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THE STRUCTURAL STABILITY OF ZIRCONIA CERAMICS IN WATER AND ACID SOLUTIONS

STABILNOŚĆ STRUKTURALNA TETRAGONALNEGO TLENKU CYRKONU W ŚRODOWISKACH WODNYCH I KWAŚNYCH

Yttria-tetragonal zirconia polycrystals (Y-TZP) are used as a material for dental applications, e.g., inlays, crowns, and bridges. However, the Y-TZP may undergo a phase transformation, which results in micro-cracking. For this reason its stability in an oral environment is of great importance.

In this paper, the hydrothermal stability of low-porous yttria-doped zirconia in water and acid solutions was investigated. Ceramics with a fractional density of tetragonal phase ranging from 90% to nearly 100% were produced by sintering of dry-pressed pellets at different temperatures in an ambient air atmosphere. The flexural strength and phase composition were determined for samples before and after exposure to various environments. The influence of phase transformation on the surface morphology was investigated using a scanning electron microscope.

The results showed that specimens sintered at 1450°C to a density of more than 95% of the theoretical maximum exhibit a strong tendency to undergo a tetragonal-to-monoclinic phase transformation during autoclaving in water at 200°C for 24 hours. The volume expansion due to phase transformation results in micro-cracking, which has a detrimental effect on mechanical properties of the investigated material.

Keywords: Y-TZP, Zirconia ceramics, Aging, dental materials

Tetragonalny tlenek cyrkonu stabilizowany itrem (Y-TZP) jest stosowany w stomatologii jako materiał na korony, wypełnienia lub mostki. Wadą tej ceramiki jest skłonność do przemiany fazy tetragonalnej w fazę jednoskośną – bardziej stabilną w niskich temperaturach. Przemianie tej towarzyszy wzrost objętości materiału (około 3%) i powstawanie mikropęknięć. Dodatkowo przemianie tej sprzyja środowisko wodne typowe dla jamy ustnej. Dlatego też w niniejszej pracy podjęto problem stabilności fazy tetragonalnej tlenku cyrkonu w środowiskach wodnych.

Ceramikę wytworzono poprzez spiekanie wyprasek w atmosferze obojętnej w różnych temperaturach. Zastosowanie różnych temperatur spiekania pozwoliło uzyskać materiał o gęstościach w zakresie od 90% do 100% gęstości teoretycznej. Wytworzone próbki poddano starzeniu w wodzie oraz roztworach kwasów siarkowego, solnego i azotowego. Określono skład fazowy oraz wytrzymałość na zginanie próbek w stanie wyjściowym i poddanych starzeniu w różnych środowiskach. W celu analizy wpływu przemiany fazowej na morfologię powierzchni przeprowadzono obserwacje mikrostruktury przy użyciu skaningowego mikroskopu elektronowego.

Uzyskane wyniki pokazały, że największą skłonność do przemiany w fazę jednoskośną mają próbki spiekane w najwyższej temperaturze (1450°C). Dodatkowo skłonność tą potęguje środowisko wodne – w wyniku starzenia w 200°C przez 24 godzin przemianie uległo 80% fazy tetragonalnej. W próbkach starzonych w roztworach kwasów w temperaturze 75°C stwierdzono tylko kilkuprocentowy udział fazy jednoskośnej. Nie zaobserwowano wpływu rodzaju użytego roztworu kwasu na stabilność fazy tetragonalnej. Obserwacje mikroskopowe pozwoliły zlokalizować miejsca degradacji ceramiki, widoczne jako kratery, będące wynikiem zmiany objętości i powstawania pęknięć podczas przemiany fazy tetragonalnej w jednoskośną. Powstawanie tej fazy powoduje także obniżenie właściwości mechanicznych Y-TZP.

1. Introduction

Biscuit-sintered yttria-tetragonal zirconia polycrystalline (Y-TZP) have become a popular ceramics suitable for dental restorations, such as crowns and bridges, due to their relatively simple way of manufacturing [1].

