

HYDROTHERMAL AGEING OF TETRAGONAL ZIRCONIA CERAMICS

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The effect of hydrothermal treatment on the phase stability, microstructure and mechanical properties of tetragonal zirconia ceramics stabilized with 3 mol% yttria was studied. At temperatures of 140-260°C the tetragonal phase transformed into monoclinic zirconia. The degree of transformation increased with increasing temperature and time of ageing. Changes in the microstructure and mechanical properties were observed for the samples used at temperatures of 180°C and higher. The thickness of transformed layer increased with increasing temperature and at 260°C it reached a thickness of 170 µm after 10 hours. The changes in mechanical properties (hardness and fracture toughness) corresponded to the structural changes in the material caused by hydrothermal ageing. Temperatures of 180°C and higher were critical for the mechanical and structural properties of the material.

INTRODUCTION

Due to their mechanical properties, materials based on yttria stabilized tetragonal zirconia (t-ZrO₂) stand out among ceramic materials. However, they are known to be sensitive to their surrounding environment, whose action can lead to changes in these properties. It is in particular the aqueous medium, the water vapour medium [1] or the medium of other liquids [2-6] that cause (at relatively low temperatures from 65°C) a degradation of material, the reason is the transformation of metastable t-ZrO₂ into the monoclinic phase (m-ZrO₂). Several possible mechanisms have been proposed by which the transformation may proceed [1]. Regardless of the type of mechanism, the following facts are characteristic of the transformation:

- the degradation process is most intensive at a temperature of 200-300°C [1, 7],
- the transformation is accompanied by the appearance of micro- and macro-cracks formed along the grain boundaries [1],
- the transformation proceeds from grain boundaries to the grain centre, from the surface of specimen into the inside, with the degradation depth growing with the time of ageing [8],
- smaller grain size and higher stabilizer content retard the transformation [9-12].

Three basic mechanisms of t-ZrO₂ transformation in aqueous medium have been presented, which are based on the above facts. The first one, the *corrosion*

mechanism, is based on the interaction of water and zirconia and leads to formation of Zr-OH bonds. The stress appears at points of these bonds and contributes, simultaneously with the motion of OH⁻ ions in the lattice (by occupying the oxygen vacancies), to the nucleation of the monoclinic phase and thus to the appearance of micro- and macro-cracks. The second mechanism, the *destabilization mechanism*, is based on the reaction of OH⁻ ions with yttria, leading to the formation of Y(OH)₃ or Y(O)OH. Reducing the content of yttrium leads to the destabilization of t-ZrO₂ and to the formation of the monoclinic phase. The third mechanism is the *stress-induced transformation*. The stress caused by water vapour acting on ceramic grains on the material surface has been referred to as thermal expansion anisotropic stress. An accompanying phenomenon is the formation of Y(OH)₃ as the consequence of water diffusing through the material. Due to volume changes the transformed grains cause microcracks and the material becomes degraded [13].

As mentioned above, the properties of the material (grain size, stabilizer content, etc.) affect significantly the process of degradation. It is possible to affect by these factors the free energy of phase transformation ($\Delta G_{t \rightarrow m}$) and thus to control the transformation. For a given material to be stable in the tetragonal phase it must hold that $\Delta G_{t \rightarrow m} > 0$. Usually, all the free energy components (chemical, surface and stress energy components) are negative during the transformation. The value of the free energy change can be increased by

adding a stabilizing oxide (which apart from the most widely used Y₂O₃ can be, for example, CeO₂ [14], MgO or CaO [15, 16]) or also by dispersion the second phase in zirconia. It has been established that adding 5-10 wt.% of Al₂O₃ reduce the volume of phase changes associated with phase transformation [7, 17]. Another possibility for increasing ΔG_{t→m} is to reduce the grain size, e.g. by adding sintering additives that reduce the sintering temperature [1].

Via the above modifications of the material it is possible to prepare ceramics of an optimum grain size and phase composition that minimizes transformation and thus reduces degradation caused by the action of an OH- containing environment.

TZ-3YSB-E zirconia ceramic (Tosoh, Japan) used in the present study is a material, whose composition (zirconia + 3 mol.% yttria + 0.25 wt.% alumina) offers optimum properties for application in biomedicine. The manufacturer claims that the grain size of TZ-3YSB-E ceramics sintered at 1350°C is below 0.3 μm, and after interaction with water vapour at 140°C/20 h less than 3% of t-ZrO₂ transform into m-ZrO₂ [18]. This is 20 times less than in the case of the same material without alumina addition [9]. The aim of the present work is to describe the effect of hydrothermal ageing on ceramics prepared from the Tosoh powder in the temperature range from 140 to 260°C and, for various times from 5-20 h to establish the change in mechanical properties.

