Original Article

The effect of titania doping on structure and mechanical properties of calcia-stabilized zirconia ceramic

Andrey O. Zhigachev*, Vyacheslav V. Rodaev, Darya V. Zhigacheva

Research Center for Nanotechnology, Tambov State University, Tambov, The Tambov Region, Russia

ARTICLE INFO

Article history:
Received 11 June 2019
Accepted 1 October 2019
Available online 28 October 2019

Keywords:
Zirconia
TZP
Titania
Dopant
Mechanical properties

ABSTRACT

The effect of titania doping on density, phase composition, and mechanical properties of calcia-stabilized tetragonal zirconia ceramics (Ca-TZP) was investigated. The samples were prepared via milling, spray drying and consequent uniaxial pressing of the powders of the chosen composition. The concentrations of titania of up 1 mol% were investigated. Addition of titania moderately improved relative density of the sintered ceramics from 98.2% in titania-free material to 99.3% in 0.5 mol% titania ceramic. Introduction of titania resulted in increase of transformability of tetragonal zirconia phase deduced from the change of lattice parameters and content of monoclinic zirconia phase on fracture surfaces. It was revealed that hardness of titania-doped Ca-TZP decreased from 12.2 GPa in undoped ceramic to 11.3 GPa in material with 0.75 mol% titania. Fracture toughness, on the contrary, demonstrated a clear extremum of 9.1 MPa·m$^{0.5}$ in 0.5–0.65 mol% titania range as compared to ~5 MPa·m$^{0.5}$ in undoped Ca-TZP.

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1. Introduction

Ceramics and composites based on zirconia are among the most promising engineering materials. It is due to an advantageous combination of their hardness, fracture toughness and flexural strength along with resistance to thermal shock, chemical inertness, and biocompatibility [1–4]. These properties allow zirconia ceramics to be used in a number of industries, including restorative medicine (dentistry and orthopedics); chemical industry and in ore processing as milling media; they can also be used for heavy-duty parts in various applications [3].

Remarkably high fracture toughness of zirconia ceramics is achieved by transformation toughening mechanism present in the material. Transformation toughening of zirconia ceramics has been first reported by Garvie et al. [5]. The mechanism consists in suppression of crack propagation by phase transformation of tetragonal zirconia phase (t-ZrO$_2$) to monoclinic phase (m-ZrO$_2$). The transformation is triggered by the stress...
field of the propagating crack. It is accompanied by increase in material volume by 3-5%, resulting in local dilatational and shear stress. The stress hinders the crack propagation or even stops it and, thus, increases toughness of the material [6].

Pure ZrO₂ exhibits no transformation toughening at room temperature since t-ZrO₂ in pure zirconia is only stable at temperatures above 1170 °C [2]. Tetragonal phase can be retained in metastable state at room temperature by addition of various oxides, often referred to as “stabilizers”. The most frequently used t-ZrO₂ stabilizers are MgO [1,2], Y₂O₃ [7-9], CeO₂ [10-12], and CaO [13-15].

The properties of zirconia ceramics stabilized in tetragonal phase depend greatly on their density (or porosity) and grain size. In order to reach high density of sintered ceramics, one often employs sintering additives, lowering porosity and improving mechanical properties of the material [3]. For sintering of zirconia ceramics numerous sintering aids may be used. Among the most frequently mentioned in the literature aids are alumina [16,17], iron oxide [18,19], niobia [20,21], and titania [22-24].

The effect of titania on density, phase composition and microstructure [23] has mostly been studied for zirconia ceramics with traditional stabilizers, such as yttria and ceria. It has been shown, for example, that addition of 10% titania to 8YSZ had little effect on hardness but significantly improved its fracture toughness. However, the effect of titania as a sintering aid, to our knowledge, has not been reported for Ca-TZP ceramics. Ca-TZPs may have properties like those of ceramics stabilized with yttria or ceria [25,26], while having an economical advantage because of much higher availability of calcia.

