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Article

Yttria-Calcia-Co-Stabilized Tetragonal Zirconia Polycrystals Made by Powder Mixing

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Highlights

Main findings:

- Yttria-calcia-co-stabilized zirconia can be obtained by powder blending
- Values of mechanical properties and LTD resistance are between Y-TZP and Ca-TZP
- Low sintering temperature favors strength and LTD resistance

Implications of the main findings:

- Y-Ca-TZP materials may be interesting materials for biomedical applications
- Further improvements may be possible by adjusting fractions and stabilizer contents of the starting powders
- Powder mixing provides easy access to some standard compositions

Abstract

In this study 1.5Y-2.2Ca-TZP materials were obtained by hot pressing of a mixed and milled blend of 3Y-TZP and 4.4Ca-TZP powders. The materials were sintered at temperatures between 1250–1400 °C and characterized with respect to mechanical properties, microstructure phase composition and stability against low temperature degradation. In the tested range, the bending strength of the TZP decreases with increasing sintering temperature from 1300 MPa to 1050 MPa while the toughness shows a rising trend from 5 MPa√m to 8 MPa√m. The microstructure is bimodal with grain sizes increasing from 140 nm to 300 nm with rising sintering temperature. LTD tests revealed high ageing resistance for TZP sintered at 1300 °C. The Y-Ca-co-stabilized TZP equilibrates the properties of Ca-TZP and Y-TZP.

Keywords: zirconia; mechanical properties; microstructure; phase composition

1. Introduction

Yttria stabilized zirconia materials have become commodities in recent decades. They are applied in mechanical engineering and biomedical applications such as dental implants due to their high strength, fine grain size and high fracture resistance [1]. The excellent mechanical properties result from transformations toughening, a stress-induced martensitic phase transformation from metastable tetragonal to stable monoclinic phase [2]. Yttria added as stabilizer forms a solid solution with zirconia. As yttrium is trivalent oxygen vacancies are introduced for charge compensation. These vacancies reduce the coordination number of the zirconium cations and distort the zirconia lattice [3]. Hereby, the high temperature polymorphs can be retained metastable after sintering. Yttria as an oversize dopant tends to segregate to the grain boundaries which slows down grain growth due to solute drag. Alumina is frequently added in small amounts to slow down grain growth [4]. The most common formulation 3Y-TZP contains 3 mol% Y₂O₃. In industrial scale the powders are produced by co-precipitation or hydrolysis of yttrium and zirconium salts which leads to an initially homogeneous stabilizer distribution [5,6]. With respect to thermodynamics, 3Y-TZP is a composition

in the t+c field (miscibility gap) at a typical sintering temperature of ~1400 °C [7]. Hence, we may expect a segregation into tetragonal and cubic phase. However, this segregation is kinetically hindered as it requires uphill diffusion. Complete segregation requires high sintering temperatures and/or long dwell [8,9]. The most prominent disadvantage of Y-TZP is the vulnerability against low temperature degradation (LTD) [10]. In moist environments hydroxy species such as water enter the oxygen vacancies increase the coordination number of zirconium cations and, thereby, de-stabilize the tetragonal phase. The degradation is slow but relevant for applications in medical implants which are implanted into the body for decades [11]. It is commonly believed that LTD follows a nucleation and growth process in which single surface grains transform, expand and put the surrounding grain boundaries under stress which favors the penetration of the fluids into the volume of the component [12]. However, Keuper et al. showed that LTD actually follows a linear kinetics [13]. LTD may lead to surface roughening or even breakout of lumps or detachment of whole surface layers which may destroy the TZP components [14].

Calcium stabilized zirconia as Ca-PSZ in which tetragonal grains embedded into a cubic matrix was the first technically applied transformation toughened zirconia material [15]. Ca-TZP consisting entirely of tetragonal grains was first described by the group of Haberko [16,17]. It was produced by sintering ultrafine powders at low sintering temperature (~1200 °C). The material offers a strength, slightly lower and toughness slightly higher than 3Y-TZP. The most prominent issue is, however, the very low critical grain size of 100-140 nm. Above the critical grain size spontaneous failure is observed [16,18]. Calcium being larger than Yttria tends to segregate even more to the grain boundary and retard grain growth. This effect was used by Li et al. to limit the grain growth of Ce-TZP by co-doping with calcium [19]. Until recently Ca-TZP was more or less a scientific curio. However, recently a high-quality powder became available which makes the material attractive for use in medical applications as the studies performed showed a combination of excellent mechanical properties and LTD resistance [20,21].

