



Full length article

Effect of cation dopant radius on the hydrothermal stability of tetragonal zirconia: Grain boundary segregation and oxygen vacancy annihilation



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ABSTRACT

The hydrothermal aging stability of 3Y-TZP-xM₂O₃ (M = La, Nd, Sc) was investigated as a function of 0.02–5 mol% M₂O₃ dopant content and correlated to the overall phase content, *t*-ZrO₂ lattice parameters, grain size distribution, grain boundary chemistry and ionic conductivity.

The increased aging stability with increasing Sc₂O₃ content and the optimum content of 0.4–0.6 mol% Nd₂O₃ or 0.2–0.4 mol% La₂O₃, resulting in the highest aging resistance, could be directly related to the constituent phases and the lattice parameters of the remaining tetragonal zirconia.

At low M₂O₃ dopant contents ≤0.4 mol%, the different aging behavior of tetragonal zirconia was attributed to the defect structure of the zirconia grain boundary which was influenced by the dopant cation radius. It was observed that the grain boundary ionic resistivity and the aging resistance followed the same trend: La³⁺ > Nd³⁺ > Al³⁺ > Sc³⁺, proving that hydrothermal aging is driven by the diffusion of water-derived mobile species through the oxygen vacancies. Accordingly, we elucidated the underlying mechanism by which a larger trivalent cation segregating at the zirconia grain boundary resulted in a higher aging resistance.

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1. Introduction

Tetragonal zirconia, especially yttria-stabilized tetragonal zirconia polycrystals (Y-TZP), possesses an excellent combination of high toughness and strength, which is mainly attributed to the transformation toughening effect of the metastable tetragonal zirconia phase [1]. Furthermore, Y-TZP ceramics are wear, corrosion and high-temperature resistant with low thermal conductivity, good ionic conductivity, good biocompatibility and superior esthetic appearance [1–3]. Therefore, they are very attractive for a wide range of applications such as fixed-partial denture in restorative dentistry, femoral heads in orthopedics and solid electrolytes

in solid oxide fuel cells [2,3].

However, Y-TZP ceramics suffer from low temperature degradation, in which the tetragonal zirconia (*t*-ZrO₂) phase spontaneously transforms to the monoclinic (*m*-ZrO₂) phase in the presence of water or water vapor (hydrothermal aging) without any applied stress over the temperature region from room temperature up to about 400 °C [4,5]. This problem was considered to be minor until hundreds of Y-TZP total hip prostheses (THP) ball-heads catastrophically failed in a very short time between 1999 and 2000, leading to its withdrawal from the market [5,6]. Hydrothermal aging is a progressive process triggered by water molecules, which starts from the surface and propagates into the ceramic component, resulting in surface roughening and microcracking [2,5,7,8]. The performance and reliability of zirconia components thereby will be inevitably influenced when used in aqueous environments such as for biomedical applications.

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The aging resistance of Y-TZP ceramics can be improved by increasing the yttria content [2,8], using an alternative stabilizer (CeO₂ for instance) and using alumina–zirconia composites [9–11]. However, some properties of Y-TZP ceramics such as strength or esthetic appearance cannot be simultaneously maintained by these approaches. Different research reports show that (co-)doping of Y-TZP with a small amount of other ions, e.g., Al³⁺ [12,13], Fe³⁺ [14], Pr³⁺ [15], Ce⁴⁺, Bi³⁺ [16], La³⁺ [17], Si⁴⁺ [13], provides a satisfactory balance between aging resistance, mechanical properties [7,13,16,17] and esthetic appearance, including color [14–16] and translucency [14,17]. Although many oxides have been tested, there is no systematic guideline for choosing a suitable doping. Recently, we reported that the cation dopant radius can be used as a controlling parameter, and larger trivalent cations segregating at the zirconia grain boundary can effectively retard the aging rate of 3Y-TZP ceramics without sacrificing the excellent mechanical properties [17]. Although different studies have reported that grain boundaries play a key role in enhancing/retarding the aging kinetics [2,5,12,13,18] and dopant cations segregated at the grain boundary (including Al³⁺, La³⁺, Cu²⁺, Mg²⁺ and Ge⁴⁺) could effectively retard the aging rate of 3Y-TZP ceramics [17–22], the underlying mechanism is still not completely clarified.

In addition, from the perspective of hydrothermal aging mechanism, the behavior of oxygen vacancies in Y-TZP ceramics should be assessed in order to explain the different aging kinetics. Although the mechanism of hydrothermal aging is not fully understood, the involvement of oxygen vacancies is widely realized and the most prevailing mechanism emphasizes the primary role of oxygen vacancies annihilation [2,21,23–25]. It has been reported that the tetragonal zirconia phase may be stabilized by oxygen vacancies adjacent to the Zr⁴⁺ ion [24,26]. The apparent activation energy of the aging kinetics (73–106 kJ/mol for various stabilizer and grain sizes [8,9,11,27]) is reported to be comparable to the activation energy for ionic conductivity in 3Y-TZP below 500 °C (88–89 kJ/mol) [28,29]. Thus, it is commonly accepted that the diffusion of water-derived species into the zirconia lattice and the filling of oxygen vacancies (V_O^{••}) is responsible for the hydrothermal aging process of Y-TZP ceramics [21,23–25,30].

