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Journal of the European Ceramic Society 25 (2005) 1597–1602

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Stability of Y-TZP during hydrothermal treatment: neutron experiments and stability considerations

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Received 12 February 2003; received in revised form 3 March 2004; accepted 13 March 2004
Available online 8 September 2004

Abstract

The degradation of yttria-stabilised zirconia in humid atmospheres at temperatures around 250 °C is influenced by a number of microstructural parameters. The corrosive attack starts from the surface and is associated with the tetragonal to monoclinic transformation. In order to investigate structural changes chemically homogeneous single phase t-powders had been hydrothermally treated in a D_2O-atmosphere and subsequently investigated by neutron diffraction. Slight structural changes were observed after water treatment: a general contraction of both *a* and *c* parameters, hence, the "free" structural *z*(oxygen) parameter as well as the *c*/*a*-ratio are closer to the values of cubic zirconia. In this paper the structural changes due to the penetration of water radicals during hydrolysis are discussed. They give rise to stresses which then have an impact on the energy balance between the tetragonal and the monoclinic phase (martensitic transformations). Since the powder state can be assumed to be mostly free from macro-straining, the changes of the lattice constants were used to deduct a shape change tensor. Hence assuming linear elastic behaviour (isotropic elastic modulus of 200 GPa for both a surface grain and its environment) maximum stresses of 328 MPa for the *a*-axis and 488 MPa for the *c*-axis were found. Thus, water radicals basically lead to further tensile stresses in the surface which increase the energy difference between the t and m phase, i.e. a further destabilisation.

Keywords: Corrosion; Degradation; Martensitic transformation; Elastic recoil detection analysis; Neutron diffraction; TZP

1. Introduction

1.1. Stability of zirconia and martensitic transformations

The stability of tetragonal zirconia material is certainly a multi-parameter problem. It has been treated in the literature by considering the stability of grains or, even further, the stability of the crystallographic structure. According to the basic work of Christian,[1] the free energy balance between the tetragonal (t-) and monoclinic (m-) phases contains a contribution of the pure lattice in its unconstrained state (ΔG_{chem}) and additional terms which only occur within a constrained dense microstructure[2–4]

$$-\Delta G = \Delta G_{\text{Chem}} + \Delta G_{\text{Eigenstresses}} + \Delta G_{\text{Transformation}} + \Delta G_{\text{Surface}} + \Delta G_{\text{Twinning}}$$

$$-\Delta G = \Delta G_{\text{Chem}} + \left(\frac{1}{2\sigma_{ij}^{\text{T}}} + \sigma_{ij}\right)\varepsilon_{ij}^{\text{T}} + \Delta\gamma\frac{\delta A}{\delta V} + \gamma_{\text{twin}}\frac{\delta A}{\delta V}$$

where ΔG_{chem} is the difference in chemical free energy; σ_{ij}^{T}, transformational stresses; σ_{ij}, residual Eigenstresses after sintering; $\varepsilon_{ij}^{\text{T}}$, transformational strain tensor; γ, surface energy; γ_{twin}, surface energy of the twin planes; *A*, area and *V*, volume.

According to the work of Schmauder and Schubert[4] the two elastic contributions are the dominating influences and both twinning and surface energy terms are of lesser importance. Thus, the stability of the t-phase is henceforth discussed on the basis of these two elastic terms.

The term 1/2 $\sigma_{ij}^{\text{T}}\ \varepsilon_{ij}^{\text{T}}$ denotes the elastic energy due to transformation. The atomic structure in a t–m transforming grain undergoes a lattice expansion which is hindered due

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doi:10.1016/j.jeurceramsoc.2004.03.025

to the surrounding elastic matrix. The situation leads to a compressive stress stabilising the t-phase.[5,2,3]

The term $\sigma_{ij}\ \varepsilon_{ij}^{\mathrm{T}}$ represents the Eigenstresses which are present in the manufactured body. They could be either due to tension, compression or shear forces and depend on a number of processing related microstructural parameters. This term is basically the only direct tool to manipulate the materials stability.[4] For tough materials unstable t-phase grains are needed, i.e. the shear and tensile stresses should increase the energy difference between t- and m-phase which is a destabilisation. Its level should be sufficiently smaller in order to avoid an unwanted self transformation on cooling but be close to elastic transformational energy term as described above. Until now a corrosion resistant Y-TZP requires very stable, i.e. non-transformable t-grains. In this sense, stability is traded against toughness.