The first paper combining yttria and calcium as stabilizers in TZP was published last year [22]. Feng et al. obtained co-stabilized powders by coprecipitation and tried compositions of with 2 and 3 mol% CaO with additions of 0.5–2 mol% of Y₂O₃. The powders were ultrafine; the pressureless sintered samples showed a fine microstructure and mechanical properties strongly depending on the recipes. As the samples were small only a basic mechanical characterization (excluding bending strength) was carried out.

The co-stabilization with yttria and calcium seems attractive. Powders with BET surface areas of > 100 m²/g which were used in the study by Feng [22] are, however, almost unprocessable in conventional shaping processes for ceramics components. Hence, in the present study we tried a mixing and milling method combining equal amounts of commercially available 3Y-TZP and 4.4-Ca-TZP powders (which we had previously tested separately) to obtain a powder blend for a 1.5Y-2.2Ca-TZP [20,23]. The aim was to check whether this simple approach is capable to obtain such co-stabilized TZP with attractive mechanical properties and LTD resistance and if the blending process leads to particular changes compared to the more homogeneous starting materials applied by Feng et al. [22].

2. Materials and Methods

The starting powders used for this study are 4.4Ca-TZP (HSY-481, Daiichi Kagaku Kigenso Kogyo, Tokyo, Japan, S_{BET} = 23.1 m²/g, alumina content 0.25 wt.%) and 3Y-TZP (Innovnano, Portugal, primary particle size 50 nm, alumina content 0.4 wt.%). A 300 g batch composed of equal amounts of both powders was attrition milled in 500 ml 2-propanol with 3Y-TZP balls of 2 mm diameter for 4h at 1000 rpm. Subsequently the milling media were separated and the suspension was dried overnight at 70 °C. The dry powder was screened with a 200 µm mesh.

The samples were consolidated by hot pressing in a boron nitride clad graphite die at 60 MPa axial pressure for 1 h in vacuum. The sintering temperatures were varied between 1250 °C and 1400

°C in 25 °C increments. Two disks of 40 mm diameter and 17 g weight separated by a graphite spacer were sintered simultaneously.

The disks were manually de-burred with a 40 µm diamond disk and lapped on both sides with 15 µm diamond suspension until the sintering skin was removed and the disks were level. One side was polished subsequently with 15 µm, 3 µm and 1 µm diamond suspension to a mirror like finish. The disks were then cut into bending bars of 4 mm width with a diamond wheel. 12 bending bars were obtained per sample set.

The density by buoyancy method (Kern, Lörrach, Germany) and the Young's modulus and Poisson's ratio by ultrasonic excitation (IMCE, Genk, Belgium) were determined on entire disks prior to cutting. Vickers hardness HV10 (five indents, Bareiss, Oberdischingen Germany) was measured by indentation of the polished samples. The bending strength was determined by 4pt bending tests in a setup with 20 mm outer and 10 mm inner span at a crosshead speed of 0.5 mm/min (Zwick-Roell, Ulm, Germany). The fracture toughness was measured by three indentation-based methods. Firstly, by direct crack length measurement of the crack patterns of the HV10 indents (K_{DCM}), the toughness was calculated according to the Palmqvist crack model of Niihara [24]. Secondly, by indentation strength in bending (K_{ISB}). Two bending bars were notched with four HV10 indents, aligned at a distance of 2 mm, along the middle of the polished tensile side of the bending bar. The indented region was placed in the inner span of the above-mentioned 4pt setup and the residual strength was determined at a crosshead speed of 2.5 mm/min immediately after indentation. The toughness was calculated using the model of Chantikul et al. [25]. The third method introduced by Braun and Lawn is an extension of the ISB protocol [26]. As only one of the four indents leads to failure, the extended crack lengths of the survivors can be employed to calculate the toughness K_{LWN} . Both the LWN and ISB methods are originally based on the assumption of semicircular cracks (geometry factor $\psi = 1.27$). In case of tough TZP materials the crack profiles are considerably flatter [27], hence a tentative correction of the geometry factor to $\psi = 1.08$ was applied. This value was determined for 3Y-TZP by Dransmann et al. [28]. Hereby the ISB and LWN toughness values are reduced by a factor of 1.08/1.27.

