The effect of silica sol infiltration on the properties of dental 3Y-TZP ceramics

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Abstract. The effect of adding silica on the phase composition, microstructure, mechanical properties and low temperature degradation (LTD) of 3 mol% yttria-stabilised zirconia (3Y-TZP) ceramics, produced from two ready-to-press granulated powders of the same nominal chemical composition, but differing in content of alumina, is presented. Silica doped 3Y-TZP materials were prepared by the infiltration of silica sol *in situ* synthesized by the sol–gel method using dynasylan as a precursor into the biscuit-sintered porous zirconia discs followed by sintering at 1450 °C. The results of transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analyses revealed that silica was mainly present as an amorphous phase concentrated at triple grain junctions. The presence of silica substantially decreases the amount of transformed monoclinic fraction in sintered 3Y-TZP after accelerated ageing, compared to the monolithic 3Y-TZP sintered at the same temperature and does not show any significant effect on flexural strength, Vickers hardness and indentation toughness.

Keywords: zirconia, infiltration, X-ray diffraction (XRD), microstructure, LTD.

1   Introduction

Yttria partially stabilized tetragonal zirconia (Y-TZP) is becoming increasingly popular as an alternative material in restorative dentistry. Nowadays dental zirconia frameworks are produced by computer-assisted design and manufacturing (CAD/CAM) technology followed by pressure-less sintering to nearly-theoretical density [1].

One of the issues concerning tetragonal Y-TZP ceramics, not only in dentistry, is their sensitivity to low temperature degradation in aggressive environments, i.e. ageing [2]. Such degradation occurs by a slow surface transformation from metastable tetragonal phase to a more stable monoclinic phase in the presence of water or water vapor. Being subject to a volume increase, tetragonal to monoclinic (t-m) transformation induces the formation of microcracks at the surface. This offers a path for the water to penetrate and exacerbate the process of surface degradation and the transformation process. The growth of the transformation zone results in severe microcracking and grain pull out, and finally surface roughening which leads to strength degradation.

LTD resistance of dental zirconia can be improved by decreasing grain size or increasing the yttria content in the starting powder. However, both of these approaches lead to the reduction of the mechanical properties of zirconia, thus making it unattractive. Another way to tackle the problem is by adding of dopants. It was also reported that the addition of silica to Y-TZP ceramic improves the LTD resistance [3-5]. All studies were carried out by introducing appropriate levels of SiO_2 as dopants to a commercial Y-TZP powder. Another way of introducing silica into the Y-TZP ceramic could be the pressureless infiltration of pre-sintered specimens with silica precursors or with silica sol synthesized *in situ* by the sol-gel method. In this way, silica can be easily included into the already soft milled zirconia frameworks.

In the present work, silica was added through the infiltration with silica sol into the pre-sintered porous ceramic specimens. After final sintering ceramic specimens were verified for fractional density, mean grain size, mechanical properties and subjected to accelerated ageing. The final aim was to improve LTD resistance without affecting mechanical properties.

2   Experimental

Two commercially available, ready-to-press, granulated, biomedical-grade Y-TZP powders (Tosoh, Japan) with different amount of alumina were used for the preparation of specimens: TZ-PX-242A contains 0.05% alumina and the TZ-3YB

grade is essentially alumina-free. Both powders contain 3 mol% yttria in the solid solution to stabilize the tetragonal structure and 3 wt% of an acrylic binder.

Uni-axial dry pressing at 150 MPa in a floating die was used to shape green disks of 20 mm in diameter and 2 mm in thickness. Afterwards they were pre-sintered in air for 2 h at 900 ˚C. After pre-sintering specimens of each material were randomly divided into two groups. One group was left untreated and served as a control group. Other group of specimens was infiltrated with silica sol, synthesized in situ by the sol–gel method through hydrolysis of dynasylan (Dynasylan® 6490, Evonik, Germany): specimens were immersed in a mixture of absolute ethanol and dynasylan; the hydrolysis was carried out by dropwise addition of an aqueous ammonia (25%) at room temperature. The concentration of SiO_2 in final solution was 0.24 mol/l. Specimens were infiltrated for 1 cycle, soaking for 30 min. Thereafter they were dried and finally sintered at 1450 ˚C for 4 h together with the controls. After sintering ceramic specimens were verified for fractional density, mean grain size, mechanical properties and subjected to accelerated ageing.

