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Role of H_2O on the degradation process of Y–TZP

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Yttrium-doped tetragonal zirconia (Y–TZP) is expected to be a good structural ceramic material because of its high strength, high toughness and wear resistance. However, the instability (degradation) of Y–TZP around 150 to 400° C in air and above 100° C in water during ageing is a severe problem which must be solved before the direct application of this material.

Since the first report by Kobayashi *et al.* [1], many works [2–16] have been devoted to the study of degradation of Y–TZP. Their phenomological observations are summarized as follows:

1. The degradation proceeds most rapidly at temperatures of 200 to 300° C in (humid) air.
2. The degradation is caused by the t–m transformation accompanying micro- and macro-cracking.
3. The transformation progresses from the surface to the interior of the specimen.
4. Water or water vapour enhances the transformation.
5. The decrease in grain size and the increase in stabilizer content retard the transformation.

In order to explain these observations, some mechanical and chemical degradation mechanisms have been proposed. In the latter, the role of water has been suggested to form OH^- by the chemisorption at the surface of Y–TZP grains [9, 10], or to form $Y(OH)_3$ leading to the depletion of yttrium [12, 13]. In the present study we have examined the effects of H_2O on Y–TZP under hydrothermal conditions to emphasize the influence of water.

The Y–TZP specimen used has similar characteristics to those reported previously [5]; Toray Industries Inc., 2.66 mol % Y_2O_3, sintered 1450° C for 2 h then HIPed at 1400° C under 200 MPa for 1.5 h, grain size ~0.5 μm, bending strength ~140 MPa, $3 \times 4 \times 36\,mm^3$ in size. The specimen was hydrothermally treated in re-distilled water under 5 and 100 MPa for < 48 h in a test-tube type vessel. After the treatment, the vessel was quenched in cold water, and then dried and weighed. The phases present and the lattice parameters were examined by X-ray diffraction using silicon and SiO_2 as the standard materials. Infrared spectroscopy and weight change were also studied for the hydrothermally treated and thereafter reheated samples.

The constituent phases of the starting sintered specimen were 90% tetragonal and 10% cubic. The tetragonal phase was transformed to monoclinic when well ground for X-ray diffraction. Its lattice parameters are given in the first column of the Table I. Hydrothermal treatment brought about the formation of monoclinic phase from the surface to the interior of the specimen. This phase had an expanded lattice compared to the starting lattice regardless of the temperature of the hydrothermal treatment, whereas the cubic phase changed neither in content nor lattice parameter. Subsequent re-heating, at 400° C in vacuum for 6 h or 1300° C in air for 1 h, of the hydrothermally treated samples brought about the returning of the lattice parameters to the original values with a decrease in weight of 0.233 wt %. This reversible expansion and shrinkage of the monoclinic lattice seems to be caused by the introduction and exclusion of OH^- in the lattice. If the depletion of yttrium by the formation of $Y(OH)_3$ or by the dissolution of Y^{3+} had occurred on hydrothermal treatment, such a reversible recovery of the lattice parameters could not be expected in a short period and/or at a lower temperature.

Infrared spectroscopy (Fig. 1) clearly showed the introduction of OH^- by the hydrothermal treatment and the exclusion of OH^- by the subsequent re-heating. Raman spectroscopy also confirmed the existence of OH^- in the sample treated hydrothermally. The above results undoubtedly indicate the introduction of OH^- into the zirconia lattice at least under the hydrothermal conditions studied. According to the weight change, the compositional change caused by H_2O is shown by

$$Zr_{1-x}Y_xO_{2-x/2}\square_{x/2}$$
$$\xrightleftharpoons{\delta H_2O} (Zr_{1-x}Y_x)O_{2-2/x-\delta}(OH)_{2\delta}\square_{x/2-\delta}$$
$$x = 0.0518, \qquad \delta = 0.0159$$

that is, the ≈ 60% oxygen vacancies were occupied by OH^-. These OH^- would migrate faster than O^{2-}, because OH^- has less charge and a size similar to O^{2-}.