The most important microstructural parameters such as stabiliser content, grain size and shape, amount of intergranular glassy phase, secondary crystalline phases can be traced back by considering their influence on the energy balance between t- and m-phase.[6]

1.2. *Degradation*

The degradation of the mechanical properties of tetragonal zirconia under the influence of water has been subject of many investigations.[7–13]

As a consequence of the transformability, the material is necessarily metastable at room temperature. After an aging treatment in the temperature range around 250 °C in a humid atmosphere a degradation of the material occurs. This degradation is accompanied by a t–m transformation of the grains. The degraded layer grows in thickness with further aging time, i.e. it is not passivating. Matsui et al.[8] attributed the further growth of the layer to large and therefore instable surface grains, which created stresses and fracture in the adjacent grain boundaries. The water can then proceed deeper into the ceramic via these microcracks.

The influence of microstructural parameters on stability could be understood by considering of the energy balance between the t- and the m-phase. Based on the understanding of homogeneous nucleation an increase of this difference would result in a smaller activation barrier, i.e. in a less stable material.[1]

2. Experimental set-up

The role of water, however, was still unclear. In spite of the commonly used martensite theory the role of water was discussed by other arguments such as hydrolysis or defect filling. This paper wants to give an explanation on the role of water based the investigation of structural changes during penetration of water radicals which then have an impact on the t–m energy balance.

Thus, experiments were needed sensitive enough to monitor the structural changes during degradation. Since the depth of penetration is only in the order of 500 nm investigations on bulk materials are not promising. Instead, chemically and crystallographically similar powders were used. They are small enough to be completely penetrated by water radicals, hence, they can be made in unlimited quantities and they are unconstrained.

As a most promising experimental approach a combination of neutron scattering (high volume of specimens possible, outstanding precision and well describable peak shape) and an isotope labelling of the water radicals by D_2O (high scattering cross section for neutron radiation) was chosen.

2.1. *Sample preparation*

For comparison both standard sintered bodies as well as conditioned powders had to be processed.

Fig. 1 show a process scheme for the model experiment comparing the sample preparation and corrosion test for a sintered body with that of conditioned powder.

The ceramic bodies were made from commercial 3 mol% yttria stabilised zirconia powder (Tosoh, Japan). For dense materials the powders were isostatically compacted at 600 MPa and sintered in air at 1400 °C for 2 h (Nabertherm, Germany). During sintering both densification and homogenisation occurred which led to microstructure of approximately 0.3 μm grain size. The stabiliser was entirely homogenised and the material showed only the reflexes of the t-phase in the diffractogram.

In contrast, common commercial zirconia powders show a relatively wide distribution in stabiliser content.[14] The primary particles are in the size range of 100 nm but being interconnected to form particles and agglomerates. Additionally these starting powders are multiphase materials. In standard processes the homogenisation proceeds during sintering, finally showing a single phase tetragonal XRD spectrum. For this experiment, one had to find a compromise between small unconstrained particles on the one hand and a homogenised, single phase composition on the other hand. Thus, the starting powder (wide distribution, t-phase with about 25% of m-phase) needed to be conditioned prior to the neutron experiments (1200 °C for 4 h in air). The material was then single phase tetragonal with sharp XRD peaks. This temperature is high enough to reach the tetragonal phase field and enabled a certain amount of homogenisation by diffusion. As a consequence, the particle sizes were in the range of 200 nm which matches well to the size of a nucleus of the m-phase in t-ZrO_2.[15] The growth of the particles from 100 to about 200 nm had be traded in for reaching chemical homogeneity.

This conditioned powder as well as the sintered and polished bodies were exposed to D_2O in a 100 ml PTFE-lined autoclave for 2 h at 200 °C, which created a vapour pressure of 16 bar. The powder was filtered, dried at room temper-