The fractional density of sintered disks was determined with Archimedes method using distilled water as the immersion liquid. The relative densities were calculated by adopting a theoretical density of $\varrho_T = 6.08$ g/cm^3. The grain size evaluations were made on FE-SEM (Jeol JSM-7600F, Japan) micrographs of polished (3 μm diamond paste) and thermally etched (1350 ˚C, 1 h) specimens, using the linear interception method, based on the ASTM E112-96(2004)e2 standard. The specimens for the TEM were prepared by cutting 3-mm diameter discs from the ceramic bodies. These discs were reduced to ∼120 μm by grinding. A region about 20-μm thick at the centre of the disc was produced using a dimple grinder. Finally, the specimens were thinned by argon-ion erosion at 4 kV with an incident angle of about 10˚.

The biaxial flexural strength of the pellets was measured using a piston-on-three-balls test, at a loading rate of 1 mm/min (Galdabini Quasar 50, Italy). The indentation technique was used to determine fracture toughness of SiO_2-doped and undoped Y-TZP. A load of 30 N was applied to the specimens with a Vickers hardness indenter. Fracture toughness was calculated using the length of the cracks emanating from the Vickers impression.

No surface treatment, such as grinding and/or polishing was applied to specimens' surface before *in vitro* ageing experiments. These were conducted in distilled water under isothermal conditions at 134 °C for 6–48 h.

X-ray diffraction patterns in the 25–40° 2θ range were collected from the specimen's surfaces before and after accelerated ageing experiments using Cu Kα radiation (Endeavor D4, Bruker AXS). The relative amount of the transformed monoclinic zirconia (m-ZrO_2) on all the surfaces was determined from the integral intensities of the monoclinic ($\bar{1}$ 1 1)$_m$ and (1 1 1)$_m$, and the tetragonal (1 0 1)$_t$ peaks according to the method of Garvie and Nicholson [6], which is the most commonly applied to determine the phase composition of zirconia powders and compacts with randomly distributed m-ZrO_2 and t-ZrO_2 phases at any distance from the surface exposed to the XRD analysis.

3 Results and discussion

The relative densities of pre-sintered TZ-PX-242A and TZ-3YB bodies were 58.8% and 56.3% respectively. The relative densities of sintered at 1450 °C silica doped and undoped TZ-PX-242A and TZ-3YB disks are listed in Table 1.

Table 1: Relative density of sintered at 1450 °C monolithic and SiO_2-doped sintered TZ-PX-242A and TZ-3YB disks.

	TZ-PX-242A	TZ-3YB
As sintered	98.6±0.3	96.0 ± 0.7
SiO_2-doped	99.2±0.5	96.5±0.4

The mean of grain size for monolithic TZ-PX-242A and TZ-3YB materials sintered at 1450 °C were 0.29±0.03 and 0.31±0.04 μm respectively. SiO_2-doped TZ-PX-242A and TZ-3YB materials sintered at the same temperature exhibit average grain sizes 0.28±0.02 and 0.32±0.04 μm. This result revealed, that the addition of silica into the Y-TZP ceramic by the infiltration of pre-sintered specimens with silica sol for 30 min practically does not change the grain size of material.

