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Low temperature degradation of Al_2O_3-doped 3Y-TZP sintered at various temperatures

Zhi-kai Wu*, Ning Li, Chao Jian, Wan-qian Zhao, Jia-zhen Yan

Department of Materials Processing Engineering, College of Manufacturing Science and Engineering, Sichuan University, Chengdu 610065, China

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Abstract

The low temperature degradation of Al_2O_3-doped 3Y-TZP sintered at 1400–1600 °C was investigated by aging at 140 °C for various hours. X-ray diffraction and field emission scanning electron microscopy were used to study the microstructure of specimens. The results showed that the mean grain size of samples sintered at 1400–1600 °C was between 0.3 μm and 0.9 μm, addition of Al_2O_3 slightly promoted the coarsening of tetragonal grain during densification. Introduction of 0.5–5.0 wt% Al_2O_3 addition into 3Y-TZP effectively delayed the tetragonal-monoclinic phase transformation and the degradation of mechanical property during aging. Sintering temperature had a significant effect on the aging sensibility of 3Y-TZP. The aging resistance of 3Y-TZP decreased rapidly with the increase of sintering temperature, especially for the control group which is free of Al_2O_3 addition. This can be interpreted by the increase in grain size and the heterogeneous distribution of Y^{3+} ions within tetragonal grains.

Keywords: A.Sintering; B.Grain boundary; D.ZrO_2; Low temperature degradation

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) is an important biomaterial due to the superior mechanical properties, high wear resistance and excellent biocompatibility [1]. Today, more than 600 000 zirconia femoral heads have been implanted worldwide [2]. In addition, Y-TZP ceramic has become increasingly popular as an alternative high-toughness core material in dental restoration [3]. However, Y-TZP ceramic undergoes an unfavorable tetragonal-monoclinic ($t \rightarrow m$) phase transformation at relatively low temperatures (65–400 °C), especially with the presence of water or water vapor [4,5]. The transformation strain (about 8% shear strain and 4–5% volume increase) and stress would cause surface roughing, grain pull out, macro or microcracks and degradation in mechanical properties. This is the so called low temperature degradation (LTD) which is detrimental to the biomedical application of Y-TZP ceramics [2].

Since the first report of LTD in 1981 by Kobayashi [6], many researchers had studied the aging sensibility of Y-TZP ceramic. The susceptibility of Y-TZP to LTD depends on several factors including the grain size, the type and concentration of stabilizer, the applied or residual stress and even the formation of cubic phase [7–9]. Besides, some studies showed that addition of Al_2O_3 had a positive effect on the aging resistance of Y-TZP ceramics. For example, Tsukama [10] reported that supplementing zirconia with 5–40 wt% Al_2O_3 addition suppressed the LTD of Y-TZP, but did not fully inhibit the transformation. Tsubakino et al. [11] found that introduction of 1.2–12 wt% Al_2O_3 limited the $t \rightarrow m$ phase transformation to the surface layer of Y-TZP ceramic. Li [12] and Elshazly [13] were able to suppress the LTD of Y-TZP by addition of Al_2O_3 respectively. However, the role of Al_2O_3 in retarding the LTD of Y-TZP is still unclear. Several hypotheses [10–12] such as the increase of Young's modulus resulted from Al_2O_3 particles, the presence of Y_2O_3–Al_2O_3 compounds at the grain boundaries and the formation of protective $Al(OH)_3$ on the surface of aged zirconia were proposed to explain the role of Al_2O_3 in retarding LTD.

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*Corresponding author. Tel.: +86 28 85405320.
E-mail address: wuzhikai@163.com (Z.-K. Wu).

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Recently, Matsui [14] and Ross [15] have reported that Y^{3+} and Al^{3+} ions segregated at the grain boundaries of Y-TZP and the concentration of segregation increased with the increase of sintering temperature. Since the $t \rightarrow m$ phase transformation during aging follows a nucleation and growth mechanism and grain boundaries are preferred nucleation zones for transformation [16].The segregation of Y^{3+} and Al^{3+} ions may have a large effect on the structure of grain boundary, therefore affect the low temperature degradation of Y-TZP ceramic.

