Degradation of yttria stabilized zirconia at 370 K under a low applied stress

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Abstract

The tetragonal-to-monoclinic phase transformation in ZrO_2–3mol.%Y_2O_3 containing 0–5% Al_2O_3 during aging in hot water (370 K) under 100 MPa stress is investigated. It is found that while a small tensile stress accelerates the degradation, a compressive stress has little affect on the degradation. The degradation of PSZ under tensile stress is considered to be caused by the reaction between Y_2O_3 and H_2O. Small amount of Al_2O_3 addition does not change the degradation mechanism of PSZ, but it prevents further continuation of degradation when the transformed volume reaches a certain value. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Partially stabilized zirconia has been extensively studied and used in many engineering applications, such as engine parts, valves, and moulds, etc., because of its high strength and good fracture toughness. These excellent mechanical properties are related to the stress-induced martensitic transformation from the metastable tetragonal to stable monoclinic phase. However, these mechanical properties are greatly degraded during aging at relatively low temperatures. Many studies [1–6] on this phenomenon have shown that the degradation is due to the t → m transformation that initiates on the surface and proceeds into the bulk, accompanied by micro- and macro-cracking. The degradation is strongly influenced by: (a) the content of yttria, (b) the grain size, (c) the temperature, and (d) the partial water vapor pressure. Among the additives, such as SiO_2, Fe_2O_3, Al_2O_3, etc., only Al_2O_3 can effectively suppress the degradation [2,7,8]. The main hypotheses to explain the degradation phenomenon can be summarized as follows [2–5]: (1) The transformation is controlled by the breaking of Zr–O–Zr bonds during reaction with water, which would result in a relief of constraint acting on the tetragonal grains and consequently leads to a transformation of the stable monoclinic phase. (2) The nucleation of the monoclinic phase is caused by the strain accumulation due to the diffusion of OH^- by the formation of Zr–OH and Y–OH bonds and the expansion of the lattice. (3) The destabilization of the t-phase is caused by the decrease of yttria content in the tetragonal grains due to the formation of yttrium hydroxide. Although there are many studies on the degradation of PSZ, studies on the degradation under stressed condition are still rather few. Matsui et al. [6] studied creep of Y–TZP under the stress ranging from 200 to 600 MPa. The degradation under small load has not been reported so far.

This paper discusses the effect of small applied stresses, both tensile and compressive (100 MPa), on the degradation of partially stabilized zirconia exposed to low temperature water (370 K). The effect of alumina addition on degradation mechanism has also been investigated.

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2. Experimental

The starting powders of ZrO_2–3 mol.%Y_2O_3 and ZrO_2–3 mol.%Y_2O_3 with Al_2O_3 were prepared by a co-precipitation method using $ZrOCl_2 \cdot 8H_2O$, Y_2O_3 and $Al(NO_3)_3 \cdot 9H_2O$. The greens were taken shape at 200 MPa by CIP, then were sintered burying in ZrO_2 powder at 1723 K for 2 h. The sintered compacts were ground into bars of size $2 \times 3 \times 25$ mm. The relative densities were determined by Archimedes's method. The degradation tests under load were carried out in an experimental setup as shown schematically in Fig. 1. The applied stress was 100 MPa. The specimen was soaked in hot water (370 K) during aging. For comparison, tests were carried out without application of load at the same time. The surface phases were identified by X-ray diffraction analysis. The ratio of monoclinic/(tetragonal + monoclinic) is estimated by Garvie and Nicholson [9]:

$$V_m\% = \frac{I_{m(11\bar{1})} + I_{m(111)}}{I_{t(111)} + I_{m(11\bar{1})} + I_{m(111)}} \times 100\%. \qquad (1)$$

Here $I_{m(11\bar{1})}$ and $I_{m(111)}$ is the diffraction intensity of the monoclinic [11$\bar{1}$] and [111] reflection, respectively. $I_{t(111)}$ is the diffraction intensity of the tetragonal [111] reflection.