In the present research we consider the effect of titania as a sintering additive on microstructure, phase composition and mechanical properties of Ca-TZP ceramic.

2. Methods

Samples of Ca-TZP ceramics doped with titania were prepared from reagent grade m-ZrO₂ powder (Sigma-Aldrich, USA), reagent grade calcia (Reachem, Russia) serving as a stabilizer and 99.5% pure titania (Reachem, Russia). All the starting powders had average particle size below 200 nm as was claimed by the manufacturers.

All prepared samples contained 8.4 mol% of calcia. The CaO concentration was chosen according to previously reported results for Ca-TZPs [15]. Zirconia stabilized with 8.4 mol% calcia contained about 95% of t-ZrO₂. Although ceramics with the chosen concentration did not exhibit the best combination of hardness and fracture toughness, [15], it was still chosen to account for possible chemical interactions between calcia and titania [27], which could reduce amount of calcia acting as stabilizer in titania-doped Ca-TZPs. It should be noted that though titania is also known to act as a stabilizer of tetragonal zirconia, its stabilizing effect is negligible as compared to that of calcia. For example, in [28] it was shown that even zirconia with 20 mol% titania transformed to monoclinic phase. For this reason, we assumed that addition of minor amounts of titania would not notably increase stability of t-ZrO₂ by formation of ZrO₂-TiO₂ solution.

Choice of titania content was based on preliminary experiments which have shown that addition of more than 1 mol% of titania led to complete transformation of t-ZrO₂ to m-ZrO₂. Such ceramics have poor mechanical properties and are of little interest for research. For this reason, we have investigated titania contents in the 0–1 mol% range. We have used titania molar contents of 0, 0.1, 0.25, 0.35, 0.5, 0.65, 0.75, and 1% to observe changes in phase composition, structure and mechanical properties with rising titania content. The samples were labeled TX, where T is TiO₂ content expressed in hundreds of percent, e.g. T65 stands for the sample with 0.65 mol% titania added.

Zirconia, calcia and titania were milled and mixed in a Netzsch MiniCer (Netzsch, Germany) ball mill for 5 h to ensure homogeneous distribution of the components. For this purpose the appropriate amounts of dry powders of the components were mixed with distilled water to obtain suspension with 10 wt% solid content. Dolapix CE64 as a dispersant (0.1 wt%) was added to the mixture to prevent agglomeration of the particles during milling. Since Dolapix CE 64 is ammonium salt of organic acid it introduced no additional impurities to sintered ceramics. Milling was carried out with 0.4 mm zirconia balls. Milling media was weighed prior to and after milling. The change in the mass of media was negligible as compared to the mass of the milled solid fraction. Average zirconia crystallite size after milling was about 20–30 nm; estimates were made by SEM observations and by analysis of X-ray diffraction peaks broadening.

The milled suspensions were then spray dried in a YC-015 machine (Shanghai Pilotech Instrument Equipment Co, China) to avoid agglomeration of the powder particles. The powders contained no detectable amount of residual water as was confirmed by thermogravimetric analysis. The dried powders were uniaxially pressed at 50 MPa in a steel die to green pellets with the diameter of 10 mm and the height of 2 mm. Polyethylene glycol 1500 was used as a binder, and glycerol was used as a plasticizer.

We sintered green ceramics using two-stage sintering process [29]. The samples were first heated to 1300 °C, held at this temperature for 5 min, cooled to 1200 °C and soaked at 1200 °C for 4 h. After soaking the samples were cooled to room temperatures. Heating and cooling rates during heat treatment were controlled to be 4 °C/min, so that not to cause significant thermal gradients and microcracking of the ceramic. Sintered samples were dense pellets with no visible defects, such as cracking or laminations, except for T100 ceramic, which had extensive network of cracks through the sample. Apparent density of the sintered samples was measured by the Archimedes method in distilled water. Theoretical densities of the samples were calculated according to mixture rule. Relative density was found as ratio of apparent and theoretical densities.

