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Ageing of Zirconia-Toughened Alumina Ceramics under Different Hydrothermal Conditions

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Abstract

Changes in the crystalline phases of ZrO_2 in different zirconia-toughened alumina (ZTA) compositions were studied at lower temperature (150–250°C) by exposing them in a stream of humid air for a period of 24 h. Fresh samples of these compositions were also aged in an autoclave with superheated water for 2·5 h in the same temperature range, and the degree of phase transformation was compared with data from the previous samples to establish the effect of pressure on this phenomenon. It was observed for all the ZTA compositions that phase transformation increased monotonically with ageing time, temperature and pressure, although for the compositions with a lower percentage (15 vol%) of zirconia (3 mol% Y_2O_3), ageing in an autoclave was more detrimental particularly at lower temperature. As the ageing temperature increased in the composition with 15 vol% ZrO_2 (3 mol% Y_2O_3), the influence of ageing duration on phase transformation of ZrO_2 increased and the effect for 24 h of exposure time was found to be even more catastrophic than that of autoclave pressure at 250°C. On the other hand, for the ZTA compositions containing more than 15 vol% zirconia (3 mol% Y_2O_3), the damaging effect of ageing in the autoclave was greater and this difference increased with increase in temperature.

1 Introduction

Y_2O_3-doped partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZP) have found application in different engineering fields as a result of their favourable room temperature mechanical properties.[1,2] High transverse rupture strength (TRS) and fracture toughness of these ceramics have been considered to be due to stress-induced martensitic transformation of the zirconia phase from its metastable tetragonal to the stable monoclinic state.[3–7] However, the use of these ceramics in the temperature range from 150 to 300°C has been reported to be severely limited as a result of degradation in mechanical properties,[8–10] due to the instantaneous phase transformation of zirconia resulting from microcracks on the surface. This degradation effect has been reported to be more severe in humid atmosphere[11–16] and even in hot non-aqueous solutions[17] of glycol, glycerol, propylamine, etc. A number of studies has been conducted to eliminate the ageing effect on Y_2O_3-doped PSZ or TZP[18,19] and it has been claimed that this degradation phenomenon can be greatly reduced by either replacing Y_2O_3 completely or partially by CeO_2, or by adding alumina in zirconia matrix.[20]

It has been reported[21,22] that the dispersion of metastable tetragonal zirconia in an alumina matrix can form a new class of ceramics with improved strength and toughness, which shows much better resistance to ageing even under humid conditions.[23] However, there has not been any systematic and extensive study on the ageing behaviour of zirconia-toughened alumina (ZTA) in hydrothermal conditions under simultaneous exposure to elevated temperature and pressure. In the present study different ZTA samples with varied amount of yttria-stabilized ZrO_2 (3Y-TZP) additions were aged in a stream of humid air in the temperature range from 150 to 250°C for 6 to 24 h. Similar samples were aged in an autoclave for 2·5 h and the effect of pressure and ageing duration on the degree of phase transformation was studied.

2 Experimental Procedure

Different ZTA compositions having 5, 10, 12, 15 and 20 vol% 3Y-TZP were prepared by milling in a planetary mill in isopropanol medium. Starting materials were A-16 grade of alumina (Alcoa, USA) having crystallite size of 7000 Å and 3Y-TZP (Tosoh Corporation, Japan) having 278 Å

Table 1. Chemical analysis of Alumina and 3Y-TZP powders, and some physical properties

Constitutent (wt%)	*Alumina*	*3Y-TZP*
Y_2O_3	–	5·07
Al_2O_3	–	0·005
ZrO_2	–	–
SiO_2	0·020	0·002
Fe_2O_3	0·006	0·002
Na_2O	0·070	0·015
Loss on ignition	—	0·710
Crystallite size (Å)	7000	278
Specific surface area ($m^2\ g^{-1}$)	—	15·4

crystallite size. Chemical analysis of these materials is given in Table 1. Test samples in the form of plates (20 × 20 × 3 mm^3) and bars (55 × 4·5 × 3·5 mm^3) were prepared in a single-acting hydraulic press at 100 MPa. The green samples were sintered at 1550°C with 1 h soaking. The bulk density of the sintered samples was measured by Archimedes' principle and thereafter the samples were thoroughly characterized for different mechanical properties (Table 2). Subsequently the samples were polished down to 0·5 μm surface finish (R_A). Photomicrographs of the polished and thermally etched samples were taken in a scanning electron microscope. The grain size was measured by the line intercept method.[24] The polished samples were aged in an air–steam mixture of controlled humidity with a steam flow rate of 10 $cm^3\ min^{-1}$ at 150, 200 and 250°C for 6 to 24 h. Fresh samples were subsequently aged in an autoclave at three different hydrothermal conditions—150°C/1MPa, 200°C/2MPa and 250°C/4MPa—to study the effect of pressure. In these cases the period of exposure was 2·5 h. The phases were identified by X-ray diffraction analysis on the plate surface before and after ageing, and the *m*-ZrO_2 content was determined by the Garvie–Nicholson method.[25]