3. Results and discussion

3.1. Degradation of Y_2O_3–ZrO_2

The phase content of sintered 3 mol.% Y_2O_3–ZrO_2 detected by XRD is nearly 100% tetragonal zirconia. The relative density is over 99.5%. The transformed volumes under different experimental conditions are shown in Fig. 2. From Fig. 2 we can observe that the transformation from t-ZrO_2 to m-ZrO_2 occurs on the surface after aging in hot water, and the transformed volume increases with the aging time. The amount of m-ZrO_2 under the compressive stress surface is similar to that of the unstressed specimen; but the amount under the tensile stress surface is noticeably higher. The results show that the compressive stress does not affect degradation significantly, but the tensile stress obviously accelerates the degradation of Y-TZP.

From the condition of the stress-induced phase transformation of ZrO_2, the load should be over a critical stress. The value of the critical stress σ_c can be estimated from Eq. (2)[10]:

$$\sigma_c = \beta^2 \sigma^T [K/(K_c - K_0)](1 + v)/3. \qquad (2)$$

Here β is the constant of proportionality. σ^T Is the compressive stress generated by the transformation, K is the stress intensity factor, K_c is the steady-state toughness, K_0 is the toughness of the matrix, and v is the Poisson's ratio.

For a typical example, assuming $\beta^2\sigma^T = 1.9$ GPa, $K_0 = 4$ MPa m$^{1/2}$, $v = 0.31$, $K = K_0$, $K_c = 12$ MPa m^{-2} [10], and σ_c is about 415 MPa. This value is much higher than the applied stress of the present experiment. It illustrates that the experimental load alone cannot induce the transformation. This can also be verified by the loading test at room temperature: there is no monoclinic phase in XRD pattern of the tensile surface under 100 MPa load after 42 h (Fig. 3).

On the other hand, the crack lengths of the sample degraded range from several micrometers to several tens of micrometers when the specimen was exposed test environment for 60 h, under 100 MPa tensile stress (Fig. 4). It is easily proved that the critical stress (σ') extending the crack is much higher than the applied load. ($\sigma' = K/yC^{1/2}$, where K is the stress intensity factor, C is half-length of the crack and y is the geometry factor). So the applied load cannot extend the cracks either.

H₂O (370K)

Compressive surface

Tensile surface

1-pallet   2-container   3-pressure bar
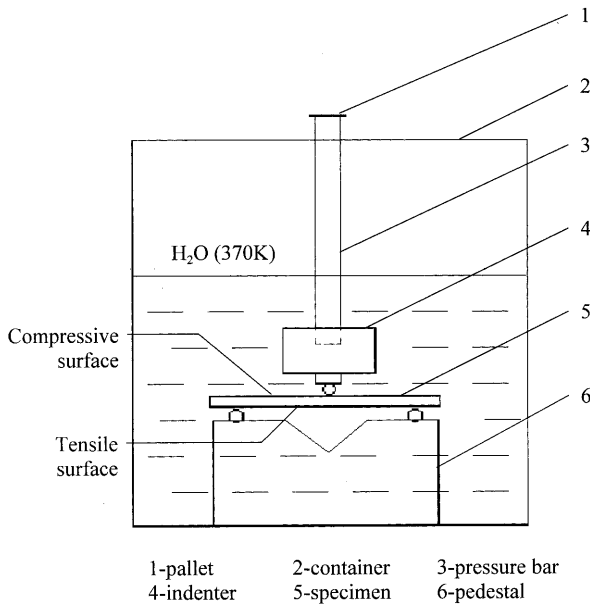4-indenter   5-specimen   6-pedestal

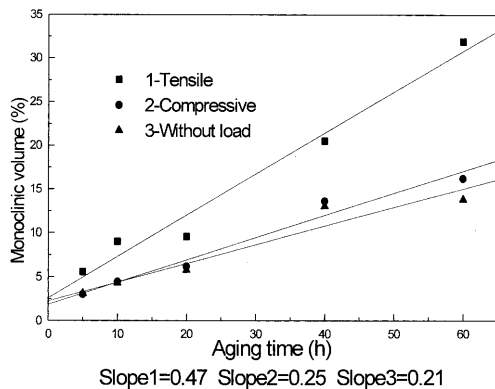Fig. 1. Schematic diagram of the degrading device

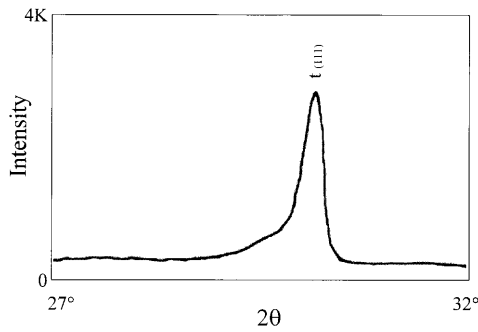Fig. 2. Degradations under different stress conditions.