The phase composition of the polished material was determined by XRD (X'Pert MPD, Panalytical, Eindhoven, the Netherlands, $CuK\alpha_1$, Ge-monochromator, Bragg-Brentano setup, accelerator detector). The characteristic diffraction peaks in the 27-33° 2 θ scale were integrated to quantify tetragonal and monoclinic phase according to Toraya et al. [29]. The 72-75° 2 θ range allows to calculate the tetragonality of the zirconia from the location of the fourth order tetragonal peak pair and identify formation of cubic phase. The quantification of the tetragonal and monoclinic phase in fracture surfaces allows to determine the transformability of the zirconia. The depth of the transformation zone [30] as well as the transformation toughness increments were calculated according to McMeeking and Evans from XRD data, Young's modulus and Poisson's ratio [31].

High resolution SEM images were taken from polished and thermally etched (1150 °C/1min air) surfaces. The average grain size of the microstructure was determined by line-intercept method using a size correction factor of 1.57 as described by Mendelson [32].

Low temperature degradation was determined by an accelerated autoclave test. It is commonly assumed that 1 h in the autoclave at 134 °C corresponds approximately to 3 years in vivo. For this test some cold pressed binderless compacts of 30 mm diameter and 1 mm thickness were sintered in air at 1300 °C and 1350 °C for 2 h. These materials were polished and exposed to saturated water vapor in an autoclave at 134 °C for durations of 1 h, 3 h, 10 h, 30 h and 100 h. The phase composition was tested by XRD at the respective aging times. Assuming a MAJ (Mehl Avrami Johnson) nucleation and growth mechanism as proposed by Chevalier $\ln(\ln(1/(1-(V_{m,t}-V_{m,0}))))$ was plotted vs. $\ln(t)$ with $V_{m,t}$ the monoclinic content at the respective time and $V_{m,0}$ the initial monoclinic content of the pristine sample [33]. According to MAJ, the relationship between ageing time and monoclinic formation can be expressed as $f = 1 - \exp [(-bt)^n]$, with f the monoclinic content $V_{m,t}-V_{m,0}$ (in our case $V_{m,0} > 0$), b the rate constant which is temperature dependent and n the nucleation factor. The nucleation n can be obtained as the slope of the above-mentioned plot. $\ln(b)$ is the value at $\ln(t) = 0$ (t in hours).

3. Results

3.1. Microstructure

Figure 1 shows SEM images of polished and thermally etched surfaces of TZP sintered at 1250–1400 °C. Except for very few sporadic pores, the samples are dense and defect-free. A trend to coarsening is clearly visible. The average grain size (Fig.2) continuously increases from 145 nm at 1250 °C to 310 nm at 1400 °C. The SEM images, however, also reveal another interesting detail. The grain size distribution is bimodal at 1250 °C and stays bimodal up to 1350 °C. This indicates that the initial inhomogeneous stabilizer distribution is retained to a certain extent even at higher sintering temperatures.