In this work, the low temperature degradation of Al_2O_3-doped 3Y-TZP sintered at 1400–1600 °C was investigated with special attention focused on the effect of the distribution of Y^{3+} and Al^{3+} ions.

Table 1
Chemical composition and some parameters of the synthesized nano-zirconia powders.

Samples	Chemical composition (mass%)					Powder parameters	
	ZrO_2	HfO_2	Y_2O_3	Al_2O_3	others	D_{50}(μm)	BET(m^2/g)
TZ000	Bal	2.30	5.58	≤0.02	<0.1	0.375	14.4
TZ050	Bal	2.20	5.71	0.54	<0.1	0.428	11.3
TZ250	Bal	2.24	5.52	2.37	<0.1	0.419	12.4
TZ500	Bal	2.21	5.45	4.82	<0.1	0.430	11.2

2. Materials and methods

2.1. Powder synthesis

High-purity $ZrOCl_2 \cdot 8H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as starting materials to prepare Al_2O_3-doped 3Y-TZP nanopowders by coprecipitation method. $Zr(OH)_4$, $Y(OH)_3$ and $Al(OH)_3$ were coprecipitated from a mixture of $ZrOCl_2 \cdot 8H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ by dropwise adding ammonium hydroxide into the solution to PH 9.5. The precipitated gels was filtered and repeatedly washed with deionized water and ethanol, then dried at 100 °C for 24 h in vacuum and calcined at 600 °C for 2 h to obtain Al_2O_3-doped 3Y-TZP nanopowders. The chemical composition determined by X-ray fluorescence spectroscopy (XRF-1800, Shimadzu, Japan), the median particle diameter (D_{50}) measured by Zetasizer Nano ZS (Malvern, UK) and specific surface area characterized by BET method are listed in Table 1. TZ000, TZ050, TZ250 and TZ500 represent 3Y-TZP doped with 0 wt%, 0.5 wt%, 2.5 wt% and 5.0 wt% Al_2O_3 respectively.

2.2. Specimen preparation and hydrothermal aging

The synthesized powders were uniaxially pressed under 20 MPa, followed with cold isostatic pressing at 200 MPa.

