0.01
Zpex Yellow	428 ± 171	13.1 ± 0.3	4.8 ± 0.2	3.6 ± 0.3	885 ± 134	0.65 ± 0.07
Zpex-0.5Fe	488 ± 206	12.6 ± 0.1	4.7 ± 0.2	3.5 ± 0.3	/	/
Zpex-1Fe	599 ± 265	12.2 ± 0.1	4.8 ± 0.2	3.6 ± 0.3	/	/
Zpex-2Fe	641 ± 395	11.6 ± 0.1	4.5 ± 0.1	3.3 ± 0.1	/	/

H_v: Vickers hardness; K_{IC}: Fracture toughness; σ_b: Bending strength; CR: Contrast ratio

Table 2: Density, grain size and mechanical properties of the zirconia ceramics

3.2 Influence Fe₂O₃-doping on the mechanical properties of 3Y-TZP ceramics

The highest Fe₂O₃ additions (0.5-2 mol% Fe₂O₃) resulted in a significantly larger average grain size and a bimodal grain size distribution was formed, as can be observed in the SEM pictures in Fig. 4 and as reported in Table 2. The large grains are most probably cubic grains [39]. All mechanical property data can be found in Table 2. The hardness decreased for samples with a Fe₂O₃ content above 0.5 mol%. The indentation fracture resistance data are within the 4.5-4.9 MPa m^{1/2} range, corresponding to what is reported in literature [40]. Only Zpex-2Fe shows a decrease in fracture toughness. The bending strength of Zpex and Zpex Yellow is similar and comparable to what can be found in literature [41]. A strong decrease in bending strength was observed for the Fe₂O₃-doped admixed ceramics.

Figure 4: Scanning electron micrographs of iron oxide doped zirconia ceramics.

The addition of Fe₂O₃ promotes grain growth, most explicitly for the cubic phase [30] and the cubic grains in a 3Y-TZP grow faster than the tetragonal grains [42], which explains the increase in average grain size. The increase in grain size combined with the increase in porosity for the three highest (0.5-2 mol%) Fe₂O₃-content ceramics explains the decrease in hardness of these zirconia ceramic formulations [43,44]. Pure Fe₂O₃-free Zpex, Fe₂O₃ coloured Zpex Yellow and 0.01-0.1 mol% Fe₂O₃-doped Zpex have a rather small grain size around 440 nm. Zhang *et al.* reported a minimum Anstis fracture toughness of $\sim 3.8 \text{ MPa m}^{1/2}$ for non-transformable 3Y-TZP with an uncorrected grain size of 200-250 nm [45]. With increasing grain size, the fracture toughness slightly increased to $\sim 4.0 \text{ MPa m}^{1/2}$ due to an increased phase transformability and concomitant transformation toughening contribution [45]. A smaller *t*-ZrO₂ grain size lowers the transformation toughening mechanism [46,47]. The grain size could be increased by sintering the ceramics at higher temperature [45,46,48]. However, by increasing the transformability of zirconia ceramics, hydrothermal ageing will also become a bigger issue [49]. The higher amount of cubic phase explains the slightly lower fracture toughness of the 2 mol% Fe₂O₃-doped zirconia ceramic, since there is less tetragonal ZrO₂ that can transformation toughen. The 0.5 and 1 mol% Fe₂O₃-doped ceramics remarkably did not show a decrease in fracture toughness, whereas they contain a higher amount of non-transformable cubic phase. The (400) and (004) tetragonal peak shifts in Fig. 2 indicate that the separation between the tetragonal (400) and (004) peaks increased with increasing Fe₂O₃ content above 0.18 mol%. The tetragonality of the *t*-ZrO₂ phase also increased with increasing Fe₂O₃ content, especially above 0.18 mol%. This tetragonality increase should be attributed to a lower amount of Y₂O₃ in the tetragonal grains, since more Y₂O₃ is consumed to stabilize the cubic phase. The higher tetragonality in these ceramics could also facilitate the *t*→*m* transformation toughening [35]. Despite the reduced *t*-ZrO₂ content in the ceramics with an Fe₂O₃ content above 0.18 mol%, the fracture resistance was maintained due to an increased *t*-ZrO₂ phase tetragonality and concomitant transformability.