EXPERIMENTAL

TZ-3YSB-E (Tosoh) powder was formed by cold isostatic pressing into the shape of a cylinder. The disks of 37 mm in diameter and 2 mm in thickness were prepared by machining the outer diameter and dividing of the cylinder. The specimens were then dried, annealed at 700°C and subsequently sintered at 1530°C.

The specimens were aged in a hydrothermal reactor at 140°C for 5, 10, 15 and 20 h, or at 180°C, 220°C and 260°C for 10 h. The specimen in the reactor was held in a teflon vessel in distilled water. The reactor was heated

under normal pressure from an initial temperature of 25°C to the reaction temperature. After the reaction it was naturally cooled. After the test the specimen was washed in distilled water, dried and analysed. Experimental conditions are given in table 1.

The phase composition of the surface of specimens before and after hydrothermal ageing was determined using by X-ray diffraction analysis on an X'pert diffractometer (Philips, the Netherlands). The mass ratio of analysed phases was calculated by means of Rietveld analysis.

The microstructure of a cross-section specimen was analysed by scanning electron microscopy (SEM) using an XL 30 microscope (Philips, the Netherlands). The specimens for analysis were ground, polished and thermally etched at 1400°C for a period of 10 min. The chemical composition of the specimen cross-section (determination of yttrium content) was determined by means of energy dispersive spectroscopy (EDS) microprobe attached to the electron microscope.

The micro-hardness of specimens was established with an M-400 Vickers micro-hardness tester (Leco, USA) on cross-sections of the specimens. To study the hardness of surface films the micro-hardness tester indentations were placed in the specimen cross-section on a line perpendicular to the disk surface. The spacing of indentation centers was 25 μm. The loading force was 0.98 N. The hardness and fracture toughness of specimens were determined with the aid of Vickers hardness tester 2Rc (Amsler, Germany) - in keeping with CSN EN ISO 6507-1 Standard and JIS R 1607 Standard. To study the effect of indentation depth, indentations were performed by a force of 9.8 N - 196 N acting on the disk surface.

From geometry of Vickers hardness tester tip and from the diagonal size of the hardness imprint 2.a to the material we were able to calculate the penetration depth *h* of hardness tester tip according to the relation:

$$h = a \cdot \frac{\cos 45^\circ}{\operatorname{tg} \frac{\alpha}{2}} \quad (1)$$

where α is angle of Vickers hardness tester tip.

Table 1. Hydrothermal conditions of tests of zirconia ceramic.

specimen	hydrothermal conditions	
	temperature (°C)	time (hours)
reference	-----	-----
1	140	5
2	140	10
3	140	15
4	140	20
5	180	10
6	220	10
7	260	10

Table 2. Results of surface quantitative phase X-ray analysis and cross-section SEM analysis of hydrothermally aged zirconia ceramics.

specimen	conditions	m-ZrO ₂	layer thickness
reference	-----	0 wt.%	-----
1	140°C/5h	6.9 wt.%	-----
2	140°C/10h	11.7 wt.%	-----
3	140°C/15h	19.5 wt.%	-----
4	140°C/20h	21.4 wt.%	-----
5	180°C/10h	54.3 wt.%	15 μm
6	220°C/10h	not established	150 μm
7	260°C/10h	61.9 wt.%	170 μm

RESULTS AND DISCUSSION

Phase composition and microstructure

Table 2 summarizes the results of X-ray phase analysis of the surface of zirconia disk and the thickness of transformed layer as established on the cross-section specimens using the SEM. The reference specimen contained on its surface only t-ZrO₂. In all the specimens tested, X-ray analysis revealed tetragonal zirconia and the transformation-produced monoclinic phase (see figure 1), in different ratios. As can be seen from the results of tests performed at 140°C, the amount of transformed phase increased with increasing time of hydrothermal action (see table 2). In comparison with the data provided by the manufacturer of the powder used (TZ-3YSB-E Tosoh) the amount of transformed phase at 140°C/20 h is ca 7 times higher than for the same material sintered at a lower temperature (1350°C) [17]. Evidently, this is due to the larger grain size of our specimen sintered at 1530°C (0.5-1 µm, see figure 2) compared with ceramics sintered at 1350°C. It is therefore clear that grain size strongly affects the degree of tetragonal phase transformation.