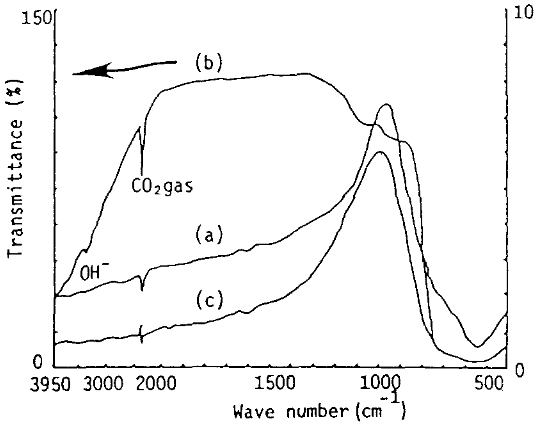

Figure 1 Infrared absorption spectra of the Y–TZP samples, (a) before hydrothermal treatment, (b) hydrothermally treated at 250° C under 100 MPa for 6 h, (c) reheated at 1300° C in air for 1 h.

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TABLE I Latice parameters of monoclinic zirconia phases transformed from tetragonal phase after various treatment

Treatment	Conditions			Lattice parameters				
	Temp. (° C)	Pressure (MPa)	Time (h)	a (nm)	b (nm)	c (nm)	β (deg)	V (nm^3)
Before hydrothermal treatment				0.5165	0.5254	0.5258	98.51	0.1411
Hydrothermal treatment	250	5	6	0.5172	0.5251	0.5281	99.08	0.1416
	250	100	6	0.5174	0.5252	0.5275	99.06	0.1415
	400	100	6	0.5169	0.5246	0.5283	99.10	0.1414
	600	100	6	0.5173	0.5251	0.5276	99.06	0.1415
	800	100	6	0.5172	0.5250	0.5278	99.03	0.1415
	800	5	6	0.5172	0.5246	0.5278	99.06	0.1414
Re-heating after hydrothermal treatment (250° C, 100 MPa)	400	vac	6	0.5169	0.5253	0.5266	98.89	0.1413
	400	vac	10	0.5171	0.5254	0.5265	98.95	0.1413
	1300	air	1	0.5169	0.5250	0.5261	98.49	0.1412

Recently, Lange *et al.* [12] suggested that water vapour drew yttrium out of the solid solution to form $Y(OH)_3$ crystallite of 20 to 50 nm and that the yttrium-depleted volume element can act as monoclinic nuclei. Schubert [13] excluded the hydroxide formation by the diffusion of Y^{3+} because of its extreme slowness, but adopted the formation of $Y(OH)_3$ by faster diffusion of H_2O in the lattice. The existence of H_2O in the zirconia lattices has not yet been confirmed. In addition to this, even if the diffusion of H_2O were fast enough, the formation of $Y(OH)_3$ crystallite must be controlled by the slow diffusion of Y^{3+}. Supposing the $(D_{Y^{3+}})_{250^\circ C} \approx 1 \times 10^{-43}\,\mathrm{cm^2\,sec^{-1}}$ extrapolated from the diffusion coefficient of Y^{3+} in 16 mol % Y–FSZ [17], we can estimate 10^{29} sec ($= 10^{21}$ year) for the time required for 1 nm diffusion according to the relation, $x \approx (Dt)^{1/2}$. The formation of $Y(OH)_3$ crystallite of 20 to 50 nm from the zirconia solid solutions, therefore, cannot be considered as an essential mechanism of the nucleation of the t–m transformation. The dissolution of Y^{3+} in the water is also disproved by analysis of the solvent carried out by Sato and Shimada [9] and our results on the hydrothermal dissolution of YSZ [18].

Based upon the above discussion where anion diffusion (not cation diffusion) should be responsible for the t–m transformation, and the observation that OH^- was formed at the surface and in the lattice of zirconia solid solutions, we propose the following degradation mechanism of Y–TZP by water (Fig. 2):

1st step: the chemical adsorption of H_2O at the surface.