Phase composition of the sintered samples was investigated using X-ray diffraction (XRD) with D2 Phase diffractometer (Bruker AXS, Germany). Diffraction patterns were taken in Bragg-Brentano geometry in 10–30 2θ degrees range. The patterns were assigned using PDF-2 Diffraction Database File compiled by the International Centre for Diffraction Data. Molar fractions of various crystallographic phases were calculated using Rietveld refinement procedure in TOPAS software.
Microstructure of the sintered samples was investigated with scanning electron microscopy (SEM) with a Merlin (Carl Zeiss, Germany) microscope. Images were taken on both as-made fracture surfaces and on polished and thermally etched surfaces. Grain size was estimated from the latter images by line intercept method. An energy-dispersive X-ray spectrometer (EDS) INCA Energy 350X-Max 80 Coupled with SEM and INCA software (Oxford instruments, UK) were used to assess homogeneity of the elements distribution.

Flexural strength of the samples was measured using biaxial bending test. For the test we used ten disks with a thickness of 1.5 ± 0.1 mm and a diameter of 8 mm. Three hardened steel balls with a diameter of 2 mm were used a specimen support. The load was applied with a flat steel punch with a 1 mm wide tip.

Hardness and fracture toughness of the sintered samples were measured using indentation technique. Surfaces of the samples were polished prior to the measurements and were carefully washed with distilled water to remove any contaminants left after the polishing procedure. Hardness was measured by Vickers indentation with 50 N load on Duramin A300 (Struers, Denmark). Values presented in the paper were averaged over 3 samples, 3 indentations on each.

Fracture toughness was calculated from lengths of radial cracks starting at the indents corners made by Vickers indentation with loads of 50–200 N. These loads were high enough for adequate cracks formation. The equation by Anstis [30] was used:

$$K_C = 0.016 \left( \frac{E}{H} \right)^{0.5} \frac{P}{C^{1.5}}$$

where $H$ is Vickers hardness, $E$ is Young’s modulus, $P$ is indentation load and $C$ stands for crack length from the center of the indent. Young’s modulus measurements were performed on a G200 nanoindenter (MTS Nano Instruments, USA). Its values for samples in question were in 210–220 GPa range. Cracks lengths were measured with Axio Observer.A1m (Carl Zeiss, Germany) optical microscope.

3. Results

The sintered samples were dense pellets without visible defects, except T100 pellets, which had numerous cracks and could be fractured by hand. Relative density of the samples T0–T75 was above 98%. It gradually increased from 98.3% for T0 sample to a maximum of 99.2% for T50 and slightly decreased to 98.5% for T75. It was difficult to carry out reliable measurements on T100 samples because of the extensive cracking and, consequently, because of air bubble that could remain in the cracks and falsify the measurements. Data on density of the samples is summarized in Table 1.

SEM images confirmed that the sintered ceramics had low porosity as shown in Fig. 1 for some of the studied titania concentrations. The images not only show low porosity of the material but also demonstrate that fine grain structure is preserved in nearly fully densified material. Calculations carried out on the SEM images of polished surfaces (not given in the paper) showed perceptible difference in average grain size between ceramics with different titania contents. In T0 ceramic the average grain size was $78 \pm 2$ nm, addition of titania lead to increase in grain size to, for example, $87 \pm 3$ nm in T50 sample and, finally, to $105 \pm 4$ nm in T100 ceramics. Interestingly, spread of grain sizes distribution increased with growing titania concentrations, that is in T100 both fine (much

![Fig. 1 - Typical SEM images of polished and thermally etched surfaces of titania-doped Ca-TZPs.](image)