Dense Y-TZP ceramics exhibit excellent mechanical properties as a result of a reduced crack-propagation rate. It results from the local volume change during the tetragonal to monoclinic phase transformation at the crack tip [2]. However, tetragonal zirconia degrades in humid environments, especially at temperatures near 250°C. This

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phenomenon was observed in a fully dense sintered zirconia by Kobayashi et al. [3] more than twenty years ago. In contrast, there are only a few reports about the structural instability of porous tetragonal zirconia. Masaki [4] suggested, for example, that a density threshold exists (as function of the amount of yttria and the grain size), below which hydrothermal degradation will not occur. For the 3Y-TZP (3 mol% yttria-tetragonal zirconia polycrystals) ceramics with an average grain size of 0.2 μm, this density would be about 95% of the theoretical maximum. Shojai and Mantyla [5] investigated the structural stability of 3Y-TZP porous membranes in water solutions. After 34 days of ageing in water at 80°C the samples did not show any trace of phase transformation, however in acidic and alkaline solutions they were partly transformed into monoclinic phase up to 13%.

There are also a few research reports on the mechanical properties of porous Y-TZP ceramics. For the 3Y-TZP ceramics several equations have been formulated to describe the relationship between the porosity and the elastic moduli. Hardness can also be estimated with these equations using a relationship between the hardness and porosity that is similar to the ones for bulk modulus and porosity [6]. The effect of low-temperature aging on the flexural strength of dental Y-TZP ceramics was investigated by Ardlin [7], who found that for aged specimens the strength was not significantly different to that of the unexposed specimens.

The purpose of this study was to evaluate the effect of aging in water and acids on the rate of tetragonal-to-monoclinic phase transformation for the Y-TZP ceramics manufactured by sintering dry-pressed powder compacts to various degrees of densification. Since the transformability of zirconia ceramics determines their mechanical properties, the relationship between the flexural strength and the aging conditions was also investigated.

2. Materials and methods

Samples were prepared from commercially available coarse-grained TZ-3YSB-E zirconia powder (Tosoh, Tokyo, Japan). The powder contained 3 mol% yttria and 0.25 wt% of alumina to moderate the tetragonal-to-monoclinic transformation during aging. The crystallite size of the polycrystalline powder was 35 nm and the specific surface area was 7 m^2/g. The ready-to-press granulates contained a few percent of an acrylic binder. Green pellets (20 mm in diameter and 2 mm thick) were prepared by uniaxial pressing at 147 MPa. The sintering was carried out in an electrical resistance chamber furnace for 4 hours. The specimens were sintered at three different temperatures (1350°C, 1400°C, 1450°C) to obtain three different porosities.

The relative density of the sintered specimens was determined by Archimedes' method using distilled water as the immersion liquid. The grain size was determined by calculating the equivalent spherical diameters of grains on SEM micrographs of polished and thermally etched specimens.

Hydrothermal aging tests were carried out at 200°C for 24 hours in distilled water and at 75°C for 15 days in acid solutions with pH = 2. Three acids were used to prepare the solutions: HCl, HNO_3, and H_2SO_4. X-ray diffraction (XRD) was used to determine the amount of transformed monoclinic zirconia. The amount of transformed monoclinic zirconia was calculated from the intensities of the monoclinic M (11-1) and M (111), and the tetragonal T (111), peaks according to the method of Garvie and Nicholson [8]:

$$Xm = \frac{I_{M(111)} + I_{M(11\bar{1})}}{I_{M(111)} + I_{M(11\bar{1})} + I_{T(111)}}.$$

The surface damages due to the phase transformation were observed using a scanning electron microscopy (SEM).

In order to determine the mechanical properties of Y-TZP before and after degradation the biaxial flexural strength was measured using a piston-on-three-balls test. The applied loading rate was 1 mm/min, in accordance with ISO 6872:1995. Three specimens for each aging condition were fractured during the tests. Vickers indentation measurements were performed under a 10 N load applied for 15 s.