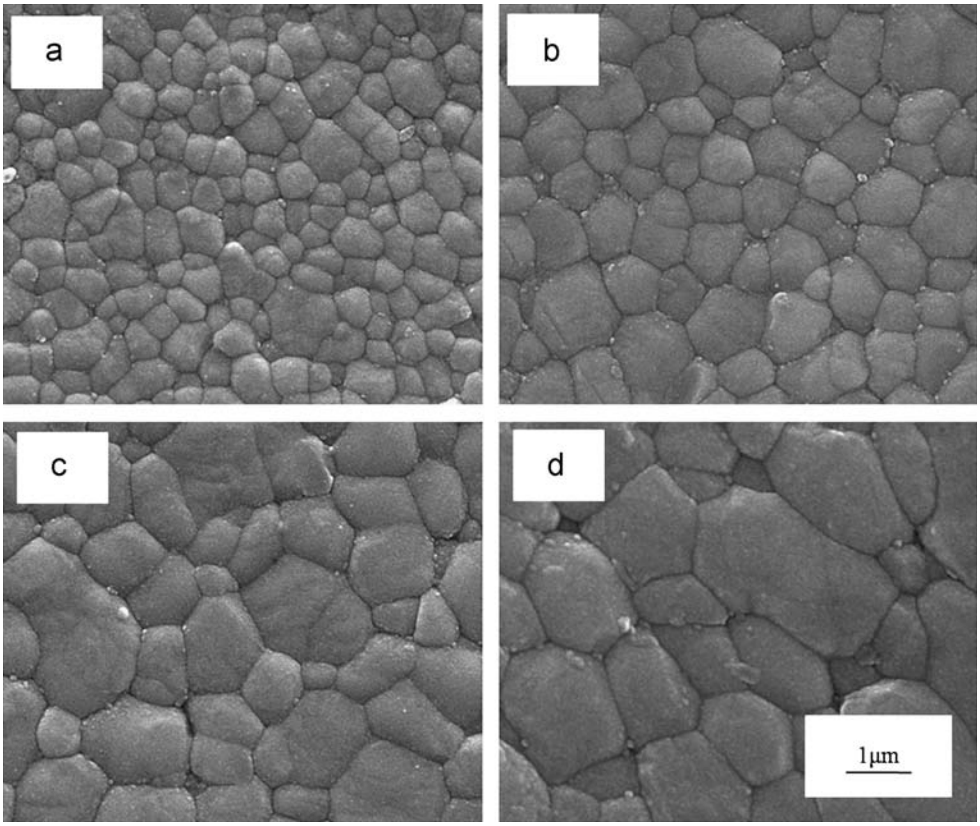

Fig. 1. SEM images of thermally etched TZ050 sintered at (a) 1400 °C, (b) 1500 °C, (c) 1550 °C and (d) 1600 °C for 2 h.

The obtained green compacts were densified by pressure less sintering at 1400–1600 °C for 2 h with a heating rate of 3 °C/min. Specimens in a dimension of 10 mm × 10 mm × 5 mm were fabricated by cutting the densified ceramic into blocks. Before aging, all specimens were polished using diamond paste of 0.5 μm and then thermally etched at 1300–1400 °C for 30 min to eliminate the surface stress caused by polishing. For LTD tests, specimens were aged in an autoclave with the presence of water vapor at 140 ± 2 °C under 0.36 Mpa for different times up to 48 h.

2.3. Characterization

The surface topography of specimens before and after aging was observed with field emission scanning electron microscopy (SEM). The mean grain size of specimens was determined by the linear intercept method from the SEM micrographs.

The phase composition of aged specimens was determined by X-ray diffraction analysis using an X'pert diffractometer (X'Pert PRO MPD, Panalytical, Holland). Diffraction data (2θ) from 26° to 38° was collected with a step size of 0.02° and a counting time of 5 s/step using Cu-K_a radiation. The amount of monoclinic phase on the surface of aged specimens was calculated by the Garvie and Nicholson method [17]:

$$X_m = \frac{I_{m(\bar{1}11)}+I_{m(111)}}{I_{m(\bar{1}11)}+I_{m(111)}+I_{t(111)}} \tag{1}$$

where $I_{t(1\,1\,1)}$, $I_{m(\bar{1}11\;)}$ and $I_{m(1\,1\,1)}$ represent the integrated intensity of the tetragonal (1 1 1), monoclinic ($\bar{1}$11) and monoclinic (1 1 1) peaks respectively.

Vickers hardness (H) was measured according to the standard ASTM C 1327-03 and calculated with Eq. (2), where P is the load (kgf), d is the average length (mm) of the two diagonals of the indentation. Fracture toughness (K_{IC}) was determined by the indentation technique using a load of 196 N. The value of K_{IC} was calculated by Eq. (3), where E is the Young's modulus (GPa), H the Vickers hardness (GPa), P the applied load (N) and c the crack length (m) measured from the center of indentation.

$$H = 1.8544 \times (P/d^2) \tag{2}$$

$$K_{IC} = 0.016(E/H)^{1/2}P/c^{3/2} \tag{3}$$

3. Results and discussion

Fig. 1 is the SEM micrograph of polished and hot etched TZ050 sintered at various temperatures. With the increase of sintering temperature, the grain size increases rapidly. The mean grain size was calculated from the SEM micrograph by the linear intercept method. Fig. 2 shows the variation of mean grain size with sintering temperature for specimens doped with different amount of Al_2O_3. As can be seen, increase of sintering temperature leads to an obvious coarsening of zirconia grains. The mean grain size increased from about 0.3 μm at 1400 °C to 0.6–0.9 μm at 1600 °C. Addition of Al_2O_3 slightly promoted the coarsening of grains during densification.