Regardless of the time of ageing, no pronounced changes in the microstructure of the section were

observed in specimens tested at 140°C when compared with the reference specimen or rather no layer of transformed zirconia was recorded as evidenced in figure 2, which gives the microstructure of the section through a specimen tested at 140°C/15 h.

The transformed layer was found at a temperature of 180°C and higher. As can be seen from table 2, with increasing temperature the transformed layer thickness increased from ca 15 µm (180°C/10 h) to ca 170 µm (260°C/10 h). Figure 3 shows the transformed layer on the surface of a specimen tested at 180°C/10 h. A detailed view reveals the porous structure of transformed layer, which was evidently caused by the grains becoming looser due to the volume change (about +3 vol.%) related to the tetragonal-to-monoclinic phase transformation [13].

A similar structure of transformed layers was also found in specimens tested at 220°C/10 h or 260°C/10 h (see figure 4). At temperatures of 180-260°C the XRD analysis revealed together with the change in microstructure a markedly greater amount of monoclinic zirconia on the specimen surface than is the case of specimens tested at 140°C. For °C/10 h, the amount of m-ZrO₂ found on the specimen surface was 54.3 wt.%, for 260°C/10 h the content of m-ZrO₂ increased to 61.9 wt.%.

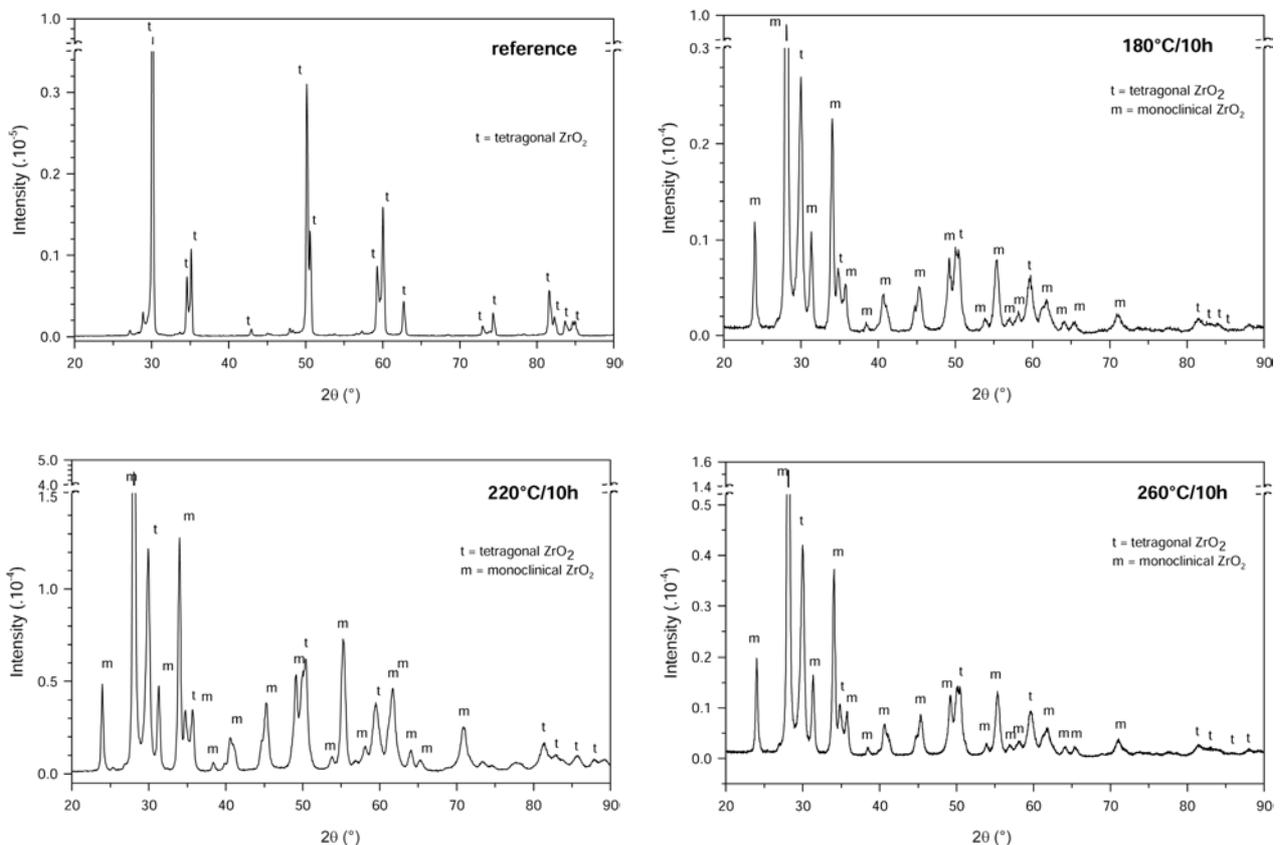


Figure 1. X-ray diffraction spectrum of zirconia ceramic (reference and after hydrothermal interaction).