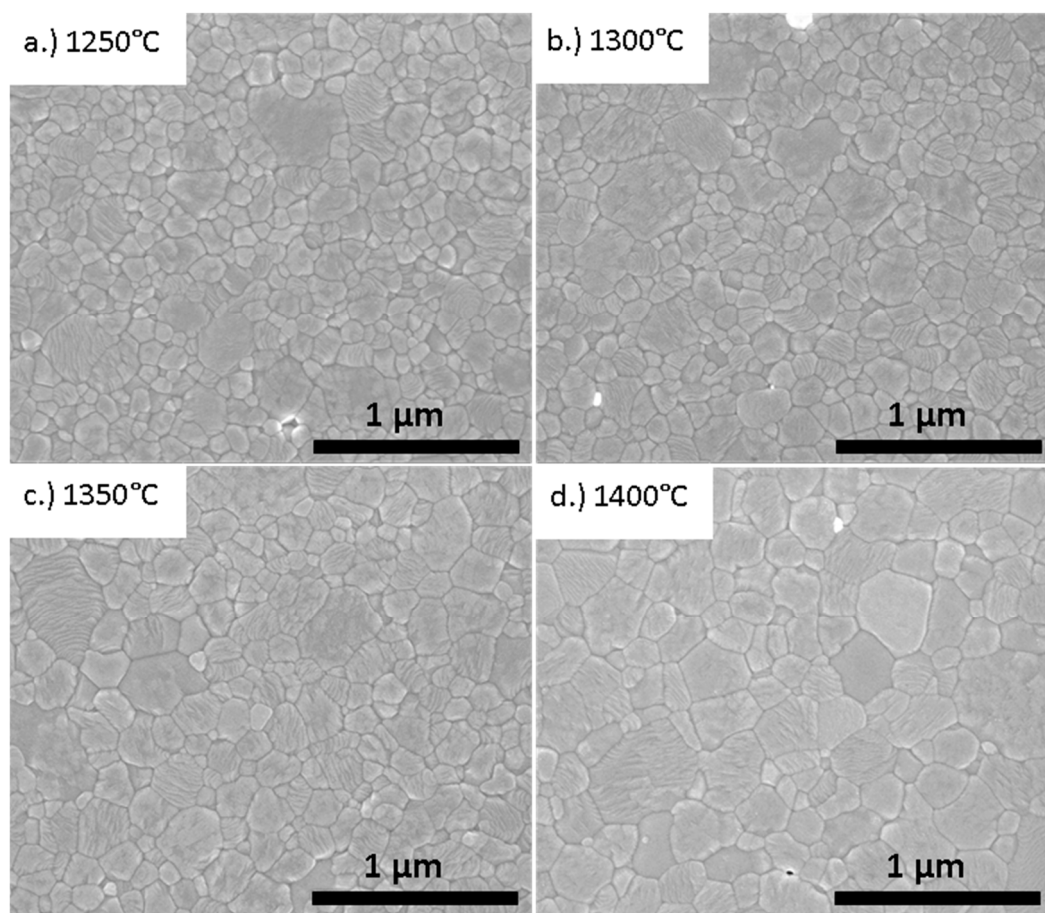


Figure 1. Microstructure of 1.5Y-2.2Ca-TZP materials sintered at different temperatures, SEM images of thermally etched surfaces 1250°C; b. 1300°C; c. 1350°C; 1400°C.

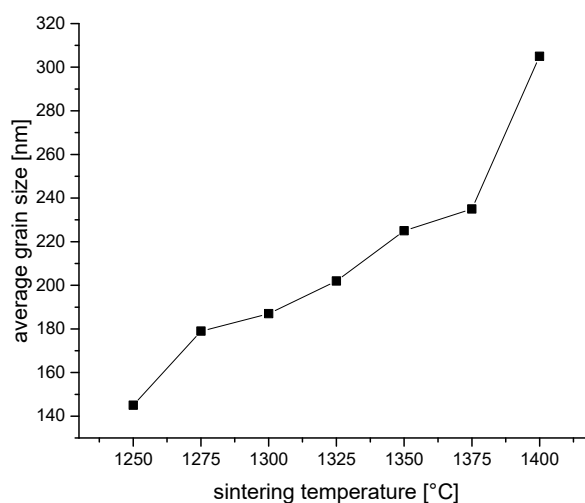


Figure 2. Average grains size vs. sintering temperature of 1.5Y-2.2Ca-TZP materials determined by line intercept method.

3.2. Density and Mechanical Properties

Assuming a theoretical density of 6.03 g/cm³ the sintered samples showed a density of 99-99.6% without any systematic trend (not shown in detail). From the SEM images we may assume complete densification. The Young's modulus values measured vary between 208.6 GPa and 211.9 GPa, the measurement error is in the range between ± 0.8 –1 GPa. These values are typical for fully dense Y-TZP materials [23]. Poisson's ratios are in the range between 0.321–0.323.

Figure 3 shows the hardness and 4pt bending strength of the TZP materials depending on sintering temperature. The Vickers hardness HV10 shows a continuous and steady decline with increasing sintering temperature from 1330 HV10 at 1250 °C to 1270 HV10 at 1400 °C. This is in good accord with the increasing trend in grain size. After an initial increase from 1180 MPa to 1280 MPa between 1250–1275 °C the bending strength values subsequently decline to a value of 1050 MPa at 1400 °C.