3. Results and discussion

Sintering of specimens at different temperatures resulted in various microstructures. The density of all specimens exceeded 93% of the theoretical maximum, and only closed porosity was observed (even in specimens sintered at 1350°C with a relatively high level of porosity) – see Table 1. It was found that the average equivalent diameter of grains rose with increasing sintering temperature up to the value of 0.26 μm for the samples sintered at 1450°C. The grain size distribution was similar for all the samples, with a variation coefficient of 0.26 (variation coefficient is defined as a ratio of standard deviation to mean value of equivalent diameter). The microstructures of the samples were reasonably homogeneous.

The microstructural parameters listed in Table 1 are important in terms of the correlation between the parameters of the sintering process and the phase stability. A large grain size can generate non-equilibrium conditions and result in phase transformations [9].

TABLE
Microstructural parameters of 3Y-TZP ceramics sintered as a function of sintering temperature

	1350°	1400°	1450°
Percent of the theoretical density [%]	93.7	99.5	99.7
Open porosity [%]	0.6	0	0
Equivalent diameter [μm]	0.19	0.22	0.26
Coefficient of variation	0.25	0.27	0.25
Max. grain size [μm]	0.39	0.41	0.53

After sintering at the temperature range from 1350°C to 1450°C the zirconia ceramics consist only of tetragonal phase which has been confirmed by XRD measurements. Aging in water at 200°C for 24 hours resulted in the phase transformation. In the case of specimens sintered at 1450°C, the amount of monoclinic phase was above 80% (Fig. 1). Samples sintered at lower temperatures exhibited less than 3% of the transformed phase. This might indicate that for each particular Y-TZP powder there is a threshold sintering temperature, above which the specimens exhibit a propensity to undergo the phase transformation. Different phase stability of the samples sintered at 1400°C and 1450°C, which have the same porosity and relative density, indicates that the grain size might be a critical factor influencing the hydrothermal stability, as was suggested by Kosmač et al. [10].

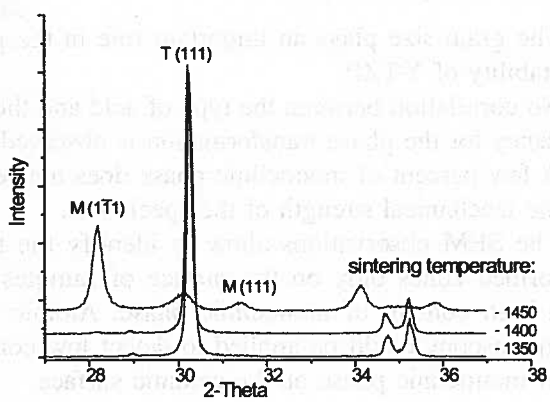

Fig. 1. XRD pattern of sintered specimens after aging in water at 200°C for 24 hours

A plot showing a relative amount of monoclinic phase on the surface of samples exposed to acid solutions is shown in Figure 2. The highest amount of monoclinic phase was observed in the specimens showing both the largest grain size and the smallest porosity. Only a small amount of monoclinic phase was found on the surface of specimens sintered at lower temperatures. No correlation between the phase stability and the acid media was found.

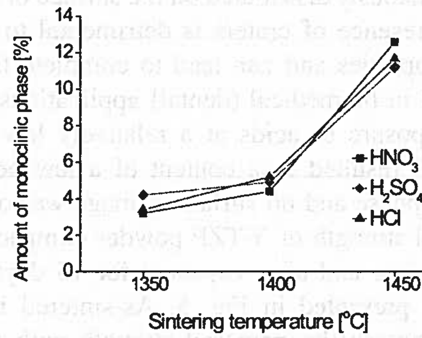

Fig. 2. The amount of monoclinic phase in specimens aged in acids at 75°C for 15 days

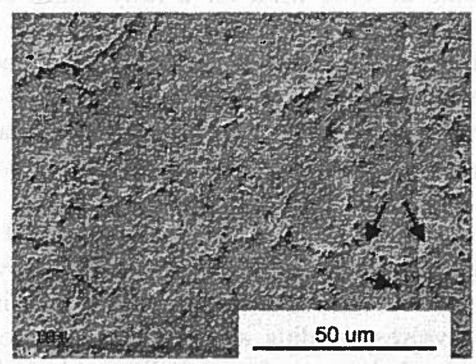

Fig. 3. Back-scattered electron image of surface of TZ-3YSB-E ceramic sintered at 1450°C. (Arrows indicate the boundaries of the powder granules)