It is apparent from the above results that the degree of tetragonal to monoclinic zirconia transformation is affected by both the temperature and the time of the action of hydrothermal medium. With increasing temperature and time of attack the content of monoclinic zirconia on the surface of the specimen tested increased and, simultaneously, at testing temperatures of over 180°C there were visible changes in the microstructure - a clearly delineated porous layer containing transformed zirconia was formed.

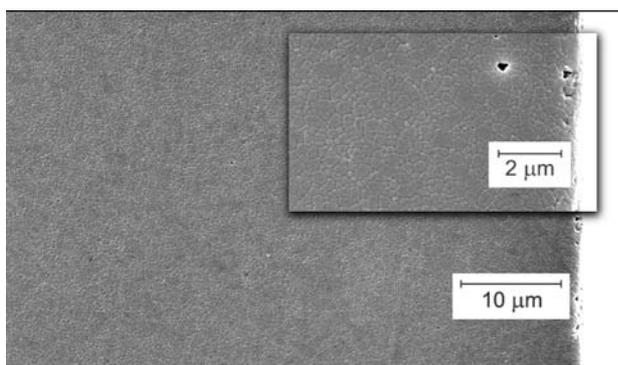


Figure 2. Microstructure of section through zirconia ceramic tested at 140°C/15h.

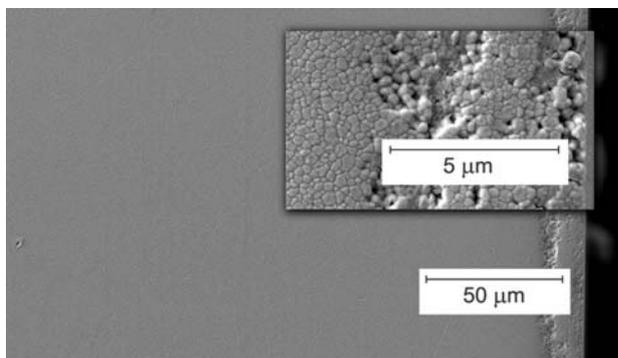


Figure 3. Microstructure of section through zirconia ceramic tested at 180°C/10h.

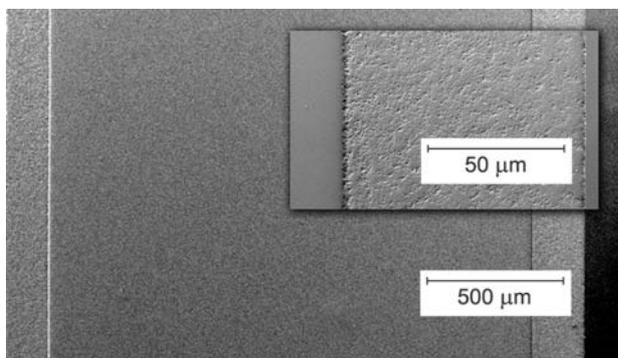


Figure 4. Microstructure of section through zirconia ceramic tested at 260°C/10h.

Yttrium content

The yttrium content analysed via EDS analysis on the crosssection through hydrothermally aged specimens was constant and in all cases comparable with the reference specimen. The average yttrium content was ca. 1.8 mol.%, which corresponds to 3 mol.% of yttrium oxide. On the basis of these results it can be said that there is no yttrium decrease in the specimen and thus Y_2O_3 does not get "washed out" from the specimen into the surrounding environment. A destabilization mechanism can therefore be assumed that is based on the Y_2O_3 content being reduced while $Y(OH)_3$ is formed.

The possibility of yttrium hydroxide being formed from yttrium oxide in hydrothermal conditions was confirmed by an analysis of pure yttrium oxide aged hydrothermally at 240°C for 10 h (see figure 5). The Figure shows the infrared spectrum of yttrium oxide before and after the hydrothermal ageing. The differences in spectra are most pronounced for wave numbers about 3600 cm^{-1} and about 700 cm^{-1} , where peaks appeared after hydrothermal ageing that correspond to the valence vibrations of -OH groups.