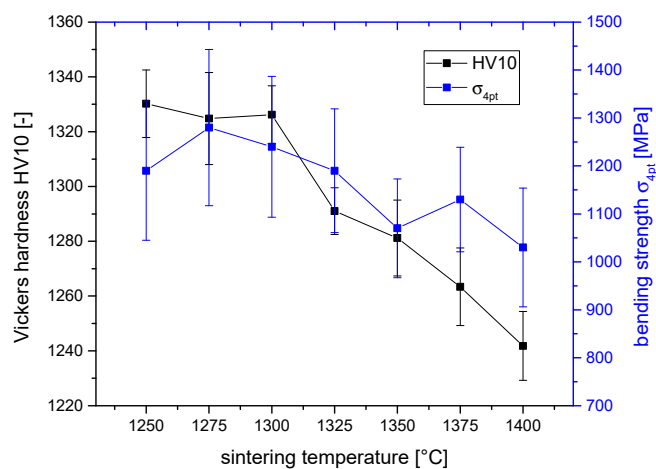


Figure 3. Hardness HV10 and 4pt bending strength σ_{4pt} of 1.5Y-2.2Ca-TZP sintered at different temperatures.

Figure 4 shows the fracture toughness values determined by different indentation-based methods. The overall trend is identical for all methods. The toughness increases with increasing sintering temperature from level of $\sim 5 \text{ MPa}\sqrt{\text{m}}$ at 1250°C to $8\text{-}10 \text{ MPa}\sqrt{\text{m}}$ at 1400°C . The highest values were determined by direct crack length measurement. This method, however, bears the risk of crack trapping especially for fine grain and very transformable materials [34]. The ISB and the LWN method based on residual strength, extended cracks and including a crack geometry correction seem therefore more reliable.

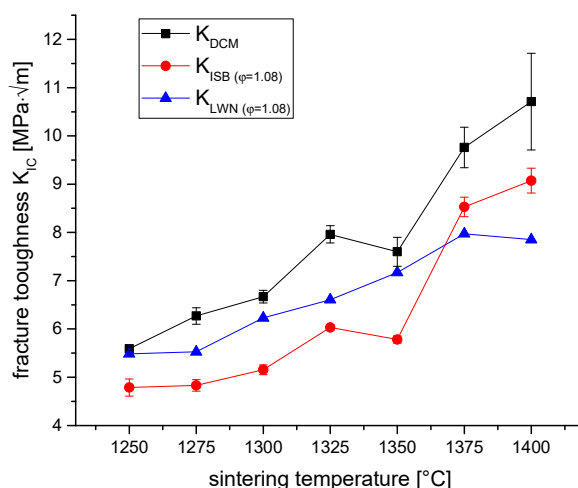


Figure 4. Fracture toughness K_{IC} of 1.5Y-2.2Ca-TZP sintered at different temperatures, determined by different methods.

3.3. Phase Composition and Transformation Characteristics

The phase composition determined on polished TZP samples sintered at different temperatures is shown in Figure 5. The monoclinic content rises from 1.3 vol.% to 5 vol.% between 1250 and 1400°C . This may – at least partly - originate from the sample preparation process. The cubic content decreases from 16 vol.% to 10 vol.% between 1250°C and 1275°C sintering temperature. Then the cubic content rises steadily to 16 vol.% at 1400°C . The high initial cubic content at 1250°C may be an artefact of the explosion synthesis process of the 3Y-TZP [35]. The progressive increase in cubic is in good accord with the rising influence of thermodynamics. Higher sintering temperatures favors the segregation of cubic phase. Accordingly, the tetragonal phase fraction has a maximum of 86 vol.% at 1275°C and declines towards higher sintering temperatures to 79 vol.% at 1400°C .

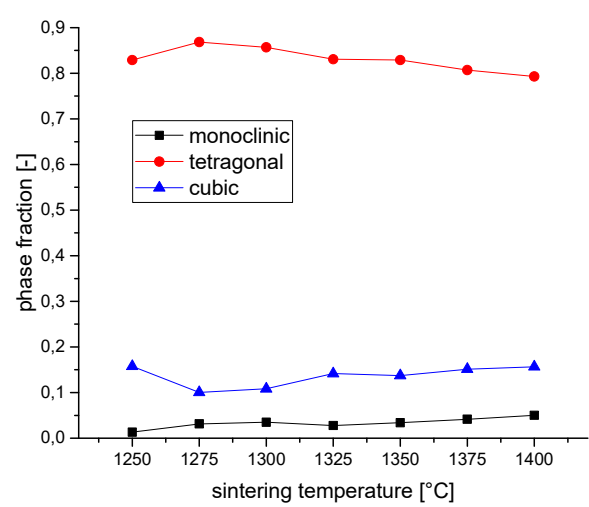


Figure 5. Phase composition of polished 1.5Y-2.2Ca-TZP TZP samples sintered at different temperatures.