Fig. 3. XRD of the surface under 100 MPa tensile stress at room temperature after 42 h.
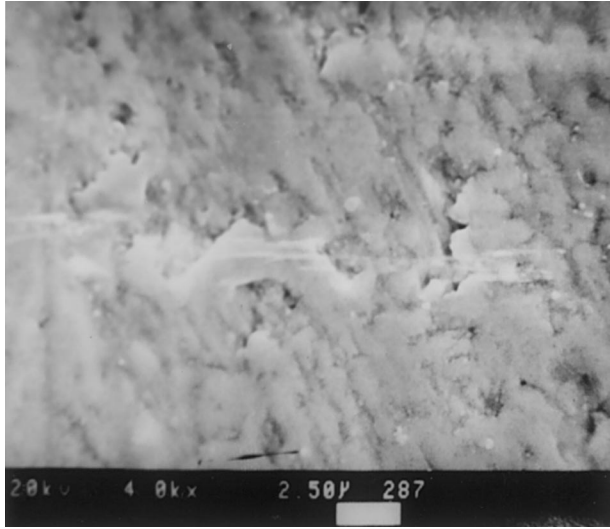

Fig. 4. Cracks on the surface of the sample under 100 MPa tensile stress after 60 h.

From the above discussion, we can conclude that the experimental load cannot induce transformation and extend the cracks. The tensile stress partially contributes to the driving force of the transformation, and then accelerates the degradation.

Comparing the transformation rate, it is known that the rate under 100 MPa of load is almost twice as that of the unstressed condition. It is more difficult to explain this phenomenon using the hypothesis of forming Zr–OH bonds or breaking Zr–O–Zr bonds. The reaction between ZrO_2 and H_2O occurs easily because ZrO_2 is exposed to water. Consequently, the reaction rate should be a constant. The rate of the strain accumulation due to the formation of Zr–OH bonds or the relief of constraint caused by the breaking of Zr–O–Zr bonds should be a constant too. Taking the relief of constrains for example: the unstressed transformation condition is [11]:

$$\Delta G_{chem} - \varepsilon \sigma^T = \Delta G_{chem} - \varepsilon(\sigma_0^T - kt) \leq 0. \qquad (3)$$

Here ΔG_{chem} is the chemical free energy difference between tetragonal and monoclinic phase, ε is the un-

constrained strain, and σ^T is the constraint stress, σ_0^T is the initial constraint stress, k is the constant of the rate, t is the time.

The transformation condition under stress is [11]:

$$\Delta G_{chem} - \varepsilon[\sigma^T + (1/2)\sigma^A]$$
$$= \Delta G_{chem} - \varepsilon[(\sigma_0^T - kt) + (1/2)\sigma^A] \leq 0. \qquad (4)$$

Here σ^A is the applied stress.

From Eqs. (3) and (4) the applied stress that doubles the transformation rate should be half of the critical stress, so the applied stress 100 MPa (nearly 1/4 of the critical stress) is impossible to double the transformation rate. Considering the hypothesis of yttrium hydroxide forming, it is easy to explain such phenomenon in the present case. The reaction between Y_2O_3 and H_2O begins on the sample's surface and the grain boundary that contacts with H_2O, and proceeds into the interior with the propagation of H_2O through the gain boundary and cracks. Y_2O_3 draws out with the reaction. The stability of the tetragonal phase decreases with the decrease of Y_2O_3 in the grains, i.e. $\Delta G \cong T\Delta S$ reduces [12,13]:

$$\Delta G \cong T\Delta S \qquad (5)$$

Here ΔS is the change of the entropy with the decrease of Y_2O_3, and T is the temperature.