It can be assumed that probably in the aqueous medium the yttrium ions reacted with free OH^- ions to form yttrium hydroxide and the tetragonal system was destabilized due to yttria depletion in the crystal lattice of partially stabilized zirconia.

The likely process of $t-ZrO_2$ degradation can be described as follows: under hydrothermal conditions at temperatures ranging from 140°C to 260°C zirconia interacted with water in 5-20 hours. The faulting of Zr-O-Zr bonds and the formation of Zr-OH bonds gave rise to a stress that initiated the nucleation of $m-ZrO_2$.

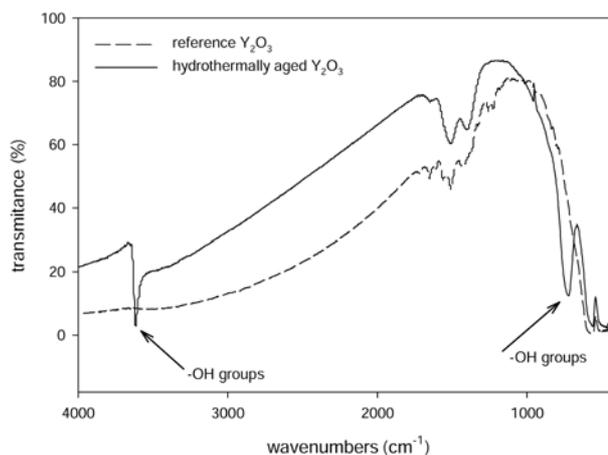


Figure 5. IR spectra of yttrium oxide before and after hydrothermal aging.

Specimen superficial hardness

Although on the surface of specimens tested at 140°C (specimens 1-4) XRD analysis revealed the presence of m-ZrO₂ in the amount of as much as 21 wt.% (specimen 4) the profile of hardness tester imprint corresponded to the deformation of t-ZrO₂ [19] (see figure 6). The deformation behaviour of specimens on whose surface the transformed layer had been detected (see table 2) differed from the behaviour of specimens tested at 140°C (figure 6). Near the impression edge the deformation of material was more pronounced (figure 6) and the transformed layer was spalling off.

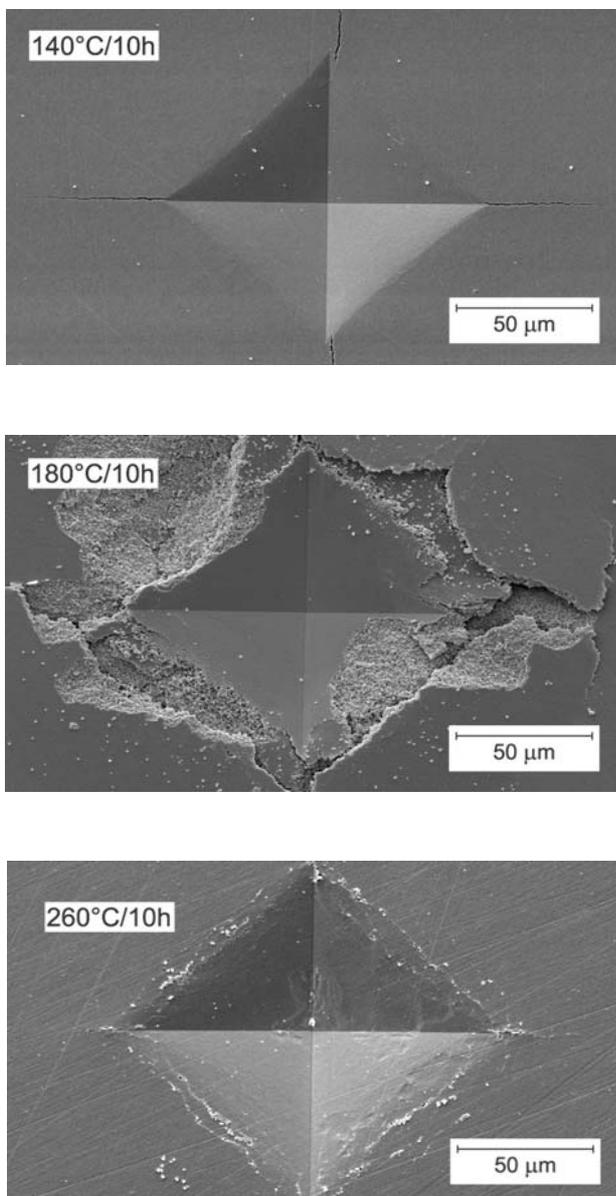


Figure 6. Hardness tester imprint at a force of 98 N into specimen surface after hydrothermal interaction.