The admixed ceramics have a sudden and strong decrease in the average bending strength. The fracture surfaces showed relatively large defects that were present in the mixed ceramics (Fig. 5). Using the formula of Griffith and the data reported in Table 2, the critical flaw size ranges from 14, 15 to 22 μm in 0.01, 0.05 and 0.1 mol% Fe₂O₃ doped Zpex respectively. The larger defects in the admixed ceramics were probably introduced during processing due to the fact that the as-received Zpex starting powder was debinded prior to Fe₂O₃ admixing and compaction was done without binder addition, in contrast to the as-received binder containing Zpex and Zpex Yellow reference grades. Skipping the debinding prior to the compaction could have minimized the formation of microdefects and improve the bending strength of the ceramics. It would have caused an inhomogeneous distribution of the Fe₂O₃ powder on the other hand.

Figure 5: SEM images of defects and pores observed on fracture surfaces of Zpex-0.1Fe 4-point bending bars: (a) defect inside the ceramic, (b) porosity and (c) surface defect with hackle lines.

The commercial Fe_2O_3 -free Zpex and 0.18 mol% Fe_2O_3 doped Zpex Yellow powder-based ceramics had a similar $t\text{-ZrO}_2$ phase tetragonality, $c\text{-ZrO}_2$ phase content, grain size, hardness, fracture toughness and bending strength. Interesting to note in Table 1 is that the Zpex Yellow grade has the highest amount of Fe_2O_3 that still corresponds to the $t+c$ content of the non-doped 3Y-TZP. Moreover, 0.18 mol% Fe_2O_3 addition is also the highest investigated dopant content, above which the unit cell parameters of both $t+c\text{-ZrO}_2$ and the $t\text{-ZrO}_2$ phase tetragonality starts to change (see Fig. 3).

3.3 Segregation of Fe^{3+} influences the low-temperature degradation

The hydrothermal ageing curves (Fig. 6(a,b)) and kinetic parameter b (Table 3) show that the Fe_2O_3 doping had a positive effect on the hydrothermal stability of zirconia ceramics up to 1 mol%. Please note that although less monoclinic content was formed in the 0.5, 1 and 2 mol% Fe_2O_3 -doped zirconia, there was less tetragonal zirconia available and the saturation level was lower. Both undoped Zpex references (Zpex and Zpex Yellow) show a rather fast hydrothermal degradation compared to 0.25 wt% Al_2O_3 containing 3Y-TZP (grade TZ-3YE, Tosoh) (Fig. 6.a and Table 3) due to the low amount (0.05 wt%) of alumina present in these zirconia ceramics [50]. Fe_2O_3 doping had a positive effect on hydrothermal stability, but is not as effective as Al_2O_3 doping of 3Y-TZP.

Ceramic	V_{ms} (vol%)	b (h^{-1})	n
Zpex	85.5	0.088	1.487
Zpex-0.01Fe	84.9	0.082	1.515
Zpex-0.05Fe	84.7	0.077	1.570
Zpex-0.1Fe	83.7	0.074	1.573
Zpex Yellow	83.1	0.084	1.599
Zpex-0.5Fe	77.0	0.048	1.176
Zpex-1Fe	57.1*	0.015*	0.570*
Zpex-2Fe	52.5	0.055	0.513
TZ-3Y-E	87.1	0.032	1.586

V_{ms} : m -ZrO₂ saturation level; b : constant describing $t \rightarrow m$ transformation; n : constant describing mechanism of nucleation and growth monoclinic grains

*Saturation level not reached, values are only indicative.

Table 3: Ageing kinetics of the sintered zirconia ceramics

Figure 6: Ageing curves of white (Fe₂O₃-free), and coloured Zpex zirconia ceramics sintered for 2h at 1450°C

Almost all trivalent cationic dopants preferentially segregate at the grain boundaries of 3Y-TZP ceramics, hereby following the space-charge layer concept introduced by Hwang *et al.* [51]. In this specific case, the Y³⁺, Al³⁺ and Fe³⁺ dopants segregate to the space charge layer, as proven by the STEM photomicrograph and EDS element mapping of the Zpex-0.1Fe shown in Fig. 7. Although Fe³⁺ cations were observed throughout the bulk of the grains, Fe³⁺ clearly had a preference to segregate at the grain boundaries. The Fe³⁺ cation was dispersed over the entire lattice because of the rather small radius difference between Fe³⁺ (78 pm) and Zr⁴⁺ (84 pm) [36,52]. Despite the small size mismatch, there is an electrical driving force that drives the Fe³⁺ cations towards the grain boundary [53]. These cations will diffuse along the forming grain