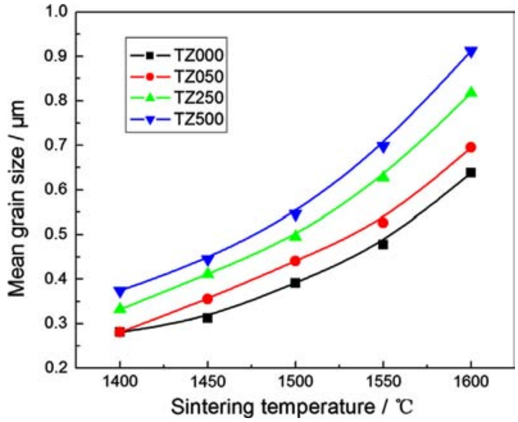

Fig. 2. Curves showing the variation of mean grain size with sintering temperature for 3Y-TZP doped with different amount of Al_2O_3 addition.

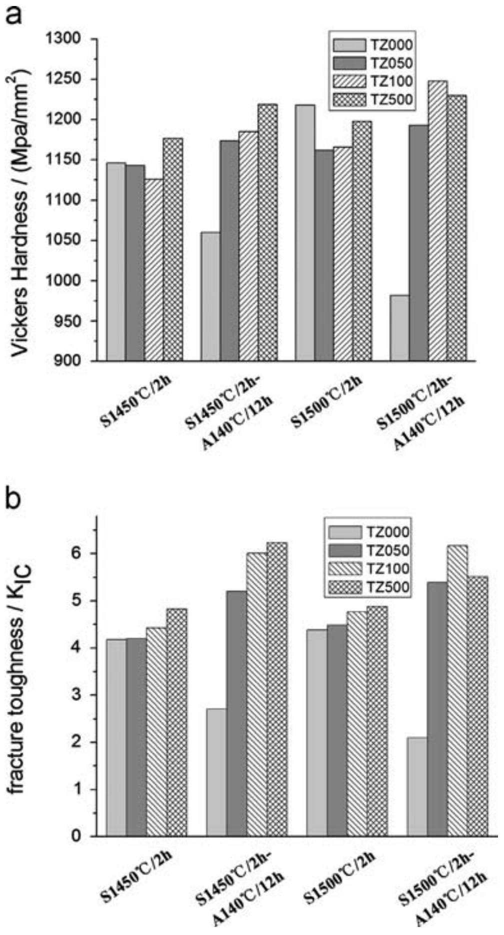

Fig. 3. Vickers hardness and fracture toughness determined before and after aging (S1450°C/2 h–A140°C/12 h represents sintering at 1450 °C for 2 h and aged at 140 °C for 12 h).

Fig. 3 shows the Vickers hardness (H) and fracture toughness (K_{IC}) of specimens determined before and after aging. The as-prepared specimens had a Vickers hardness of 1100–1300 kgf/mm^2 and a fracture toughness of 4–5 Mpa m$^{1/2}$. After aging at 140 °C for 12 h, both the Vickers hardness and the fracture toughness of TZ000 dropped to a lower value, while the mechanical property of Al_2O_3-doped 3Y-TZP was enhanced. After aging at 140 °C for 24 h, the mechanical property of all the specimens reduced to an extremely low value which can hardly be measured using the indentation method. It is likely that the surface compressive stress introduced by the $t \rightarrow m$ phase transformation during aging leads to the increase of mechanical property. However, the formation of flaws on the surface finally caused the degradation in mechanical properties. The presence of flaws is confirmed by Fig. 4 which shows the SEM image of aged specimens. No flaws except some small pores were observed on the surface of as-prepared specimens. After aging at 140 °C for 48 h, plenty of flaws including holes and microcracks presented on the surface of TZ000, while few flaws were found on the surface of Al_2O_3-doped 3Y-TZP. Addition of Al_2O_3 delayed the degradation in mechanical properties during aging.