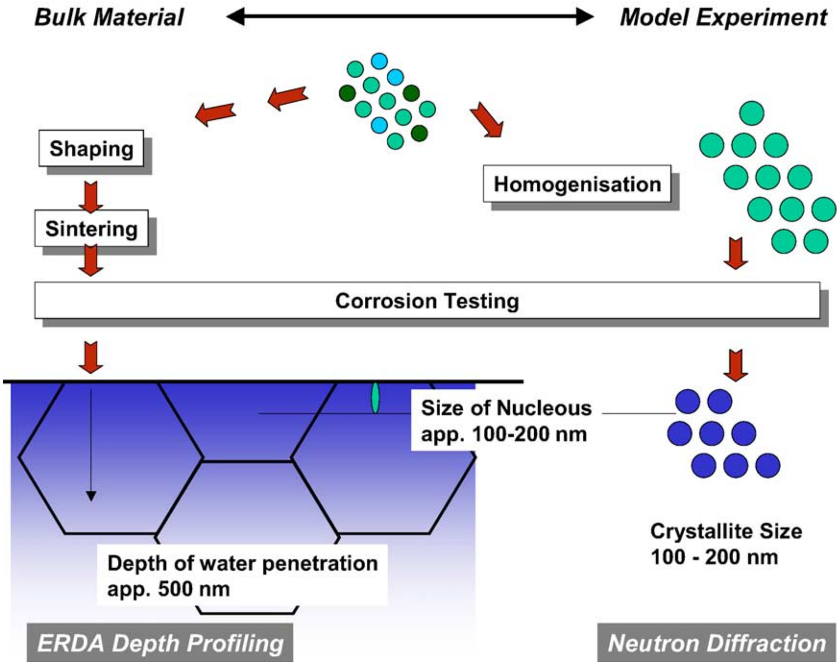

Fig. 1. Flow diagram for the preparation of water-treated (D_2O and H_2O) specimens for ERDA depth profiling (left part of the diagram) as compared to neutron measurements (right part of the diagram).

ature for a short time and finally sealed in a vacuum tight PE bag. For comparison a reference sample was prepared without water-loading. This set of samples was used for the neutron experiments. A refinement of all structural parameter was not possible because of the high incoherent scattering cross section of H, but a determination of simple lattice parameters was possible.

For comparison with technical corrosion a further set of powder specimens was prepared using H_2O (high purity distilled water) for hydrothermal treatment.

2.2. Neutron experiments

The neutron measurements have been carried out with at the powder diffractometer MAN I located at the research reactor FRM I[1] using a wavelength of 0.1075 nm from a Cu(2 2 0) monochromator. The diagrams were recorded in the angular range $2\Theta = 10–105^\circ$ using a step width $\Delta(2\Theta) = 0.1^\circ$. Further experimental details are given in.[16,17] The data were evaluated using a multiphase Rietveld program in a version of Wiles and Young.[18] The peaks were fitted with a pseudo-Voigt function $\eta G + (1 - \eta)L$ (with $0 \leq \eta \leq 1$), where G and L denote a Gaussian and Lorentzian function, respectively, but the peak profiles turned out to be basically Gaussian-shaped. The variation of their widths with scattering angle 2Θ is described by the formula

$$\Delta(2\Theta)_{\mathrm{p}}^2 = Utg^2\Theta + Vtg\Theta + W$$

Refinements of various structural parameter were carried out within the space group $P4_2/nmc$ (t-ZrO_2), in detail:

- the structural parameter z(O), the only free atomic co-ordinate,
- an occupation parameter of the oxygen site N_O to take care of oxygen vacancies and a possible occupation of this site by H/D atoms or OH groups (see below),
- the isotropic atomic displacement parameters $B_{Zr/Y}$ and B_O,
- the lattice constants a and c, and the instrumental parameters U, V, W are free parameters in the refinements.

The background is refined by a polynomial. The refinements converged with weighted profile R-factors of 4.82 and 2.72, goodness-of-fit values of 1.49 and 1.13, and intensity related R_{Bragg}-factors of 2.39 and 3.36, respectively.

3. Results and discussion

3.1. Neutron experiments

The evaluation of the neutron data showed only small effects of the lattice constant changes as given in Table 1.

The same tendency can be observed by considering the z(O) parameter which changes from 0.4588(2) to 0.4601(4) in the water-loaded sample (cubic: $z(O) = 0.5$). The occupancy of the oxygen site is 1.99(1) corresponding to the O-vacancies in the reference sample, and 2.01(2) in the water-loaded sample. For the tetragonal zirconia with a homogeneous distribution given stabiliser a content a solid so-

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[1] This reactor was shut down in summer 2000.