Table 1 - Relative densities of the sintered samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative density, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>98.3 ± 0.2</td>
</tr>
<tr>
<td>T10</td>
<td>98.5 ± 0.3</td>
</tr>
<tr>
<td>T25</td>
<td>98.6 ± 0.2</td>
</tr>
<tr>
<td>T35</td>
<td>98.9 ± 0.2</td>
</tr>
<tr>
<td>T50</td>
<td>99.2 ± 0.2</td>
</tr>
<tr>
<td>T65</td>
<td>99.1 ± 0.2</td>
</tr>
<tr>
<td>T75</td>
<td>98.5 ± 0.3</td>
</tr>
<tr>
<td>T100</td>
<td>N/A</td>
</tr>
</tbody>
</table>
less than the average grain size) grains were present alongside with grains as large as 200 nm.

EDS analysis of fracture surfaces of the sintered samples has clearly shown that the samples were chemically homogeneous, i.e. no local clusters of Zr, Ca or Ti were observed. Furthermore, EDS measurements have not discovered notable presence of any other chemical elements other than Zr, Ca, Ti or O. Such homogeneity was observed at different fields of view ranging from 3 μm to 3 mm.

Fig. 2 illustrates chemical homogeneity of the studied samples through the example of T50 sample. It shows SEM image of T50 coupled with EDS maps for the key elements: Zr, Ti, and Ca. The distribution of these elements is homogeneous on the chosen scale. Similar maps were obtained for other studied samples: the observed distribution was similar to the one presented in Fig. 2. Attempts to make EDS mapping on higher magnifications did not improve spatial resolution of the mapping because of the intrinsic limitations of the EDS method. EDS mapping showed that the samples did not contain detectable amounts of impurities.

Fig. 3 shows typical XRD patterns registered on some of the sintered samples. It can be seen from the patterns that sintered ceramics with titania content from 0% to 0.75% were composed of tetragonal (PDF 01-072-7115) and cubic (c-ZrO₂) zirconia (PDF 00-049-1642) phases and contained only trace amounts of m-ZrO₂ (PDF 00-037-1484) as can be deduced from strong t-ZrO₂ and c-ZrO₂ overlapping peaks observed at 30.5° and in 34–36° range. The XRD pattern of T100 sample have additional peaks, which correspond to m-ZrO₂ phase. The most intensive of these peaks are marked with black circles. Therefore, T100 sample contained considerable amounts of m-ZrO₂. XRD patterns of all the studied samples had no visible peaks that could be attributed to titania-containing phases such as calcium titanates (CaTiO₃, PDF 01-075-2099; CaTi₂O₅, PDF 00-025-1450; CaTi₃O₈, PDF 00-026-0333) or zirconium titanates (ZrTiO₄, PDF 01-080-1783; Zr₁Ti₂O₂₄, PDF 01-084-1019). It can be concluded that these phases do not appear in the studied materials, at least in crystalline form.

![Fig. 2 – EDS mapping of T50 sample. Only maps for Zr, Ti and Ca are shown.](image)

![Fig. 3 – XRD patterns of the sintered ceramic samples. Dark circles indicate positions of the most intensive m-ZrO₂ reflections.](image)

### Table 2 – Phase composition of sintered titania-doped Ca-TZPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>m-ZrO₂ mol%</th>
<th>t-ZrO₂ mol%</th>
<th>c-ZrO₂ mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>≤2</td>
<td>91 ± 2</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>T10</td>
<td>≤2</td>
<td>91 ± 2</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>T25</td>
<td>≤2</td>
<td>90 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>T35</td>
<td>≤2</td>
<td>91 ± 2</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>T50</td>
<td>≤1</td>
<td>92 ± 2</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>T65</td>
<td>≤1</td>
<td>93 ± 2</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>T75</td>
<td>3 ± 2</td>
<td>94 ± 2</td>
<td>3 ± 2</td>
</tr>
<tr>
<td>T100</td>
<td>48 ± 2</td>
<td>47 ± 2</td>
<td>5 ± 2</td>
</tr>
</tbody>
</table>

Amounts of t-ZrO₂, m-ZrO₂ and c-ZrO₂ are presented in Table 2. Content of c-ZrO₂ remained at roughly the same level at all the studied concentrations. Monoclinic phase was present in negligible amounts in all samples except T100.
where its content was as high as 48%. The t-ZrO₂ content went beyond 90% for T0-T75 samples, whereas in T100 it was about 50%.