Fig. 5 is the XRD pattern of aged specimens. Specimens sintered at 1400 °C displayed only one peak at approximately 30.3° after aging at 140 °C for 6 h. This peak was the combined peaks of cubic (1 1 1) and tetragonal (1 1 1) phase. For specimens sintered at higher temperatures, the monoclinic peaks ($\bar{1}$ 1 1) and (1 1 1) appeared in the XRD pattern at 2θ of 28.1° and 31.3°, respectively. The content of monoclinic phase (f_m) on the surface of aged specimens was calculated from the XRD patterns. Fig. 6 shows the evolution of f_m with aging time for Al_2O_3-doped 3Y-TZP sintered at 1450 °C. With the increase of aging time, the content of monoclinic phase on the surface of TZ000 increases rapidly, while Al_2O_3-doped 3Y-TZP showed a lower increasing trend of f_m with aging time. This indicated that a small amount of Al_2O_3 addition effectively delayed the $t \rightarrow m$ transformation of 3Y-TZP during aging. It is notable that the change of monoclinic fraction with aging time is almost the same for 3Y-TZP doped with 0.5–5 wt% Al_2O_3, which signifies that increase of Al_2O_3 addition from 0.5 wt% to 5 wt% did not further improve the aging resistance of 3Y-TZP.

The solubility of Al^{3+} in zirconia is extremely limited at room temperature. Therefore, Al_2O_3 existed in the matrix of zirconia mainly as Al_2O_3 particles which present to be black grains in Fig. 4 (c,d). Tsukama [10] insisted that Al_2O_3 particles acted to improve the aging resistance of 3Y-TZP by the increase of Young's modulus in the matrix. Recently, Matsui et al. [14] have found that Al^{3+} ions segregated at grain boundaries with a width of about 6 nm and a concentration of 3–5 mol% depending on the sintering temperature. The segregation of Al^{3+} ions was expected to enhance the stability of zirconia local to grain boundaries by an increase of oxygen vacancies, thus improve the aging resistance of 3Y-TZP [14]. Since the increase of Al_2O_3 addition from 0.5 wt% to 5 wt% did not further improve the aging resistance of 3Y-TZP, it is likely

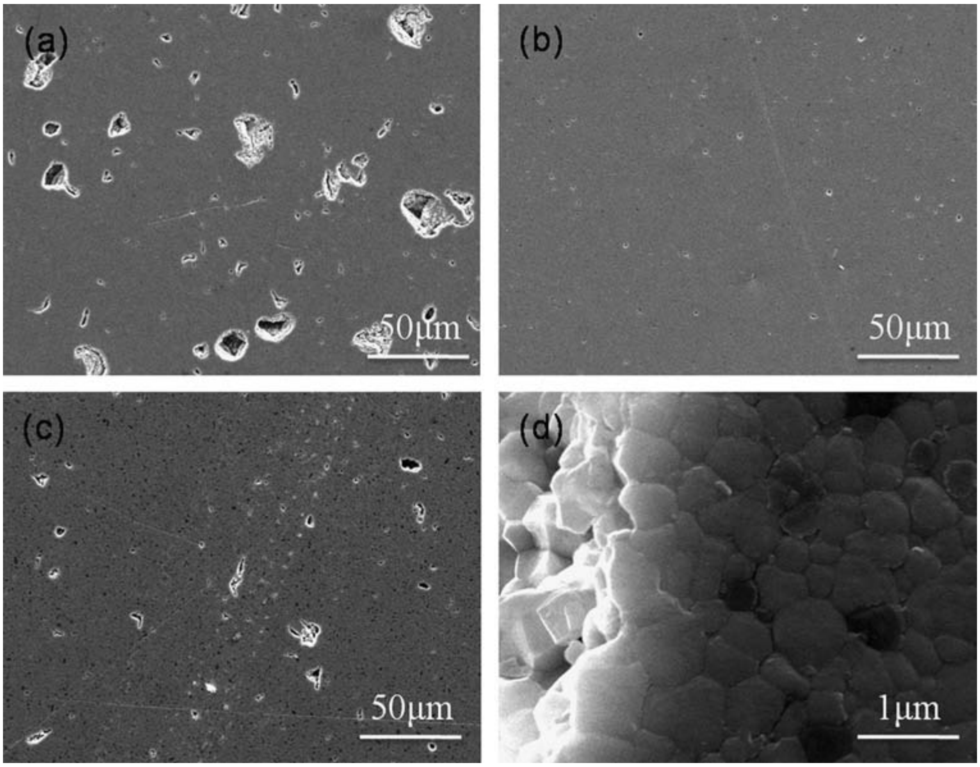

Fig. 4. SEM images showing the surface flaws of TZ000 (a), TZ050 (b), and TZ500 (c,d) after aging at 140 °C for 48 h.