As it is mentioned in the experimental section, hardness was tested at loading forces of 0.98-196 N. Each loading force produced an imprint of different depth. Figure 7 gives the dependence of superficial hardness on the indentation depth for the ceramic materials tested. Specimens tested at 140°C had a superficial hardness exceeding 10 GPa and for a loading force of over 49 N (impression depth of over 12 µm) their superficial hardness was identical: 12.5 GPa. The hardness of specimens tested at 140°C corresponded to the hardness of t-ZrO₂ [20].

The superficial hardness of specimens with transformed layer (specimens tested at 220 and 260°C) was less than 10 GPa, ranging between 7 GPa (260°C) and 9 GPa (220°C) (see figure 7). Comparing the impression depth and the thickness of transformed layer (table 2) we can see that the measured superficial hardness of specimens tested at 220 and 260°C corresponded to the hardness of transformed layer.

The superficial hardness of a specimen tested at 180°C was strongly dependent on the loading force (figure 7). When measuring at a loading force of 9.8 N (impression depth of approx. 7 µm) the measured superficial hardness of specimens was similar to the hardness of specimens tested at 220 and 260°C, namely 8 GPa. When loading with higher loading force (impression depths of 8-17.5 µm), the superficial hardness of a specimen tested at 180°C was similar to the superficial hardness of specimens tested at 140°C (11.3-12.3 GPa). This behaviour may be related to the presence of transformed layer on the specimen surface. When loading with a force of less than 9.8 N the tip of hardness tester penetrated to a small depth (less than 7 µm) and the hardness established corresponded to the hardness of transformed layer. When loading with higher loading forces the depth of hardness tester indentation (and the related deformation) was greater and the hardness measured corresponded to the hardness of the material without transformation layer (specimens tested at 140°C).

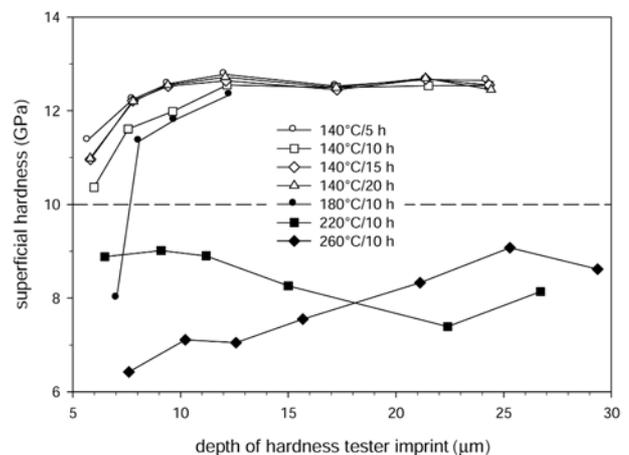


Figure 7. Dependence of superficial hardness of specimens on the depth of hardness tester imprint.

It can be seen from the results that, when the indentation is shallow enough, superficial hardness of the material is a good indicator of the presence of transformed material on the surface of specimen. Although in the case of a specimen tested at 180°C the thickness of transformed layer as established by SEM was approx. 15 μm, the effect of transformed material (with respect to the plastic deformation around the impression) on superficial hardness was evident already when the hardness tester tip penetrated to depths of less than 8 μm. The effect of the m-ZrO₂ and thus the presence of transformed layer on the surface of specimens tested at 140°C was not observed even if superficial hardness was measured at a loading force of 0.98 N, when the hardness tester tip penetrated to a depth of approx. 1.5 μm (figure 7). It follows from the above results that the transformed layer appears on the surface of specimens in the temperature range from 140°C to 180°C, which had in fact been found out by SEM.

Dependence of micro-hardness on distance from surface

The degradation of specimen surfaces and the related phase transformation of zirconia showed in the micro-hardness established on the section through specimens (see figure 8). For specimens on the surface of which no transformed layer was found (specimens tested at 140°C) corrosion did not affect the micro-hardness of specimen for the loads used- the micro-hardness of specimen surface was the same as in the centre of the specimen - ca 1500 MPa (see figure 8).

The micro-hardness in the transformed layer of a specimen tested at 180°C/10 h could not be established because of the small thickness of the transformed layer (figure 8). In spite of this, a difference between the micro-hardness on the specimen surface (0.9 GPa) and inside the specimen (1.4GPa) was found.