The positions of t-ZrO₂ peaks in the XRD patterns were used to calculate degree of tetragonality (ratio of c to \(\sqrt{2}a\), where c and a are lattice parameters) of t-ZrO₂, which can serve as a reliable indication of transformability of t-ZrO₂ [30]. The ratio grew slightly with increasing titania concentration from 1.0198 for T0 to 1.0207 for T75. This change hints at higher t-ZrO₂ transformability in titania-doped samples as compared to undoped ceramics.

In addition, content of m-ZrO₂ on fresh fracture surfaces of all samples except for T100 was calculated. It was difficult to measure content of m-ZrO₂ for the latter due to extensive cracking of the sample and, consequently, problems with preparation of flat fracture surfaces for reliable XRD measurements. For all samples area of x-ray spot on the fracture surface (2 × 12 mm) was slightly larger than cross-section of pellet (about 1.8 × 8 mm). This discrepancy was accounted for during Rietveld analysis in TOPAS software. Fig. 4 shows XRD patterns (a) and fracture surface m-ZrO₂ content (b) as a function of titania concentration. It can be seen from Fig. 4a that intensities of m-ZrO₂ peaks (marked with vertical lines) increase with rising titania content. Fig. 4b shows that m-ZrO₂ content grows steadily from sample T0 to T75, clearly correlating with change in titania content and with the mentioned above growth of the degree of tetragonality.

Mechanical properties of the studied samples are summarized in Fig. 5, where data on Vickers hardness, fracture toughness and flexural strength are presented. Hardness slowly decreases from 12.2 GPa in undoped samples to 11.3 GPa in T75 ceramics and then falls abruptly to about 8.5 GPa in T100 sample. The sudden drop in hardness value of T100 sample is clearly associated with the tetragonal to monoclinic transformaton upon cooling and with the accompanying extensive cracking of the material.

Fracture toughness changes non-monotonically from a minimum of 5.1 MPa m\(^{0.5}\) in T0 to a maximum of slightly above 9 MPa m\(^{0.5}\) in T50-T65 materials. Further increase in titania content leads to an opposite effect, namely fracture toughness drops to ~8 MPa m\(^{0.5}\) in T75. We were unable to carry out reliable fracture toughness measurements on T100 samples because of severe cracking of the sample surface, and it was difficult to find a suitable surface region. In addition, irregular cracks patterns were formed upon indentations, instead of straight radical cracks exiting indentations corners as required by Anstis method [30]. It may be safely assumed that fracture toughness value for T100 is significantly below those obtained for T0-T75 samples, because of such factors as extensive cracking reducing structural integrity of the material, and low content of t-ZrO₂, and thus low input from transformation toughening.

Flexural strength also changes non-monotonically. The strength is 630 ± 25 MPa in undoped samples; it increases to 730 ± 20 MPa in T35 composition and falls with further rise in titania concentration. So, in T65 flexural strength is 679 ± 24 MPa, and in T75 it is even lower – 542 ± 37 MPa. We were not able to measure strength of T100 samples because of the extensive cracking of the samples, likely caused by tetragonal to monoclinic transformation (see Table 2).