Figure 6 plots the monoclinic contents in polished $V_{m, pol}$ and fractured surfaces $V_{m, F}$, the difference between both values is the transformability V_f . V_f increases from values of 30-35 vol.% at sintering temperatures of 1250–1325 °C to a value of 50 vol.% at 1375–1400°C. The higher fluctuations in the values of samples sintered at low temperature are related to the relatively rough and uneven fracture surfaces of these samples which have a high strength and moderate toughness. They show catastrophic failure and frequently multiple fractures. The tougher samples sintered at 1350 °C and higher did not exhibit multiple fractures and showed much smoother fracture surfaces which provides more reliable values.

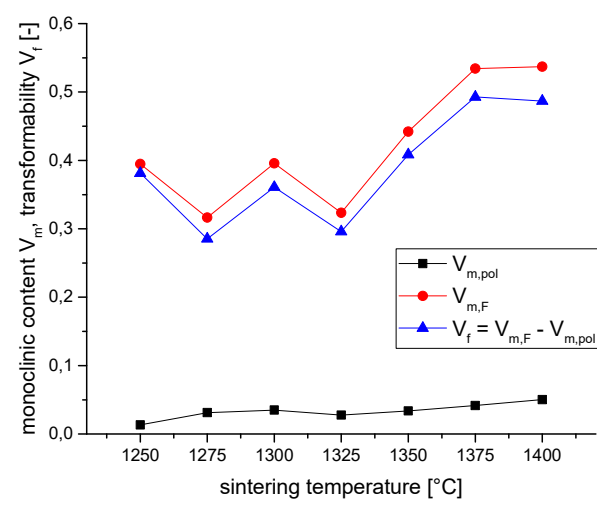


Figure 6. Monoclinic contents in polished ($V_{m, pol}$) and fractured surfaces ($V_{m, FF}$) of 1.5Y-2.2Ca-TZP samples sintered at different temperatures.

Figure 7 shows the transformation zone sizes h and the transformation toughness increments ΔK_{IC}^T calculated from the above XRD results. Note that the above-described fluctuations in monoclinic contents of fractured surfaces are transferred to values of h and ΔK_{IC}^T .

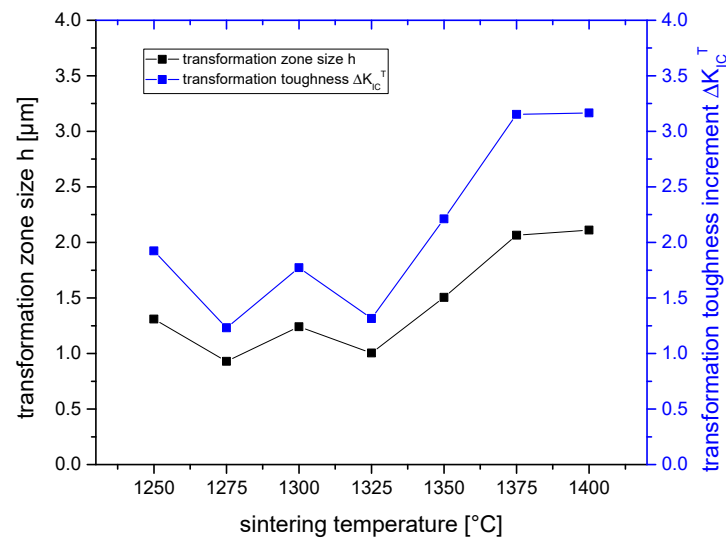


Figure 7. Calculated transformation zone sizes h and the transformation toughness increments ΔK_{IC}^T of 1.5Y-2.2Ca-TZP samples sintered at different temperatures.