2nd step: the formation of Zr–OH and/or Y–OH at the surface at which points stressed sites are created.

3rd step: the accumulation of the stresses by the migration of OH^- at the surface and in the lattice, to prepare nucleating defects [19].

4th step: the nucleation of monoclinic phase in the tetragonal grains; then the t–m transformation yields micro- and macro-cracking.

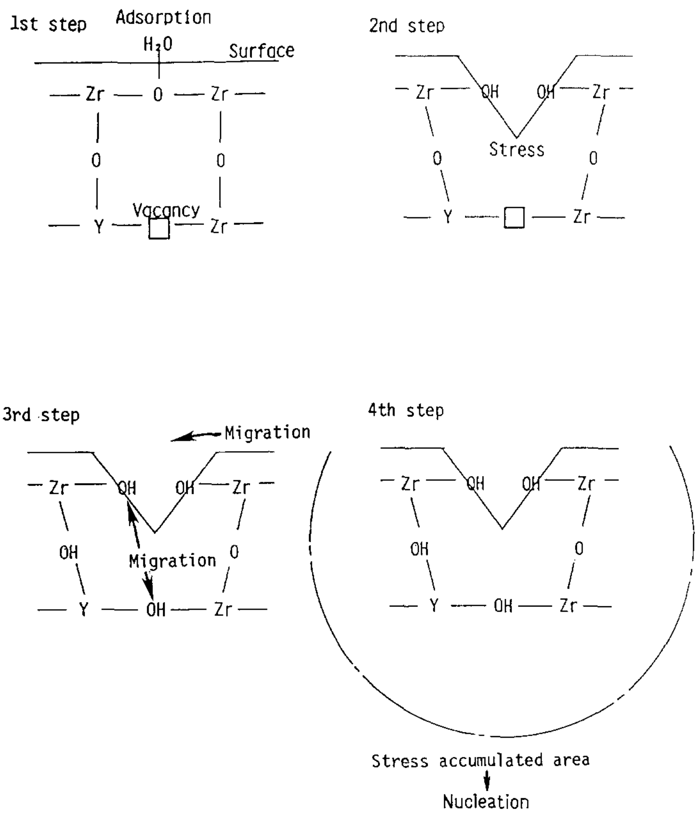

Figure 2 Proposed degradation process of Y–TZP by H_2O.

Saka *et al.* [15] and Nakanishi *et al.* [16] recently supposed the O^{2-} diffusion in the lattice to be responsible for the t–m transformation. But we suggest that OH^- rather than O^{2-} is the key, based upon the present experiments and faster diffusion of OH^- than O^{2-}. The formation of Zr–OH(Y–OH) at the surface of zirconias seems to be completely reasonable, because even hydrogen adsorbed on the surface of ZrO_2 calcined at 700° C can form Zr–OH on heating at 200° C according to the infrared study of Ohnishi *et al.* [15]. Sato and Shimada [9] also suggested the formation of Zr–OH at the surface, but they imagined that the formation of OH^- causes the release of strain which acts to stabilize the tetragonal phase. On the contrary, we think that the formation of Zr–OH brings about the stressed site.

Not only H_2O but also some polar gases such as NH_3 and non-aqueous solvents [9] of the molecules containing a lone-pair electron orbital opposite a proton donor site would also be adsorbed at the surface, and would then cut the Zr–O–Zr(Y) bonds to prepare stressed sites at the surface. Thus they also can enhance the t–m transformation through the accumulation of the stresses. Similarly to these chemical stresses, the mechanical stresses [13, 14] by mismatching the thermal expansion between the matrix and the dispersed grains, and heterogeneous thermal stresses also play a role in triggering the t–m transformation when the accumulated stresses overcome the nucleation barrier. The size, shape and location of t-grains as well as their composition may effect the accumulation of stresses in preparing nucleating defects [19].

As described above, the proposed mechanism seems to be consistent with other phenomenological observations concerning the degradation. A detailed study including macroscopic degradation of Y–TZP under hydrothermal conditions has been published elsewhere [20].

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