In this work, to elucidate how the cation dopant radius influences the hydrothermal aging kinetics of tetragonal zirconia, 3Y-TZP ceramics were doped with different trivalent oxides M₂O₃ (M = La, Nd, Sc and Al). The fundamental microstructural parameters including the constituent phases, *t*-ZrO₂ crystal lattice parameters, grain size distribution, grain boundary chemistry and oxygen ionic conductivity were investigated. Since the amount of dopant also showed a crucial impact on the aging kinetics [17,31], which can again depend on the cation radius, the hydrothermal aging kinetics of 3Y-TZP-xM₂O₃ (M = La, Nd, Sc) were systematically studied as a function of M₂O₃ dopant content from 0.02 to 5 mol%.

2. Materials and methods

2.1. Material preparation

High purity 3Y-TZP powder (grade TZ-3Y, Tosoh, Japan) was respectively doped with trivalent oxides (Sc₂O₃, Nd₂O₃, La₂O₃) having a different cation radius Zr⁴⁺ (84.0 pm) ~ Sc³⁺ (87.0 pm) < Y³⁺ (101.9 pm) < Nd³⁺ (110.9 pm) < La³⁺ (116.0 pm) [32]. 0.02–5 mol% Nd₂O₃ (Chempur, purity of 99.9%), La₂O₃ (Chempur, purity of 99.99%) and Sc₂O₃ (abcr GmbH & Co. KG, purity of 99.9%) were respectively mixed with tetragonal zirconia nanopowder on a multidirectional mixer (Turbula type T2C, WAB, Switzerland) for 24 h in ethanol using 5 mm Y-TZP (grade TZ-3Y, Tosoh, Japan) milling balls. The mixed suspension was further

processed by bead milling (Dispermat SL, Germany) for 3 h at 5000 rpm using 1 mm ZrO₂ beads (grade TZ-3Y, Tosoh, Japan). The base powder (pure 3Y-TZP) was bead milled as a reference. 0.25 wt.% (0.3 mol%) alumina-doped 3Y-TZP powder (grade TZ-3Y-E, Tosoh, Japan) was processed as well for comparison, because alumina is widely doped in 3Y-TZP ceramics and aluminum cation has a much smaller radius (Al³⁺ (53.5 pm)) than the other dopant cations.

All powders were cold isostatically pressed at 250 MPa (EPSI, Temse, Belgium) and pressureless sintered in air at 1500 °C for 2 h.

Since the yttria is co-precipitated in the TZ-3Y starting powder, we refer to the other oxide additives as dopants in the 3Y-TZP ceramics. The sintered zirconia ceramics are referred to as 3Y-TZP-xM₂O₃ (M = La, Nd, Sc and Al) with x the mol % of M₂O₃.

2.2. Phase characterization and Rietveld refinements

X-ray diffraction (XRD, 3003-TT, Seifert, Ahrensburg, Germany) using Cu–K_α radiation at 40 kV and 40 mA was used for phase analysis. XRD patterns were recorded at room temperature from polished ceramic surfaces in the 20–90° (2θ) range with a scan speed of 2 s/step and a scan size of 0.02°.

Rietveld refinements of the XRD patterns were performed using TOPAS-Academic software (Bruker AXS, Karlsruhe, Germany). The phase structures were refined as: tetragonal zirconia (*t*) unit cell with space group P4₂/nmcZ, monoclinic zirconia (*m*) unit cell with space group P21/c, cubic zirconia (*c*) with space group Fm-3m, “non-transformable” tetragonal zirconia (*t'*) with space group P4₂/nmcS and the La₂Zr₂O₇ phase with space group Fd-3mZ. The quality of the Rietveld refinement was controlled with a low R value of <10%. To simplify the discussion and clarify the interphase relationships, the tetragonal data are presented using a pseudo-cubic (distorted fluorite) unit cell and the lattice parameter of *t* and *t'* was multiplied by √2.

2.3. Microstructural characterization

Scanning electron microscopy (SEM, XL-30FEG, FEI, Eindhoven, The Netherlands) was used to characterize the microstructure on polished, thermally etched (1250 °C for 25 min in air) and Pt-coated surfaces. The grain size was measured on SEM micrographs using IMAGE-PRO software according to the linear intercept method. At least 1000 grains were counted, and the grain size distribution and the average results (±standard deviation) were reported with a correction factor of 1.56.

Transmission electron microscopy (TEM) analysis was performed to examine the distribution of dopant cations (La³⁺, Nd³⁺, Al³⁺ or Sc³⁺), Y³⁺ and Zr⁴⁺ around the grain boundaries. Electron transparent samples were prepared by ion-milling with an Ion Slicer (EM-09100IS, Jeol, Japan). High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive spectroscopy (STEM-EDS) elemental maps were obtained on a FEI Titan 60–300 “cubed” transmission electron microscope operated at 200 kV. 5–7 grain boundaries in each ceramic were analyzed. Al–K, Sc–K, Y–L, Zr–L, La–L, and Nd–L lines were used for the elemental maps. Quantitative elemental maps were acquired to calculate the element concentration profiles across the grain boundary using ESPRIT 1.9 software.

2.4. Assessment of aging kinetics

In vitro accelerated hydrothermal experiments were used to age the ceramics. Double-side mirror polished specimens were autoclaved at 134 °C and 0.2 MPa in water vapor. The amount of tetragonal to monoclinic zirconia phase transformation was

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