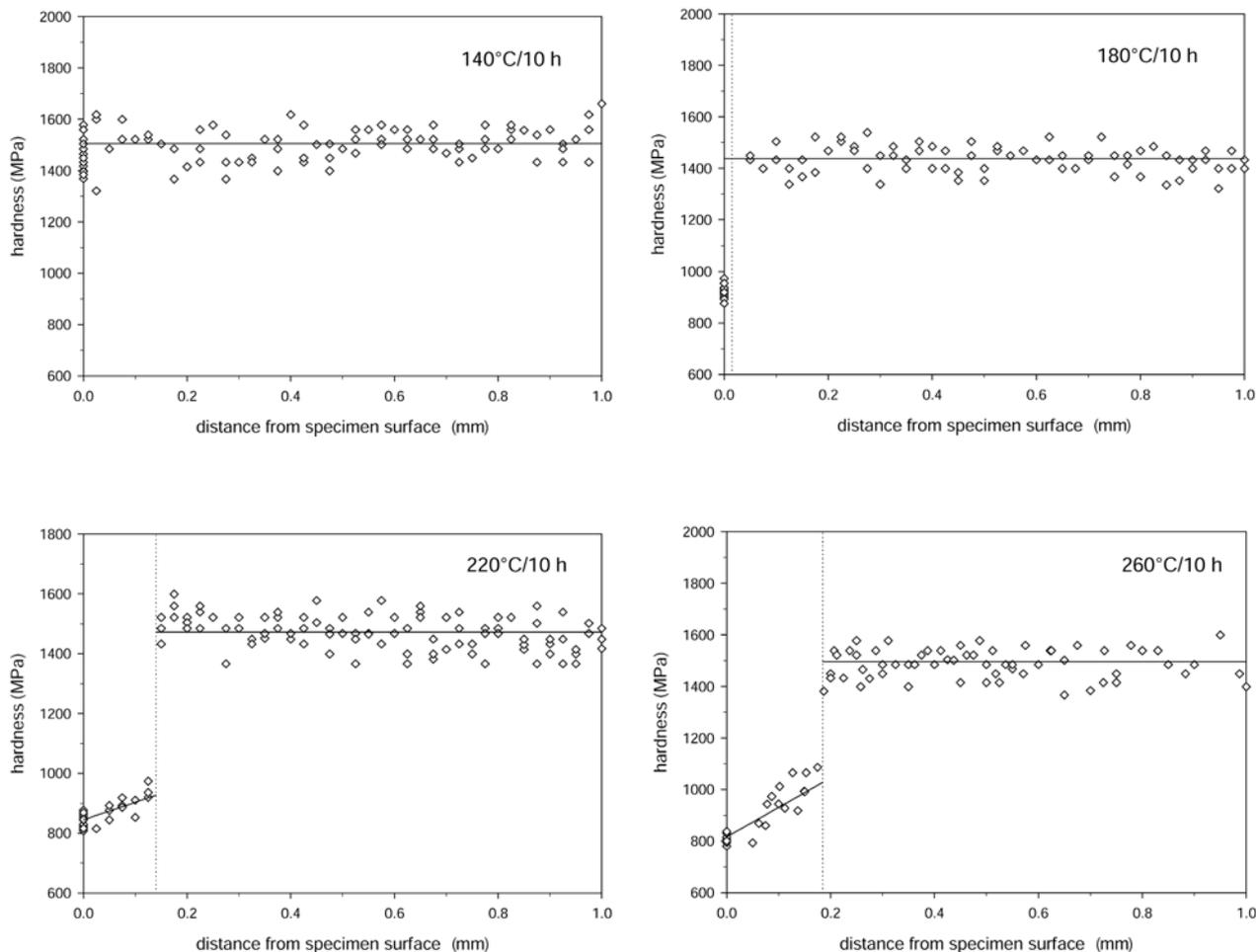


Figure 8. Dependence of micro-hardness on distance from specimen surface after hydrothermal interaction.

For the specimens on whose surface a thick transformed layer was established (specimens tested at 220 and 260°C) it was possible to measure the micro-hardness of transformed layer in dependence on the distance from specimen surface (figure 8). The lowest micro-hardness was on specimen surfaces while in the direction from specimen surface the micro-hardness increased as far as the transformed layer/nontransformed material interface. Beyond this interface, the micro-hardness changed abruptly to the micro-hardness of nontransformed material. The micro-hardness of a material consisting of two phases is directly proportional to the phase composition of material [19]. On the basis of the established dependence of the micro-hardness on the distance from specimen surface it can be assumed that the transformed layer consists of a mixture of m-ZrO₂ and t-ZrO₂, with the m-ZrO₂ predominating on the specimen surface and the t-ZrO₂ increasing in the direction towards the transformed layer/nontransformed material interface. In the non-degraded part only the t-ZrO₂ phase was present.