TEM and EDS analyses of sintered SiO_2-doped TZ-PX-242A material revealed the presence of amorphous silica phase, which is mainly located in triple grain junctions rather than grain-boundaries (Fig. 1.).
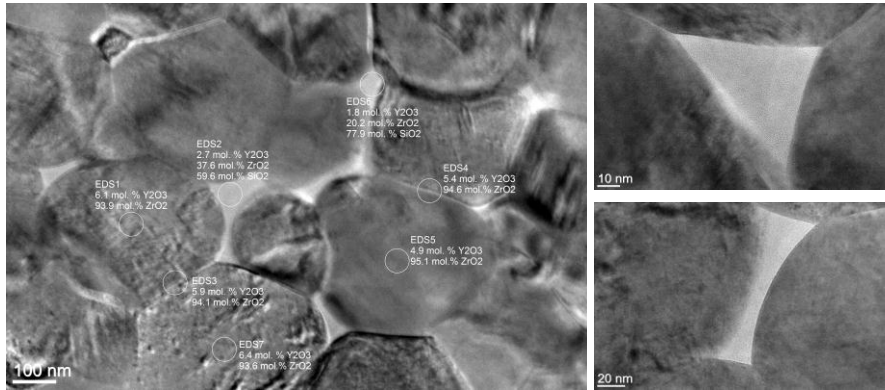
Figure 1: TEM micrographs and results of EDS analysis of TZ-PX-242A/SiO_2 specimen sintered at 1450 ˚C for 4 h, showing that amorphous silica is mainly present in the grain junctions.

The flexural strength, hardness and fructure toughness of monolithic and SiO_2-doped TZ-PX-242A and TZ-3YB materials are listed in Table 2. No significant differences in Vickers hardness and indentation toughness was observed between SiO_2-doped and monolithic specimens for all materials.

Table 2: Flexural strength, Vickers hardness and indentation toughness of monolithic and SiO_2-doped TZ-PX-242A and TZ-3YB materials.

Sample	Flexural strength, MPa	Hardness, H_v (GPa)	Indentation toughness, K_{IC} ($MPa \cdot m^{1/2}$)
TZ-PX-242A	1072 ± 48	15.2 ± 0.5	4.5 ± 0.7
TZ-PX-242A/SiO_2	1150 ± 150	14.1 ± 0.4	4.2 ± 0.3
TZ-3YB	1051 ± 136	14.5 ± 0.5	4.4 ± 0.3
TZ-3YB/SiO_2	1076 ± 114	13.9 ± 0.3	4.3 ± 0.1

Characteristic XRD patterns obtained in the 21–36 2θ range from SiO_2-doped TZ-PX-242A and TZ-3YB ceramic surfaces sintered for 4 h at 1450 ˚C, before and after

accelerated ageing at 134 °C in water for different periods of time (6, 12, 24 and 48 h), are represented in Fig. 2a and 2b, respectively. The pattern for as sintered surfaces displays three characteristic peaks positioned at 2θ of 30.2°, 34.7° and 35.2° corresponding to the $(1\ 0\ 1\ )_t$, $(0\ 0\ 2)_t$ and $(1\ 1\ 0)_t$ planes of the t-ZrO_2 phase, respectively. The amount of silica in SiO_2-doped sintered specimens was below the detection limit.
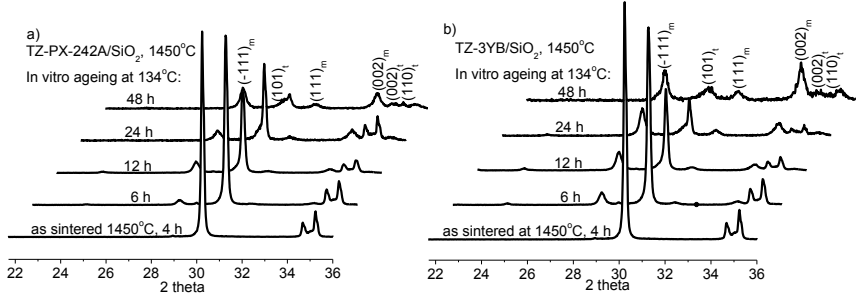

Figure 2: XRD patterns obtained from a) SiO_2-TZ-PX-242A and b) SiO_2-TZ-3YB ceramic surfaces, sintered for 4 h at 1450 °C and aged in water at 134 °C for 6, 12, 24 and 48 h.