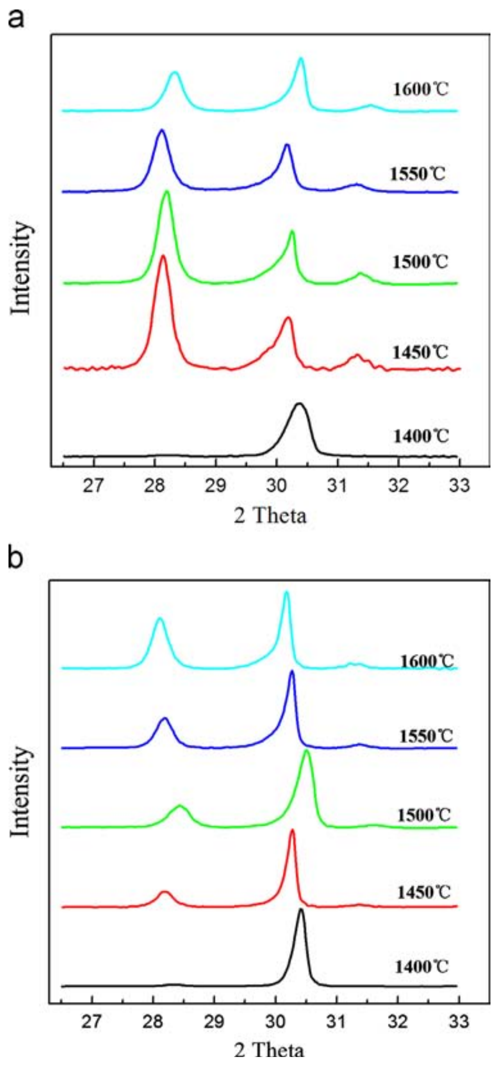

Fig. 5. XRD patterns of the aged TZ000 and TZ050 with various sintering temperatures (all the specimen were aged at 140 °C for 6 h).

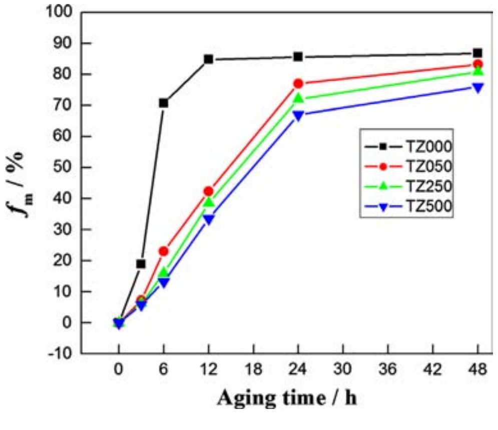

Fig. 6. Curves showing the evolution of f_m with aging time for Al_2O_3-doped 3Y-TZP sintered at 1450 °C.

that Al^{3+} ions segregated at grain boundaries, instead of Al_2O_3 particles, plays an important role in retarding LTD of Al_2O_3-doped 3Y-TZP.

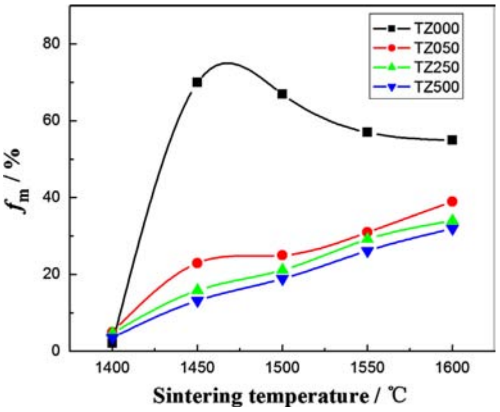

Fig. 7. Curves showing the relationship of f_m and sintering temperature for 3Y-TZP doped with different amount of Al_2O_3 addition (all the specimen were aged at 140 °C for 6 h).