The samples sintered at low temperatures (1250–1325 °C) show only moderate transformation zone sizes of 1–1.2 μm coupled with moderate transformability. Hence, a low transformation toughness increment ΔK_{IC}^T of 1.2–1.8 $\text{MPa}\sqrt{\text{m}}$ is calculated. The samples sintered at 1375 °C and 1400 °C show zone sizes of 2 μm and transformation toughness increments of 3.2 $\text{MPa}\sqrt{\text{m}}$. Assuming an intrinsic toughness K_0 of 4 $\text{MPa}\sqrt{\text{m}}$ [36] and no other toughening effects except TT we may assume that $K_{IC} = K_0 + \Delta K_{IC}^T$ [37]. The calculated toughness values are in the range between 5.3–7.2 $\text{MPa}\sqrt{\text{m}}$ and follow the same rising trend with sintering temperatures as the measured toughness values shown in Figure 4. The best match between measured and calculated toughness values is observed for K_{LWN} .

3.4. Low Temperature Degradation Resistance

The monoclinic contents of samples sintered at 1300 °C and 1350 °C after different treatment times at 134 °C in saturated water vapor in an autoclave are shown in figure 8a. The trends do not show the typical sigmoidal trend displayed in many publications on 3Y-TZP [33]. After an initial steep rise the monoclinic content tends to saturate. The LTD resistance of the material sintered at 1300 °C is considerably higher, here the monoclinic content after 100 h is only 20 vol.%. The sample was still intact. The sample sintered at 1350 °C showed a monoclinic content of > 60 vol.% at 100 h and was broken. Fig. 8b shows a MAJ plot of the collected data [38]. A linear regression over the whole range to determine the nucleation factor is not possible. The slope decreases with increasing ageing time which indicates a mechanistic change. The results show a strong similarity to the results obtained with explosion synthesized 3Y-TZP [23] which also showed a mechanistic change after 10 h of autoclave ageing. Comparing the data with existing results shows LTD stability between Ca-TZP (no ageing) [21] and detonation synthesized 3Y-TZP [33]. Interestingly the nucleation factor determined in this study which is approximate $n=1$ was also found for the detonation synthesized 3Y-TZP. $N=1$ means zero order growth, i.e. the layer thickness increases with a constant speed. This contradicts the typical nucleation and growth scenario depicted for Y-TZP (with $n=4$). The result is however in good accord with results published by Keuper et al. [13]. The rate constant $\ln b$, however, was about $\ln b = -4$ for 3Y-TZP [33] and is between -5.3 and -6 in the current study. This means the Y-Ca-TZP sintered at 1300 °C ages by a factor of ~7 slower than the 3Y-TZP sintered at 1400 °C. The fine grain size of the YCa-TZP is probably one of the main reasons for the enhanced LTD resistance.

According to Chevalier's interpretation [39] the LTD process is initiated by the transformation of isolated grains in the surface. The volume expansion of this first grains weakens the grain boundaries of the surrounding grains so that the penetration of the water into the bulk is facilitated and causes the growth of the transformed regions into the bulk. As the transformed region expands the stress on the surrounding grains constantly increases which leads to a high Avrami exponent n . In case of small grains (here: 200-220 nm, standard Y-TZP: 400-500 nm) the initial stress exerted by the first transformed grain is much lower (the stresses scale with R^3) and the growth of the transformed region is thereby impeded. Hence, an ultrafine initial grain size is favorable for high LTD resistance. The different grain boundary chemistry with a mixture of yttria and calcia at the grain boundary may also be of importance. Ca^{2+} (114 pm) has a much higher ionic radius than Y^{3+} (104 pm) and consequently tends to segregate more to the grain boundary. Stabilizer supersaturation at the grain boundary is known to be beneficial to LTD resistance.