According to statistical thermodynamics, we get Eq. (6) considering $ZrO_2–Y_2O_3$ as an ideal solid solution:

$$\Delta S' = -R[y \ln y + (1 - y) \ln (1 - y)] + yC. \qquad (6)$$

Here $\Delta S'$ is the change of the entropy of $ZrO_2–Y_2O_3$ with the change of Y_2O_3 content, C is a constant, which is the difference of entropy per mole between Y_2O_3 and ZrO_2 ($C \cong 58$ J K^{-1} mol^{-1}) [14], R is the gas constant, and y is the content of Y_2O_3, $y < 0.03$ in the present work.

Then:

$$\Delta S \cong (-R \ln y + R + C)y.$$

$\Delta S'$ can be considered to be approximately proportion to y in the present work (we know the t-phase of ZrO_2 will spontaneously transform to the m-phase when the content of Y_2O_3 is below 1.6 mol.% [15,16], so we assume $0.016 < y < 0.03$, then $(-R \ln y + R + C)$ changes very little when y changes in this range. We can express it as a constant A). The ΔS in Eq. (5) can be expressed as $\Delta S = A(y - 0.03)$. Here $(y - 0.03)$ is the decrease of Y_2O_3. The required emergence of Y_2O_3 with 100 MPa stress (only 1/4 of the critical stress) is about three-fourth of that of unstressed condition. But the emergence rate is not linear. It is faster at the beginning, and then slows down with the reaction because Y_2O_3 is dissolved in solid ZrO_2. The period before the transformation begins would shorten to half of that of the unstressed condition. From the above discussion it can be concluded that the degradation under stress is caused by the reaction between Y_2O_3 and H_2O.

3.2. Effect of Al_2O_3

The relative density of the samples with 5% Al_2O_3 and 3% Al_2O_3 is 94 and 90%, respectively (the theoretical densities are calculated by the mixture rule). The surface phase is not 100% tetragonal zirconia. There is a small amount of monoclinic phase present (this would be caused by the stress due to the difference in the expansion coefficients between Al_2O_3 and t-ZrO_2). The relationship between the transformed volume and the aging time of the unstressed samples with 5% Al_2O_3 and without Al_2O_3 is shown in Fig. 5. We can see that the slopes of the two lines are very similar. This shows that Al_2O_3 has no apparent effect on the degradation without applied stress at the beginning. The degradation mechanism of ZrO_2 (Y_2O_3) ceramic does not change with Al_2O_3 addition. Fig. 6 shows the loaded degradation with different amounts of Al_2O_3 addition. The monoclinic volume of the samples with Al_2O_3
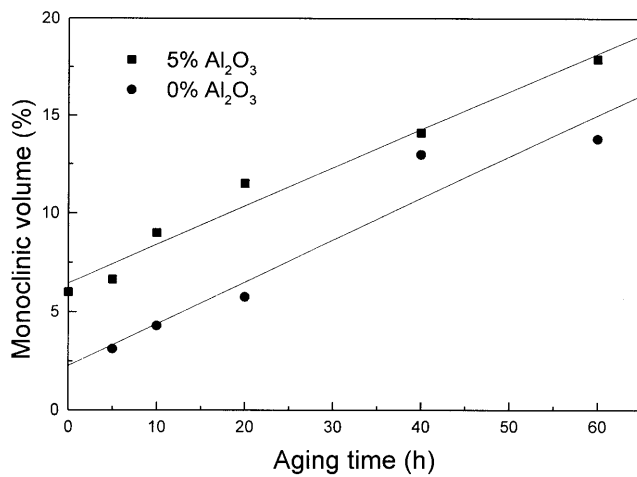

Fig. 5. Degradations in the unstressed condition with different amounts of Al_2O_3 addition.
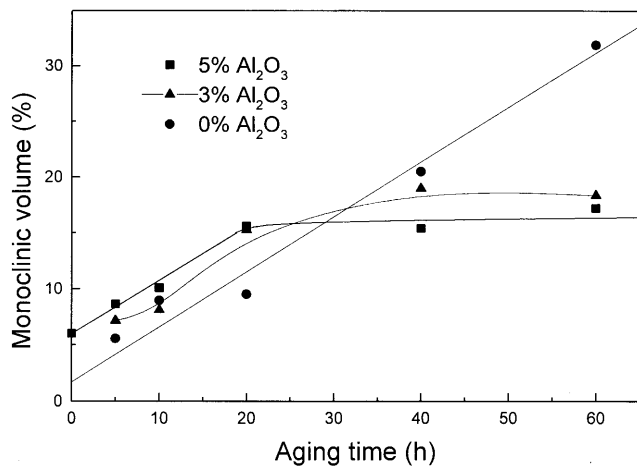