Table 1
Lattice parameters of zirconia as derived from neutron measurements for reference material as compared to H_2O- and D_2O-treated, cf.[16,17]

	Reference	H_2O-treated	D_2O-treated
a (pm)	360.47(1)	359.88(3)	360.55(3)
b (pm)	517.05(3)	515.79(6)	516.92(7)
c/a	1.014258(7)	1.01344(15)	1.01377(17)
O(z) position	0.4588(2)		0.4601(4)
B-factor ($10^{-2}\ nm^2$)	0.81(2)		1.15(2)
Occupancy of the O-site	1.99(1)		2.01(2)

lution with a defect model

$$Y_2O_3 \underset{ZrO_2}{\rightarrow} 2Y''_{Zr} 1V_O^{\bullet\bullet} 3O_O^x$$

may be assumed which leads to a solid solution

$$Zr_{1-x}Y_xV_{x/2}O_{2-x/2}$$

Thus, for a stabiliser content of 3 mol% Y_2O_3 the theoretical value for the occupancy of the oxygen site is 1.985. The measured number of the reference specimen is within the error bars, however, the occupancy of the D_2O treated specimen is slightly higher. The refinement of the population of particular sites is basically a refinement of "scattering power" at these sites. The ratio of the scattering power $\sigma(D)/\sigma(O)$ is $(0.62/0.58)^2 \approx 1.15$ which gives, therefore, a hint that the O-site is populated by some amount of D or OD or D_2O. Concomitantly the (overall) atomic displacement parameter B_O of the O/D-atoms increases from $0.81(2) \times 10^{-2}$ to $1.15(5) \times 10^{-2}\ nm^2$ indicating some "smearing" of the location of the scatterers at this site.

The stability of a free unconstrained powder particle should be determined by ΔG_{Chem} only.[1–4] Even under the influence of water radicals these materials should not transform. The phase analysis however, showed a content of 18.8(6) vol.% m-phase which is much less as compared to dense ceramic bodies (60–80 vol.%). Thus, a small strain hindrance must be taken into account, which is in accordance to the increase of particle size from 100 to 200 nm most probably due to agglomeration.

3.2. Stress evaluation

Apparently the water radicals lead to a change in lattice parameters which shows basically a lattice contraction of a tetragonal unit cell. The material remains in the t-modification. The change of the dimensions can be described by a shape change tensor ε_{korr} which contains only components

$$e_{11} = e_{22} = \frac{\Delta a}{a} \quad \text{for the } a \text{ as well as the } b\text{-axis and}$$

$$e_{33} = \frac{\Delta c}{c} \quad \text{for the } c\text{-axis.}$$

The strain in the material after treatment with H_2O and D_2O are different, i.e. the strain is larger for the H_2O system. NMR studies in literature[19] showed a larger anion–anion-distance of adjacent OH/OD groups for the D-case. This might explain the smaller strain for the D_2O treated specimen, but more investigation are required to proof the assumption. Thus, the denoted tensor was derived from the data of the H_2O-treated material, because of the comparability with technical cases and practical relevance.

$$\varepsilon_{korr} = \begin{vmatrix} -0.0016 & & \\ & -0.0016 & \\ & & -0.0024 \end{vmatrix}$$

The error of these numbers is mainly determined by the difference between the lattice parameter of the treated material and that of the reference (small difference of large numbers). The standard deviations of the neutron measurements are quite small as compared to those of standard XRD. Nevertheless an error of up to 10% for strain values has to be taken into account.

This strain tensor was gained from comparably free and mostly unconstrained powder particles. It describes the strain of a surface volume element of a Y-TZP material when water radicals are penetrating the lattice, but without any strain hindrance. In the real situation of a sintered body, the surface grains are highly strain hindered. A first estimation on the maximum stresses can be done using Hooke's law $\sigma = \varepsilon E$ use to find maximum stresses

$$\sigma_{korr} = \varepsilon_{korr} E$$

with ε_{korr} being the tensor as denoted above. For TZP a Young's modulus E of 200 GPa may be used.[20,21]

$$\sigma_a = \sigma_b \cong 328\ \text{MPa}$$

$$\sigma_c \cong 488\ \text{MPa}$$

These numbers, however, have to be seen as guiding values which are carrying high experimental errors. Since the assumed Young's modulus will also carry an error of about 5% and other influences are of importance a total error of up to 20% has to be taken into account for stress values.

In spite of the uncertainties the level of these stresses is quite high and reaches more than a third of the strength. Their level is comparable to the microstructural stresses as published by.[4]

3.3. Free energy considerations

In spite of the small changes and the high error of the stress values, the role of water may be interpreted as further increase of the difference in free energy. The water penetrating into the zirconia surface leads to a substantial increase in stresses σ_{ij}. These additional stresses are primarily tensile stresses, which are destabilising the t-phase.

The total stress state of a t-grain is given by superposition of the processing related Eigenstresses and the additional contribution σ_{korr}. This is visualised in Fig. 2.