The low temperature aging behavior of 3Y-TZP sintered at 1400–1600 °C was investigated by aging at 140 °C for 6 h and the results were shown in Fig. 7. As can be seen, the evolution of monoclinic fraction with sintering temperature was quite different for 3Y-TZP with and without Al_2O_3 addition. After aging at 140 °C for 6 h, only few tetragonal phases (about 2–4%) transformed to monoclinic phase for specimens sintered at 1400 °C. However, an obvious increase of monoclinic fraction was observed for specimens sintered above 1400 °C, especially for TZ000 which is free of Al_2O_3 addition. This could be interpreted by the change of grain size and the distribution of Y^{3+} ions with sintering temperature.

Numerous researchers [8,18–20] have reported that reducing the grain size has a beneficial effect on the stability of tetragonal zirconia, therefore on the susceptibility of Y-TZP to LTD. A thermodynamics approach proposed by Lange [21] helps to understand the role of grain size in affecting the stability of tetragonal zirconia. The total free energy change per units volume required for the $t \rightarrow m$ transformation in a constrained matrix can be expressed as follows:

$$\Delta G_{t \rightarrow m} = \Delta G_{CH} + \Delta G_E + \Delta G_S, \tag{4}$$

where ΔG_{CH} is the chemical free energy change associated with the $t \rightarrow m$ transformation, ΔG_E the change of strain free energy and ΔG_S the change of surface free energy. 3Y-TZP with smaller grain size has higher ΔG_S, therefore, specimens sintered at 1400 °C showed a higher stability of tetragonal phase and a superior resistance to LTD. An alternative interpretation is that it is more difficult to accommodate the shear and dilatational strain accompanied with transformation for smaller grain size.

Besides, the distribution of Y^{3+} ions within tetragonal grain also has a significant effect on the aging sensibility of 3Y-TZP. Matsui et al. [22] have examined the distribution of Y^{3+} and Al^{3+} ions in 3Y-TZP sintered at 1100–1650 °C, using nanoprobe EDS technology. They found that Y^{3+} ions are drastically changed to heterogeneously distribute at high sintering temperatures. Specifically, the distribution of Y^{3+} ions in grain interiors was nearly homogeneous for 3Y-TZP sintered at 1300 °C and below. However, at high sintering temperature, the tetragonal grain partitioned into Y^{3+} ions enriched regions and Y^{3+} ions depleted regions, and the partition aggravated with the increase of sintering temperature. The Y^{3+} ions depleted regions will act as nucleation sites for the $t \rightarrow m$ transformation, therefore leads to a decrease of aging resistance [9]. In addition, the formation of Y^{3+} ions enriched regions well explains the relatively lower monoclinic fraction of aged TZ000 sintered above 1500 °C, for these regions are less liable to transform to monoclinic phase during aging.

4. Conclusion

The average grain size of Al_2O_3-doped 3Y-TZP sintered at 1400–1600 °C is between 0.3 μm and 0.9 μm. Addition of Al_2O_3 slightly promotes the coarsening of zirconia grain during densification.

The Vickers hardness and fracture toughness was enhanced at the initial stage of aging. However, for longer aging time, the formation of flaws on the surface finally lead to the degradation in mechanical properties.

Addition of Al_2O_3 effectively delayed the $t \rightarrow m$ transformation and the degradation in mechanical properties during aging. Besides, sintering temperature had a significant effect on the aging resistance of 3Y-TZP. The aging resistance of 3Y-TZP decreases rapidly with the increase of sintering temperature, especially for the control group which is free of Al_2O_3 addition. This can be interpreted by the increase in grain size and the heterogeneous distribution of Y^{3+} ions within tetragonal grains.

References

[1] C. Piconi, G. Maccauro, Zirconia as a ceramic biomaterial, Biomaterials 20 (1999) 1–25.

[2] J. Chevalier, What future for zirconia as a biomaterial?, Biomaterials 27 (2006) 535–543

[3] I. Denry, J.R. Kelly, State of the art of zirconia for dental applications, Dental Materials 24 (2008) 299–307.

[4] S. Lawson, Environmental degradation of zirconia ceramics, Journal of the American Ceramic Society 15 (1995) 485–502.