4. Discussion

As mentioned earlier, the effect of titania addition on density of the sintered samples is negligible, although titania is known as an efficient sintering aid [22-24] for zirconia ceramics. Low efficiency of titania in the present study may be explained by low sintering temperatures of 1200–1300 °C of Ca-TZP as compared to those reported for titania-doped Y-TZP and alumina ceramics (1400–1500 °C) [23]. Titania with its melting point of 1843 °C cannot facilitate sintering at 1200–1300 °C because viscous flow sintering mechanism, by which titania usually works, requires higher temperatures. Additionally, low efficiency of titania as a sintering aid in the present study may be attributed to rather high densification achieved in the titania-free sample (relative density was 98.3%). The residual porosity in this case is mainly associated with large defects resulting from the pellet formation stage; these defects cannot be removed by usage of sintering aids.

However, some of the porosity was, indeed, removed in the present study by using titania, for example T50 samples had relative apparent density of 99.2%. This increase in density is likely due to removal of minor pores at multiple grain junctions at the final stage of the sintering [32]. Furthermore, slight increase in the average grain size from 87 to 105 nm with rising titania content under unchanged heat treatment conditions is a clear indication of enhanced heat treatment conditions, caused by addition of titania.
Introduction of titania resulted in certain changes in phase composition of the sintered ceramics as depicted in Fig. 3 and Table 2. The most obvious change consists in appearance of nearly 50% of m-ZrO\textsubscript{2} in T100 sample. Such behavior of phase compositions can be explained by chemical interaction between calcia, serving as stabilizer, and titania. This interaction may result in reduction of amount of calcia available for stabilization of t-ZrO\textsubscript{2} and c-ZrO\textsubscript{2}, and eventually to spontaneous t-ZrO\textsubscript{2} to m-ZrO\textsubscript{2} transition as observed in T100 composition.

Decrease in calcia concentration in zirconia-based solid solution, i.e. weaker stabilization of tetragonal phase is proved by change in the degree of tetragonality in samples with different titania contents. It is known that the lower stabilizer content in zirconia matrix is, the higher is its degree of tetragonality \cite{31}. In other words, the observed increase in degree of tetragonality indicates lower calcia content in t-ZrO\textsubscript{2} crystals. Further proof of removal of calcia from zirconia matrix either prior to sintering or after it by reaction between calcia and titania consists in increase of m-ZrO\textsubscript{2} fracture surface content. This phenomenon directly indicates higher transformability of t-ZrO\textsubscript{2}, resulting from lower calcia content in t-ZrO\textsubscript{2}. It cannot be a result of titania dissolution in zirconia matrix, since though titania solubility in zirconia at 1300 °C is rather high \cite{33,34} the solid solution tends to decompose into zirconia and zirconium titanate, i.e. the solid solution is not stable at room temperature.

Indeed, reaction between calcia and titania may result in formation of calcium titanates of various compositions, depending on local amounts of calcia and titania; and if zirconia also participates in reaction, complex ternary phases may appear \cite{33}. However, XRD patterns, presented in Fig. 3, display no new peaks that could be assigned to these new phases. Absence of these new peaks can be explained in two ways. The first possible reason is that low content of the new phases is below XRD pattern analysis software recognition threshold. The other possible reason is formation of thin amorphous layer of these new phases on boundaries between zirconia grains. The hypothesis is indirectly supported by the fact that EDS analysis of the specimens (Fig. 2) did not discover any areas of anomalously high Zr, Ti or Ca contents. If the new phases formed any large inclusions in the material, the latter would be detected by EDS mapping as a chemical composition inhomogeneity. Similar situation was observed in a previously reported study \cite{35}, where silica-doping of 3Y-TZP medical grade zirconia resulted in formation of thin amorphous layer on grains surface.

Changes in phase composition had an impact on mechanical properties as shown in Fig. 5. It should be noted that hardness drops with rising titania content despite the observed increase in density of the material. The discrepancy, presumably, might be associated with formation of new phases with hardness lower than that of zirconia matrix. For example, one of the possibly appearing phases is calcium titanate with hardness of only 5 GPa \cite{36}, well below 12 GPa of stabilized zirconia (T0 sample). Another phase that could appear, ZrTiO\textsubscript{4}, also has low hardness of 8 GPa \cite{37} as compared to zirconia. Sudden drop in hardness at 1 mol% of titania is, indeed, associated with extensive cracking of the material caused by spontaneous tetragonal to monoclinic transformation (Fig. 3).