boundaries during sintering. Since Fe^{3+} cations (78 pm) are smaller than the slow diffusing Y^{3+} cations (101.9 pm) and smaller than the Zr^{4+} cations (84 pm), it is believed they will diffuse faster and dissolve easily into the lattice up to a few mol% [42,54]. Next to the space charge layer concept, the Al^{3+} segregation at the grain boundary can also be explained by the low solubility of Al_2O_3 in zirconia at room temperature. There is only a very small amount of Al_2O_3 (0.05 wt%) present in the zirconia ceramic. The solubility of Fe^{3+} is much higher, which makes it easier for the Fe^{3+} cations to settle in the lattice [55]. The cation dopant size also has an influence on the low-temperature degradation of zirconia. A higher radius mismatch, either larger or smaller, results in a more favourable hydrothermal ageing stability due to the stronger bond of the point-defect cluster $[2M_{\text{Zr}'}\cdot V_{\text{O}}'']$ at the grain boundaries [36]. The small amount of Fe^{3+} dopant and the relatively small cation size mismatch between Zr^{4+} and Fe^{3+} could explain the small improvement in ageing resistance. The segregated Fe^{3+} cations at the grain boundary bind the oxygen vacancies (0.9 eV $[2\text{Fe}_{\text{Zr}'}\cdot V_{\text{O}}'']$ bonding energy), retarding the ageing kinetics [56]. This bonding energy is even slightly higher than for Y^{3+} cations (0.65 eV $[2\text{Y}_{\text{Zr}'}\cdot V_{\text{O}}'']$ bonding energy). [56] However, because there is only a small radius difference, the bond between the Fe^{3+} cations and the oxygen vacancies is not that strong [36,56]. This underlines the importance of alumina in zirconia ceramics. Doping zirconia with Al^{3+} can improve the ageing kinetics due to the stronger bonding with the oxygen vacancies (1.27 eV $[2\text{Al}_{\text{Zr}'}\cdot V_{\text{O}}'']$ bonding energy) [56].

Interestingly, the Zpex Yellow did not show the positive retarding ageing effect as explicitly as the coated Zpex- Fe_2O_3 mixtures. The co-precipitated Zpex Yellow powder has less grain boundary segregation of the Fe^{3+} cations than the admixed powder mixes. We can state that admixing of the Fe_2O_3 colouring dopant has a slight advantage over co-precipitating in case of ageing kinetics. Grain boundary cation segregation can further be improved by using coated 3Y-TZP powder [45].

The degradation curves (Fig. 6) and kinetic parameter b (Table 3) indicate that the Fe_2O_3 doping had a positive influence on the hydrothermal stability of Zpex up to 1 mol%. Please note that from 2 mol% Fe_2O_3 the kinetic parameter b increases again (Table 3), indicating a decrease in hydrothermal ageing resistance. The unstable, yttria-depleted tetragonal grains that surround the cubic grains, could cause this faster transformation rate because they are easier transformed into monoclinic phase [34,57]. The higher amount of non-transformable cubic phase in these ceramics can explain the decrease in the formation of $m\text{-ZrO}_2$. The 1 mol% Fe_2O_3 -doped Zpex zirconia ceramics did not reach the $m\text{-ZrO}_2$ saturation level after 400 hrs of testing, implying a substantial amount of maintained $t\text{-ZrO}_2$ and indicating that the cubic ZrO_2 grains are surrounding the leftover tetragonal grains and protect them against hydrothermal degradation. When using these ceramics to fabricate monolithic dental restorations, the ageing resistance of such zirconia is important because of the possible risk of hydrothermal degradation. As mentioned in literature, glazing the monolithic restorations could not protect the zirconia framework from hydrothermal degradation like porcelain veneering does. The glazing can make the ageing problem

even more critical because of a pit area [57]. The use of a pre-shaded zirconia block with better ageing stability can help avoiding any potential issue. The use of Fe_2O_3 as a dopant decreases hydrothermal ageing degradation and effectively colours the zirconia ceramic without the risk of fading because the dopants are incorporated in the ceramic lattice.