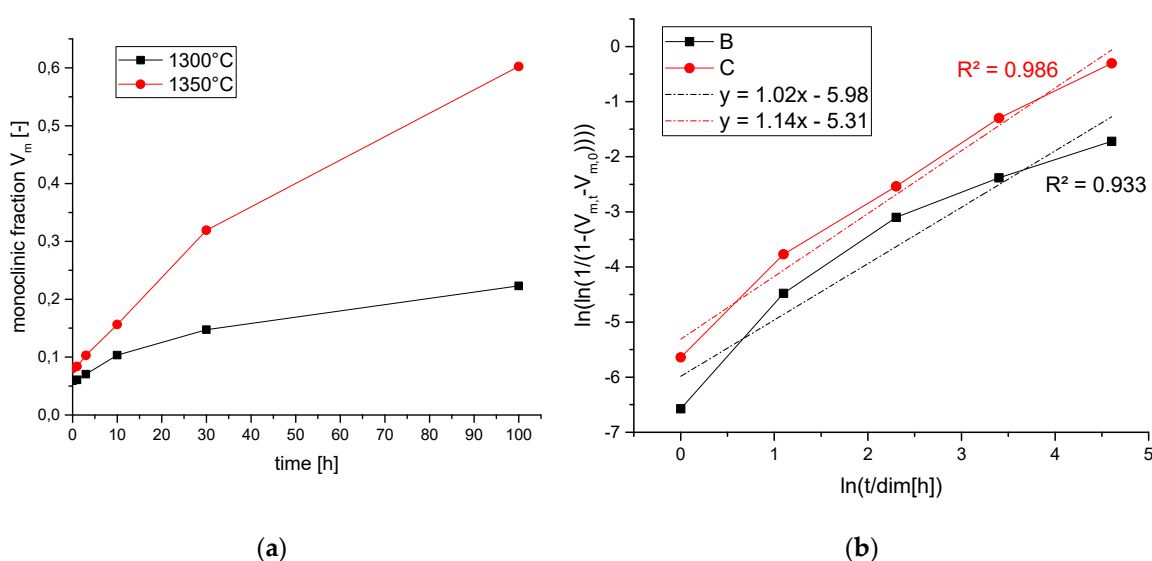


Figure 8. Low temperature degradation behavior in accelerated autoclave test at 134 °C. (a) Monoclinic fractions V_m of samples sintered at 1300 °C and 1350 °C at different ageing times in autoclave test at 134°C (b) MAJ-plot of data shown in Fig. 8a.

4. Discussion

The results from the study performed by mixing and milling Ca-TZP and Y-TZP to obtain a co-stabilized Ca-Y-TZP material shows that the concept can be applied. This simple procedure facilitates the manufacturing of such co-stabilized materials as commercially available Y-TZP and Ca-TZP powders can be used as raw materials. However, the range of possible compositions is somewhat limited as presently only one Ca-TZP powder is available and as the available Y-TZP compositions are mostly 2Y-TZP and 3Y-TZP powders.

The mechanical properties and ageing resistance of the mixed material are between the properties of 3Y-TZP and 4.4Ca-TZP. At low sintering temperature the material is strong and relatively brittle but very LTD resistant. At higher sintering temperature the toughness increases notably to a very attractive level above 7 MPa $\sqrt{m}$, however, at the expense of lower strength and LTD stability.

The phase analysis shows that the enhanced toughness at high sintering temperatures is resulting from a higher transformability. This higher transformability can be traced back to the increase in grain size but also to the segregation of cubic phase. The formation of cubic leads to a stabilizer depletion of the tetragonal phase and favors high toughness. However, this also seems to be the clue to the reduced LTD resistance at higher sintering temperature.

The analysis of microstructure shows a bimodal grain size distribution. As we may expect, the initial composition of separate Ca-TZP and Y-TZP grains does not equilibrate instantaneously. This is, however, the only apparent disadvantage in comparison to Y-Ca-TZP made from a single co-stabilized precursor.

We think that it will be worth trying different Y-Ca-TZP compositions by variation of the yttria stabilized zirconia starting powders (different BET-surface, different stabilizer content) and their fraction to learn more about this new co-stabilized TZP system. Eventually, if the 4.4Ca-TZP gets established other Ca-TZP powders with different stabilizer contents may become available. This would broaden the parameter space for elaboration of mixed stabilizer TZPs considerably.

5. Conclusions

Yttria-calcia co-stabilized-TZP materials combine excellent mechanical properties with good LTD resistance. The mixing and milling technology of commercially available starting powders provides easy access to standard compositions. The extremely fine but bimodal microstructure indicates inhomogeneous distribution of stabilizers at low sintering temperature and a progressive equilibration toward higher sintering temperatures. Strength and LTD resistance show an inverse correlation to fracture toughness. Low sintering temperatures favor strength and LTD resistance while high sintering temperatures provide higher fracture toughness. The LTD and mechanical properties of co-stabilized material lie in between the properties of 3Y-TZP and 4.4Ca-TZP. Y-Ca-TZP materials may be interesting alternatives to Y-TZP in biomedical applications such as dental implants.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

TZP	Tetragonal zirconia polycrystals
SEM	Scanning electron microscopy
MAJ	Mehl-Avrami-Johnson
SEM	Scanning electron microscopy
XRD	X-Ray diffraction
LTD	Low temperature degradation

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