Non-monotonic behavior of fracture toughness can be explained in terms of varying transformability of t-ZrO\textsubscript{2}. At low titania contents phase transformability is low, so high internal stresses are required to trigger t-ZrO\textsubscript{2} to m-ZrO\textsubscript{2} transformation. If these stresses are higher than the ones generated by the tip of the propagating crack, then transformation toughening mechanism does not work and does not improve toughness of the material. With rising titania content, so does transformability of t-ZrO\textsubscript{2} and the transformation is triggered at lower stresses. Under these conditions transformation toughening works and materials with the highest values of fracture toughness (9.2 MPa m\textasciicircum{0.5}) are obtained.
Flexural strength rises initially presumably due to higher density of the samples and, consequently, smaller flaw size. It reaches maximum while fracture toughness is still increasing and drops when fracture toughness reaches its maximum. It is a well known limitation of transformation-toughened materials, described in details in [38]. Further drop in strength is indeed caused by appearance of m-ZrO₂ and accompanying cracking of the material.

Further addition of titania reduces stability of t-ZrO₂ even greater, so transformation in the field of the initial propagating crack triggers transformation in the adjacent areas not subjected directly to the stress field of the crack. These areas have no way to relieve resulting stresses, except by cracking. At these titania concentrations material fracture toughness declines. Finally, at 1 mol% of titania considerable amounts of m-ZrO₂ appear in the material upon cooling from sintering temperature as noted earlier. These samples exhibit extensive cracking even prior to stress application and indeed have low fracture toughness.

5. Conclusions

The introduction of titania as a sintering aid to calcia-stabilized tetragonal zirconia ceramics sintered at 1200–1300 °C had some effect on the relative density of the sintered samples: slight density improvement from 98.3% in titania-free sample to 99.2% in ceramic with 0.5 mol% titania added was detected. Additionally, a slight increase in the average grain size from 78 nm in titania-free ceramic to 96 nm in 1 mol% doped material was observed.

Furthermore, the introduction of titania had a significant effect on phase composition of the material. While addition of up to 0.75 mol% titania only slightly increased content of t-ZrO₂ correspondingly decreasing the c-ZrO₂ content, doping with 1 mol% titania resulted in spontaneous tetragonal to monoclinic transformation of zirconia and extensive cracking of the material. It was suggested that such behavior was a consequence of chemical reaction between calcia and titania causing lower stability of t-ZrO₂. The reaction has not been proven conclusively but was strongly hinted at by increase in degree of tetragonality of t-ZrO₂, which could only result from lower calcia content in zirconia solid solution, and by higher m-ZrO₂ fracture surface in titania-doped samples as compared to titania-free material.

Change in the phase composition of the studied materials was accompanied with the change in their hardness and fracture toughness. Hardness almost monotonically decreased from 12.2 GPa in undoped samples to 11.3 GPa in 0.75 mol% titania doped ceramic and to even lower value of 8.5 GPa in 1 mol% titania sample. Fracture toughness changed non-monotonically with variation in titania content: starting from rather low value of 5.1 MPa·m⁰.⁵ in undoped material, it reached maximum of slightly above 9 MPa·m⁰.⁵ in 0.5–0.65 mol% titania range and then dropped at higher titania contents. The observed change in mechanical properties of the material was explained in the paper in terms of presumed formation of new phases and change in transformability of t-ZrO₂.

Authors declaration

The authors declare that there are no potential conflicts of interest associated with the manuscript.

Acknowledgements

The research was supported by the Ministry of Education and Science of the Russian Federation (project no. 16.2100.2017/4.6). The authors thank Alexey Umrikhin for his assistance in preparation of the samples for mechanical properties measurements.

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