Figure 7: HAADF-STEM image of Zpex-0.1 Fe with corresponding STEM-EDS element maps and elemental distribution profiles over the grain boundary (the arrow shows the line scan location and direction)

3.4 Translucency decreases with increasing Fe_2O_3 dopant

The translucency data are summarised in Table 2 and presented in Fig. 8. Pure Fe_2O_3 -free Zpex zirconia ceramics have the lowest contrast ratio (CR). This CR of 0.44 ± 0.01 is even more translucent than reported for Al_2O_3 - and La_2O_3 -co-doped 3Y-TZP ceramics [59], and zirconia ceramics of other brands [13]. The good translucency of Zpex zirconia ceramics results from the lower Al_2O_3 (0.05 wt%) content [9]. The Al_2O_3 particles act as a light-scattering source, decreasing the translucency of zirconia [50,59]. No secondary Al_2O_3 particles were observed in any of the ceramics (Fig. 4).

Pure Zpex, Zpex Yellow and 0.01-0.1 Fe_2O_3 doped Zpex had a similar grain size around 430 nm and an equal amount of cubic phase fraction of 13-14 vol% (Table 2). A smaller grain size improves the translucency of the zirconia ceramic [9,60]. To obtain a translucency that is comparable to that of teeth, the grain size of 3Y-TZP should be below 100 nm [9]. Since Zpex zirconia ceramics contain less Al_2O_3 , the grains could be larger for pure Fe_2O_3 -free Zpex zirconia ceramics, while still having a suitable translucency. Cubic phase zirconia shows a higher translucency than tetragonal phase zirconia, due to a lower birefringence. Increasing the yttria content to obtain this cubic phase is therefore a possibility to increase translucency [61], but would strongly

decrease the fracture toughness of the zirconia ceramics [62]. Secondary phase iron oxide particles that could scatter the incoming light were not observed in the ceramics.

With the introduction of the Fe_2O_3 dopant, there was a small increase in porosity for the admixed ceramics (Table 1). Even a small amount of porosity considerably decreases translucency [63]. Zpex Yellow is the least translucent of all tested ceramics and showed no increase in porosity. Literature reported that the decreasing translucency of Fe_2O_3 -doped Zpex is caused by the darker colour of Fe_2O_3 [64].

The Fe^{3+} cations that substitute Zr^{4+} create extra oxygen vacancies in the ceramics [31]. These colour centres will absorb light, decreasing the translucency of the material [65]. With increasing Fe_2O_3 doping, there will be more oxygen vacancies produced, decreasing the translucency, as observed by the increasing CR value in Table 2.

Figure 8: Translucency of the coloured zirconia ceramics

4 Conclusions

The present study shows that doping small amounts (0.01-0.1 mol%) of Fe_2O_3 is a promising strategy to create tooth-coloured zirconia ceramics for dental restorations: (1) homogeneous colouring can be obtained; (2) colouration was obtained by incorporating Fe^{3+} in the zirconia lattice, which gives a stable colouring effect and indicates that dis-colouration will not occur within a reasonable life span; (3) Fe_2O_3 doping improves the hydrothermal aging stability. Although the ageing problem was not critical for conventional porcelain-fused-zirconia systems, it might be problematic for monolithic restorations, since there is no covering layer. Moreover, monolithic restorations need pre-shaded zirconia blocks to provide a naturally aesthetic outlook.

The Fe_2O_3 -doped ceramics had a similar density (6.07 g/cm^3), composition (86 vol% $t\text{-ZrO}_2$, 14 vol% $c\text{-ZrO}_2$), grain size (430 nm), hardness (13.1 GPa) and fracture toughness ($4.8 \text{ MPa m}^{1/2}$) as conventional 3Y-TZPs. Due to grain boundary segregation of Fe^{3+} in the ceramics, the oxygen vacancies are strongly bound in the space charge layer and hydrothermal ageing is slowed down with increasing amount of Fe_2O_3 dopant. These Fe_2O_3 -doped ceramics were compared to Zpex Yellow, a Fe_2O_3 -containing coprecipitated zirconia powder from Tosoh. The improved hydrothermal ageing resistance of co-precipitated powder (Zpex Yellow) based ceramics was less pronounced than for the Fe_2O_3 -admixed powder-based ceramics due to the lower extent of Fe^{3+} grain-boundary segregation. The binder containing Zpex and Zpex Yellow powder-based ceramics showed a substantially higher strength after sintering, showing the importance of proper binder addition during processing of larger sized ceramics.

Higher amounts of Fe₂O₃ doping (0.5-2 mol%) not only revealed a colour that cannot be applied for dental restorations, but also resulted in a strong increase in larger grained cubic phase formation and residual porosity, and a subsequent decrease in density and mechanical properties.

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