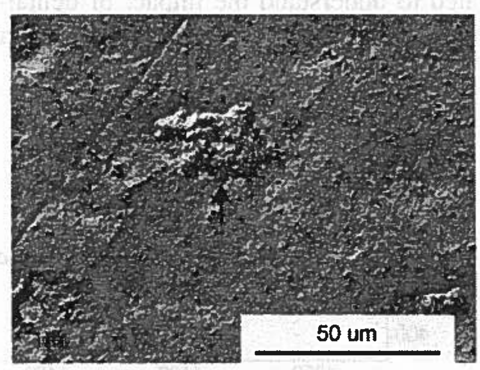

Fig. 4. Back-scattered electron image of surface of TZ-3YSB-E ceramic sintered at 1450°C and subsequently aged at 200°C for 24 h in water. (Arrow indicates transformed zone)

Observations of the surface structure using SEM revealed that a chosen sintering temperature and applied high initial pressure resulted in a smooth surface of specimens with only occasional irregularities. Small flaws were found at the boundaries between the particles of powder (Fig. 3). The surface of specimens aged at 200°C for 24 hours in water showed higher roughness. High level of monoclinic content in this sample (80%) results in a large area of degraded surface (Fig. 4). Transformed zones appear in the form of craters, which are related to monoclinic nuclei formed during the exposure. Similar effects were observed by Chevalier [11]. These craters are homogeneously distributed on the surface of the samples. The presence of craters is detrimental to the mechanical properties and can lead to complete failure of the material in biomedical (dental) applications.

The exposure to acids at a relatively low temperature (75°C) resulted in a content of a few percent of monoclinic phase and no surface damage was observed.

Flexural strength of Y-TZP powder compacts in the as-sintered state and after exposure for 15 days to acid solutions is presented in Fig. 5. As-sintered materials show a progressively increased strength with the fractional density, starting from more than 800 MPa for the ceramics with 93.7% of theoretical density and reaching a value of 1100 MPa for a fully dense ceramics. The same tendency was observed for almost all cases of exposed zirconia ceramic samples. Only the specimens treated with HCl solution exhibit strength at a constant level, with a slight decrease for higher temperatures of sintering. This is an unexpected result and will be a subject of further analysis.

In our study, flexural strength was measured on samples not exposed to any surface treatment. However, it is important to know that the use of zirconia in dental devices involves grinding and sandblasting. Kosmač et al. [12] revealed that surface grinding and sandblasting influence the strength of Y-TZP ceramics leading to conclusions that mechanical and chemical agents should be investigated to understand the impact of dental-relevant environments on the phase degradation of the material.

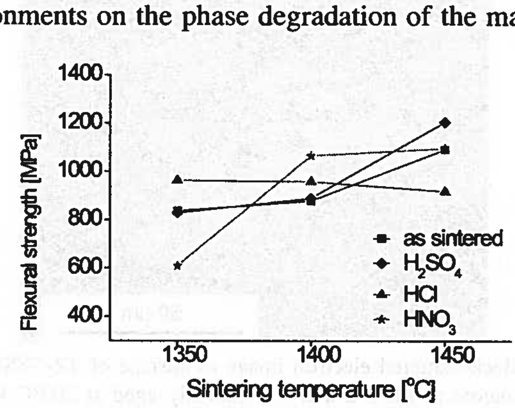

Fig. 5. Flexural strength of ceramics aged in different kinds of acid solutions

Results of hardness measurements are shown in Fig. 6. Hardness of the samples in as-sintered state depends on the sintering temperature, i.e. on the materials density. The higher the density, the higher the hardness of the material. Aging in various acid solutions does not change significantly the hardness of ceramic. This is due to the fact that only small amount of monoclinic phase is formed during such conditions. This is in agreement with the SEM observations where no surface damage was observed. However, a significant decrease of hardness was observed for the samples exposed to water. The amount of monoclinic phase on the surface of such samples was evaluated as 80%. The depth of the transformed zone is sufficient to reduce the hardness significantly.