[5] M. Cattani-Lorente, S.S. Scherrer, P. Ammann, M. Jobin, Low temperature degradation of a Y-TZP dental ceramic, Acta Biomaterialia 7 (2011) 858–865.

[6] K. Kobayashi, H. Kuwajima, T. Masaki, Phase change and mechanical properties of ZrO_2–Y_2O_3 solid electrolyte after ageing, Solid State Ionics (1981) 489–4933-4 (1981) 489–493.

[7] V. Lughi, V. Sergo, Low temperature degradation – aging – of zirconia: a critical review of the relevant aspects in dentistry, Dental Materials 26 (2010) 807–820.

[8] J.F. Li, R. Watanabe, Phase transformation in Y_2O_3-partially-stabilized ZrO_2 polycrystals of various grain sizes during low-temperature aging in water, Journal of the American Ceramic Society 81 (1998) 2687–2691.

[9] J. Chevalier, S. Deville, E. Münch, R. Jullian, F. Lairadd, Critical effect of cubic phase on aging in 3 mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis, Biomaterials 25 (2004) 5539–5545.

[10] K. Tsukama, M. Shimada, Thermal stability of Y_2O_3-partially stabilized zirconia (Y-PSZ) and Y-PSZ/Al_2O_3 composites, Journal of Materials Science 4 (1985) 857–861.

[11] H. Tsubakino, R. Nozato, M. Hamamoto, Effect of alumina addition on the tetragonal-to-monoclinic phase transformation in zirconia–3 mol% yttria, Journal of the American Ceramic Society 74 (1991) 440–443.

[12] J.F. Li, R. Watanabe, Influence of a small amount of Al_2O_3 addition on the transformation of Y_2O_3-partially stabilized ZrO_2 during annealing, Journal of Materials Science 32 (1997) 1149–1153.

[13] E.S. Elshazly, M.E.S. Ali, S.M. El-Hout, Alumina effect on the phase transformation of 3Y-TZP ceramics, Journal of Materials Science 24 (2008) 873–877.

[14] K. Matsui, N. Ohmichi, M. Ohgai, Effect of alumina-doping on grain boundary segregation induced phase transformation in yttria-stabilized tetragonal zirconia polycrystal, Journal of Materials Science 21 (2006) 2278–2289.

[15] I.M. Ross, W.M. Rainforth, D.W. McComb, A.J. Scott, R. Brydson, The role of trace additions of alumina to yttria–tetragonal zirconia polycrystals (Y-TZP), Scripta Materialia 45 (2001) 653–660.

[16] H. Tsubakino, M. Hamamoto, R. Nozato, Tetragonal-to-monoclinic phase transformation during thermal cycling and isothermal ageing in yttria-partially stabilized zirconia, Journal of Materials Science 26 (1991) 5521–5526.

[17] R.C. Garvie, P.S. Nicholson, Phase analysis in zirconia systems, Journal of the American Ceramic Society 55 (1972) 303–305.

[18] F.F. Lange, G.L. Dunlop, B.I. Davis, Degradation during aging of transformation-toughened ZrO_2–Y_2O_3 materials at 250 °C, Journal of the American Ceramic Society 69 (1986) 237–240.

[19] A. Suresh, M.J. Mayo, W.D. Porter, C.J. Rawn, Thermodynamics of the tetragonal-to-monoclinic phase transformation in fine and nanocrystalline yttria-stabilized zirconia powders, Journal of Materials Research 18 (2003) 2912–2921.

[20] J.M. Saldana, H.B. Ramirez, D.J. Vigueras, T. Iga, G.A. Schneider, Mechanical properties and low-temperature aging of tetragonal zirconia polycrystals processed by hot isostatic pressing, Journal of Materials Research 18 (2003) 2415–2426.

[21] F.F. Lange, Transformation toughening, Journal of Materials Science. 17 (1982) 225–234.

[22] K. Matsui, N. Ohmichi, M. Ohgai, Effect of alumina-doping on grain boundary segregation induced phase transformation in yttria-stabilized tetragonal zirconia polycrystal, Journal of Materials Research 21 (2006) 2278–2289.