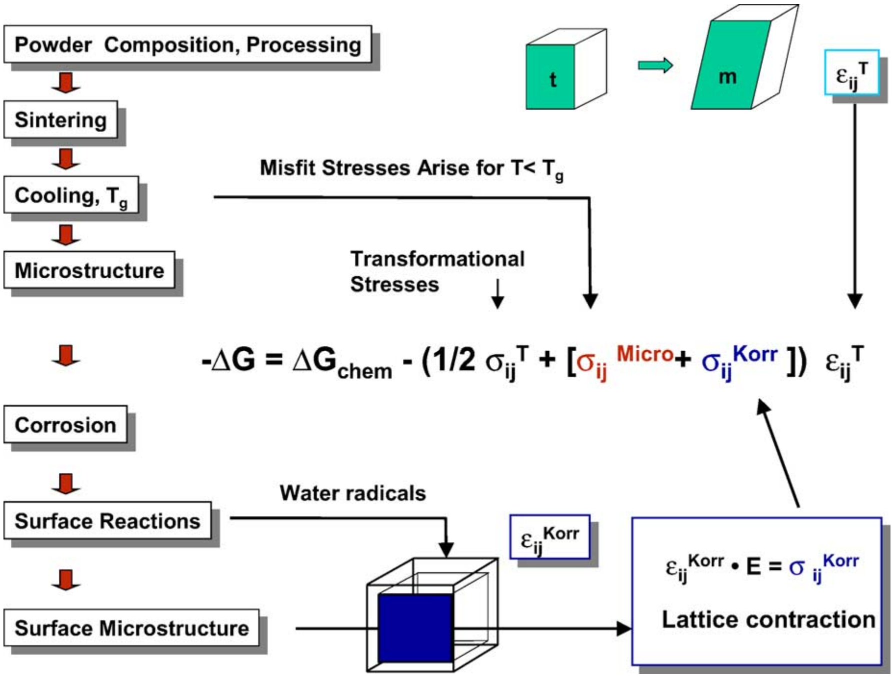

Fig. 2. Scheme for various influences on the energy balance, visualised on the basis of a process flow diagram. The upper part show the well described microstructural influence on microstructural development.[2–4] The central discussion considers the competition of transformational stresses σ_{ij} and the Eigenstresses σ_{ij}^{T}. The major influence of water is a contraction of the lattice because of the penetrating water radical. Since the surface is sufficiently strain hindered, the contraction results in a further stress contribution to the Eigenstresses.

The contraction due to proton penetration leads to a greater energy difference ΔG between t- and m-phase. This is clearly destabilising, because a higher energy difference leads to a smaller activation barrier for transformation, and promotes the transformability. The further process is then believed to proceed as described by Matsui et al.[8]

4. Summarising discussion

The water assisted degradation of zirconia can be understood entirely on the basis of martensitic transformations. The general stability of the material is clearly a function of the microstructural parameters and can be understood in a simplified manner as a competition between the transformational stresses σ_{ij}^{T} and process-related microstructural stresses σ_{ij}.

During degradation water radicals are penetrating the lattice of the t-zirconia, as could be shown in previous work using elastic recoil detection analysis (ERDA).[22,23] For these experiments isotope marking for both hydrogen and oxygen was needed in order to distinguish between the contribution of the corrosive atmosphere and contaminants (use of D_2O an $H_2{}^{18}O$). The profile showed a depth of penetration of about 500 nm, which is more than the size of nucleus for martensitic transformations.[15] The concentrations of hydrogen and oxygen are similar and both are in the order of the vacancy concentration of this material. The neutron experiments of this work showed an overpopulation of the oxygen site. Most probably the oxygen of the environmental water atmosphere is then located on vacancy sites and the hydrogen is placed on an adjacent interstitial site. This is further underlined by the higher *B*-factors.

The penetration of water radical leads to a lattice contraction and is deep enough to reach the dimensions of a nucleus. In a strain hindered situation—such as the surface near region—the contraction leads to the formation of tensile stresses. Thus, the term σ_{ij} consists of the stresses as determined by the microstructural parameters after sintering and an additional contribution due to the penetration of water radical. The superposition of a microstructural and a corrosive contribution determines σ_{ij}. Thus, the lattice contraction due to water basically increases the free energy difference between t- and m-phase.

Acknowledgements

This work was subsidised by the Deutsche Forschungsgemeinschaft under grant Schu 679/4-1. . . 3.

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