Standard hardness measurements do not fully reveal the surface degradation. Thus nano-indentation methods should be applied to characterize precise, phase transformation in a locale scale [13].

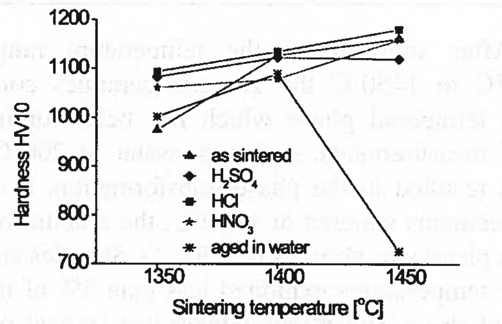

Fig. 6. Hardness of ceramics aged in different acid solutions and in water

4. Conclusions

Samples showing different microstructure were manufactured by employing different sintering temperatures. Investigations of microstructures and properties of the samples after exposure to hydro-environments led to the following conclusions:

- The grain size plays an important role in the phase stability of Y-TZP.
- No correlation between the type of acid and the tendency for the phase transformation is observed.
- A few percent of monoclinic phase does not reduce the mechanical strength of the specimens.
- The SEM observations allow to identify the transformed zones only on the surface of samples with a high content of monoclinic phase. Atomic force microscopy could be applied to detect low contents of monoclinic phase on the ceramic surface.

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REFERENCES

[1] F. Filser, P. Kocher, F. Wibel, H. Luthy, P. Scharer, L. J. Gauckler, Reliability and strength

of all-ceramic dental restorations fabricated by direct ceramic machining (DCM). Int. J. Comput. Dent. **4**, 89-106 (2001).

[2] P. Christel, A. Meunier, M. Heller, J. P. Torre, C. N. Peille, Mechanical properties and short-term in vivo evaluation of yttrium-oxide-partially-stabilized zirconia. J. Biomed. Mater. Res. **23**, 45-61 (1989).

[3] K. Kobayashi, H. Kuwajima, T. Masaki, Phase Change and Mechanical Properties of $ZrO_2Y_2O_3$ solid electrolyte after ageing, Solid State Ionics **3/4**, 489–493 (1981).

[4] T. Masaki, Mechanical properties of Y-PZS after ageing at low temperature, Int. J. High Tech. Ceram. **2**, 85–98 (1986).

[5] F. Shojai, T. A. Mantyla, Structural stability of yttria doped zirconia membranes in acid and basic aqueous solutions, J. Eur. Ceram. Soc **21**, 37–44 (2001).

[6] J. Luo, R. Stevens, Porostity-dependence of elastic moduli and hardness of 3Y-TZP ceramics. Ceramics International **25**, 281–286 (1999).

[7] Berit I. Ardlin, Transformation-toughened zirconia for dental inlays, crowns and bridges: chemical stability and effect of low-temperature aging on flexural strength and surface structure; Dental Materials **18**, 590–595 (2002).

[8] R. C. Garvie, P. S. Nicholson, Phase analysis in zirconia systems. J Am Ceram Soc **55**, 303-306 (1972).

[9] S. Lawson, Environmental degradation of zirconia ceramics. J. Eur. Ceram. Soc. **15**, 485-502 (1995).

[10] T. Kosmac, M. Andrzejczuk, K. J. Kurzydłowski, The mechanical properties and hydrothermal stability of porous partially (biscuit-) sintered Y-TZP ceramics. Proceedings of International Conference on Advanced Ceramics and Composites 2006.

[11] J. Chevalier, B. Cales, J. M. Drouin, Low temperature aging of Y-TZP ceramics. J Am Ceram **82**, 2150-4 (1999).

[12] T. Kosmac, C. Oblak, P. Jevnikar, N. Funduk, L. Marion, The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic, Dental Materials **15**, 426–433 (1999).

[13] S. A. Catledge, M. Cook, Y. K. Vohra, E. M. Santos, M. D. McClenny, K. D. Moore, Surface Crystalline Phases and Nanoindentation Hardness of Explanted Zirconia Femoral Heads, Journal of Materials Science: Materials in Medicine **14**, 863 (2003).

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