Fracture toughness of specimens

The fracture toughness of specimens tested at 140°C for different periods of time (specimens 1-4) was identical and exhibited the same dependence on loading (see figure 9). For loads exceeding 98 N the fracture toughness of these specimens was the same (4.6-5.2 MPa m^{1/2}) and corresponded to the fracture toughness of t-ZrO₂ given in the literature [18].

Specimens on the surface of which a transformed layer was found (specimens tested at 180, 220 and 260°C) exhibited different fracture behaviour (figure 9). The lowest fracture toughness was in the case of loading with a force of 9.8 N (5.3 MPa m^{1/2} for specimen 7).

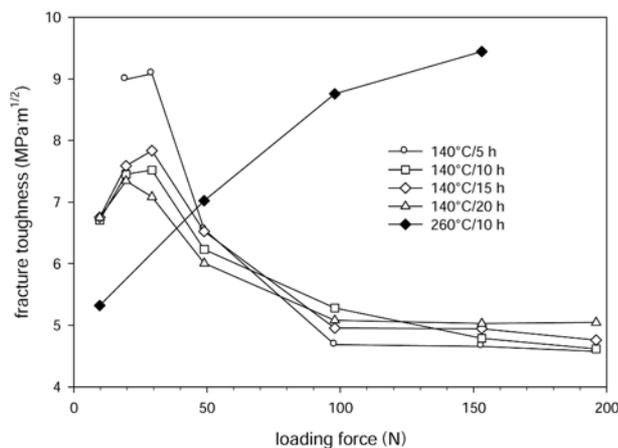


Figure 9. Dependence of fracture toughness on loading force.

With increasing loading force it increased to a maximum for a loading force of 153 N (9.5 MPa m^{1/2} for 260°C). As mentioned above, the phase transformation t-ZrO₂ into m-ZrO₂ is related to a volume change of ca +3%. At low specimen testing temperatures the internal stresses caused by the change in volume could not be relaxed and, due to the firm bond with substrate material the surface layer could not increase its volume and so pressure stresses appeared in it. The pressure stress prevented opening of the propagating crack, which led to increased fracture toughness. Another explanation for the increase in indentation fracture toughness may be the bifurcation of propagating crack into the existing network of microcracks, which appeared during the layer transformation since internal stresses related to the phase transformation may have partially relaxed due to the appearance of cracks on grain boundaries and inside the grains.

CONCLUSIONS

It has been found that hydrothermal conditions (140°C - 260°C) lead to the transformation of tetragonal zirconia into monoclinic zirconia, with the measure of transformation increasing with increasing temperature and time of action. At temperatures from 140°C to 260°C some 7-62 wt.% of tetragonal phase transformed on specimen surface into monoclinic phase. The transformation of tetragonal zirconia at temperatures of 180°C and higher was the most intensive. At these temperatures a layer of transformed material was formed on the surface of material. Its thickness increased with temperature and reached as much as 170 μm. The transformed layer consisted of a mixture of grains of the monoclinic and the tetragonal phases with varied phase content. In the non-degraded part only the tetragonal zirconia phase was present. A change in mechanical properties was observed at temperatures of 180°C and higher, and it was in correlation with a change in the microstructure of material at these temperatures.

Temperatures of 180°C and more are critical from the viewpoint of changes in the microstructure and mechanical properties for this material.

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HYDROTERMÁLNÍ KOROZE KERAMIKY NA BÁZI
TETRAGONÁLNÍHO OXIDU ZIRKONIČITÉHO

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Byl studován vliv hydrotermálních podmínek na fázovou stabilitu, mikrostrukturu a mechanické vlastnosti tetragonální ZrO₂ keramiky stabilizované 3 mol% Y₂O₃. Při teplotách 140-260°C došlo k transformaci tetragonální fáze na monoklinický ZrO₂. Míra transformace rostla s rostoucí teplotou a dobou působení. Změna mikrostruktury a mechanických vlastností byla zaznamenána při teplotách 180°C a vyšších. S rostoucí teplotou tloušťka transformované vrstvy rostla a při 260°C dosáhla tloušťky 170 μm. Změna mechanických vlastností (tvrdosti a lomové houževnatosti) odpovídala strukturním změnám v materiálu způsobených hydrotermálním působením. Teploty 180°C a vyšší byly pro mechanické a strukturní vlastnosti materiálu kritické.