After 6 h of ageing, monoclinic $(\overline{1}\ 1\ 1)_m$, $(1\ 1\ 1)_m$, and $(0\ 0\ 2)_m$ peaks (positioned at 2θ of 28.15°, 31.3°, and 34°, respectively) start emerging with a tendency for their intensity to increase with still longer ageing times at the expense of reduced intensity of the tetragonal $(1\ 0\ 1)_t$, $(0\ 0\ 2)_t$ and $(1\ 1\ 0)_t$ peaks. Notice that the intensity of the moclinic peaks of the aged SiO_2-doped TZ-PX-242A material considerably lower, compared to the aged for the same time SiO_2-doped TZ-3YB material. This result can be explained by the presence of 0.05% alumina in TZ-PX-242A powder. It is well-documented, that addition of small amounts of alumina to 3Y-TZP helps to reduce the tetragonal-to-monoclinic phase transformation upon ageing in water [7,8], but it is not clear why.

The variation of the calculated fraction of the monoclinic zirconia for SiO_2-doped and pure TZ-PX-242A and TZ-3YB materials sintered at 1450 °C with *in vitro* ageing time is represented in Fig. 3. For both materials the presence of silica substantially decreases the monoclinic fraction after ageing, as compared to the monolithic Y-TZP sintered at the same temperature. It seems, that small additions of oxides with

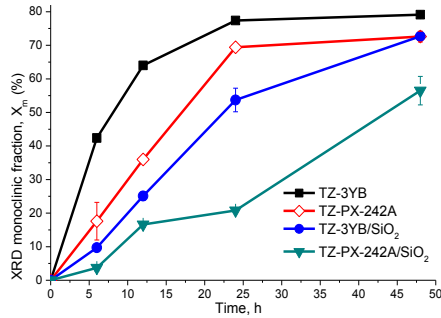limited solubility in zirconia hinders the nucleation of LTD, but the mechanism is not known.

Figure 3: Calculated monoclinic fraction versus *in-vitro* ageing time for monolithic and silica doped TZ-PX-242A and TZ-3YB materials.

4   Conclusions

Silica doped 3Y-TZP ceramics with the same grain size were prepeared by the pressureless infiltration of pre-sintered specimens with silica sol synthesized *in situ* by the sol-gel method. The results of XRD, TEM and EDS analysis revealed that silica was mainly present as an amorphous phase concentrated at triple grain junctions. No glassy phase was detected in zirconia grain boundaries. The presence of silica substantially improves the LTD resistance and does not show any significant effect on flexural strength, hardness and fracture toughness of Y-TZP ceramics.

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For wider interest

Yttria partially stabilized tetragonal zirconia (Y-TZP) is becoming increasingly popular as an alternative material in restorative dentistry. One of the issues concerning tetragonal Y-TZP ceramics is their sensitivity to low temperature degradation (LTD), i.e. ageing. LTD appears from spontaneous transformation of metastable tetragonal grains to a more stable monoclinic phase in the presence of water or water vapour.

LTD resistance of dental zirconia can be improved by decreasing grain size or increasing the yttria content in the starting powder. Unfortunately, both of these approaches lead to the reduction of the mechanical properties of zirconia, thus making it unattractive for dental applications. Other way to tackle the problem is by adding of dopants.

Our research is focused on the study of the effects of silica on the phase composition, microstructure, mechanical properties and LTD of the Y-TZP ceramics in order to understand, whether ageing resistance can be increased without decreasing mechanical properties. The other goul of work is to understand the mechanism, by which silica gives rise to increasing ageing resistance of Y-TZP. The understanding of this can helps to explain the mechanism of LTD. In order to reach the desired final properties of tetragonal zirconia ceramics, the mechanism of LTD must be known.