Fig. 6. Degradations with applied stressed with different amounts of Al_2O_3 addition.

quickly increases with the aging time at the initial period, and then almost remains at a constant level. However, the monoclinic volume of the sample without Al_2O_3 steadily increases with the aging time. This shows that the tensile stress can still accelerate the degradation, and Al_2O_3 can effectively suppress further degradation under load. It should be pointed out that the degradation rates with different amounts of Al_2O_3 addition at the beginning are similar. This indicates that Al_2O_3 has no obvious effect on the loaded degradation at the beginning.

Al_2O_3 has a high elastic modulus, and usually segregates at grain boundaries in PSZ [7,8]. It would constrain t-ZrO_2 and prevent the phase transformation. In the present work, the constraint is very weak due to the low relative density at the beginning. When the transformed volume reaches a certain level the constraint would be enhanced, therefore, further phase transformation is suppressed. More over, segregation of Al_2O_3 at the grain boundary blocks the transportation of H_2O into the interior when the transformation reaches a certain level. The reaction between H_2O and Y_2O_3 would be stopped. The degradation then stops.

4. Conclusions

A small applied tensile stress improves the driving force of the phase transformation and accelerates the tetragonal-to-monotonic phase transformation with aging in hot water. However, a compressive stress has no obvious effect on the degradation.

The degradation of Y_2O_3–ZrO_2 under the applied stress is caused by the reaction between H_2O and Y_2O_3, which leads to the decrease of the t–ZrO_2 stability.

The addition of Al_2O_3 does not change the degradation mechanism of Y_2O_3–ZrO_2, but it can prevent further degradation when the transformed volume reached a certain value.

References

[1] K. Kobayashi, H. Kuwajima, T. Masak, Solid State Ion. 3–4 (1981) 489–493.
[2] T. Sato, M. Shimada, J. Am. Ceram. Soc. 68 (6) (1985) 356–359.
[3] F.F. Lange, G.L. Dunlop, B.I Davis, J. Am. Ceram. Soc. 69 (3) (1986) 237–240.
[4] M. Yoshimura, T. Noma, K. Kawabata, S. Somiya, J. Mater. Sci. Lett. 6 (1987) 465–467.
[5] J. Li, R. Watanabe, J. Am. Ceram. Soc. 79 (12) (1996) 3109–3112.
[6] M. Matsui, T. Soma, I. Oda, J. Am. Ceram. Soc. 69 (3) (1986) 198–202.
[7] J. Li, R. Watanable, J. Mater. Sci. 32 (1996) 1149–1153.
[8] H. Tsubakino, R. Nozato, M. Hamamoto, J. Am. Ceram. Soc. 74 (2) (1991) 440–443.

[9] R.C. Garvie, P.S. Nicholson, J. Am. Ceram. Soc. 55 (6) (1972) 303–305.

[10] M.V. Swain, L.R.F. Rose, J. Am. Ceram. Soc. 69 (7) (1986) 511–518.

[11] A.G. Evans, A.H. Heuer, J. Am. Ceram. Soc. 63 (5–6) (1980) 241–248.

[12] A.G. Evans, R.M. Cannon, Acta Metall. 34 (5) (1986) 761–800.

[13] S. Schmauder, H. Schubert, J. Am. Ceram. Soc. 69 (7) (1986) 534–540.

[14] D. Ye, Applied Thermochemical Properties of Inorganic Substances (in Chinese), Metallurgical Industry Press, Beijing, China, 1979.

[15] R. Ruh, K.S. Mazdiyasni, P.G. Valentine, H.O. Bielstein, J. Am. Ceram. Soc. 67 (9) (1984) C190–192.

[16] F.F. Lange, J. Am. Ceram. Soc. 69 (3) (1986) 240–242.