3 Results and Discussion

Figure 1 presents the effect of 3Y-TZP content on the phase transformation of different ZTA compositions due to ageing at 150°C in a stream of humid air for up to 24 h and in an autoclave at the same temperature involving additional pressure

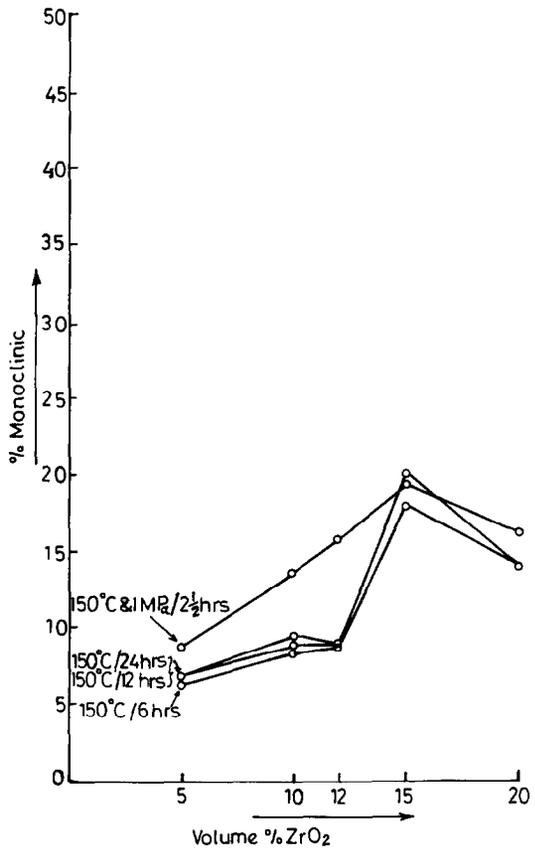

Fig. 1. Effect of ZrO_2 content on the phase transformation of different ZTA compositions when aged at 150°C in humid conditions for up to 24 h and at 1 MPa pressure for 2·5 h.

Table 2. Physical properties of different ZTA ceramics

Composition	*m-ZrO_2 content at 0 h ageing (%)*	*Density*			*Hardness (GPa)*	*TRS (MPa)*	*Fracture toughness ($MPa\ m^{1/2}$)*	*Average grain size (μm)*
		Theoretical ($g\ cm^{-3}$)	*Sintered ($g\ cm^{-3}$)*	*Relative (%)*				
A (Al_2O_3 + 5 vol% 3Y-TZP)	5·8	4·09	4·04	0·98	18·52	355·0	4·6	5·5 (Al_2O_3) + 0·5 (ZrO_2)
B (Al_2O_3 + 10 vol% 3Y-TZP)	6·6	4·18	4·13	0·99	17·40	465·0	4·6	4·5 (Al_2O_3) + 0·4 (ZrO_2)
C (Al_2O_3 + 12 vol% 3Y-TZP)	8·6	4·21	4·16	0·99	17·30	525·0	4·7	4·2 (Al_2O_3) + 0·4 (ZrO_2)
D (Al_2O_3 + 15 vol% 3Y-TZP)	10·0	4·26	4·22	0·99	17·00	775·0	5·7	3·5 (Al_2O_3) + 0·35 (ZrO_2)
E (Al_2O_3 + 20 vol% 3Y-TZP)	12·0	4·34	4·28	0·99	16·10	575·0	5·0	2·7 (Al_2O_3) + 0·3 (ZrO_2)

of superheated water. It is clear from the figure that, for 3Y-TZP additions of up to 15 vol%, the ageing effect increased with increasing ageing time and samples aged in the autoclave under pressure always showed a higher extent of phase transformation. At 15 vol% 3Y-TZP content the magnitude of transformation is maximum, and the effect of ageing for 24 h was found to be almost the same as 2·5 h hydrothermal treatment with 1 MPa pressure. Thereafter, i.e. at 20 vol% 3Y-TZP, the ageing effect decreased and the samples aged in the autoclave showed a higher degree of transformation, revealing more predominant damage. Figure 2 reveals that even at 200°C the ageing behaviour of these materials follows a similar trend, although the magnitude of transformation was found to be higher particularly in the composition with higher amount of 3Y-TZP. Furthermore, at this temperature, the difference between the effects of these two types of ageing on phase transformation was found to be much higher in ZTA compositions with 12, 15 and 20 vol% 3Y-TZP when compared with the ageing behaviour at 150°C. Figure 3 shows that during ageing at 250°C either the increase of steam pressure in the autoclave or the exposure time in hydrothermal conditions gives a lower effect up to 12 vol% 3Y-TZP. Moreover, the effect of 24 h of hydrothermal exposure was found to be more detrimental than the autoclave ageing for 15 vol% 3Y-TZP and thereafter both the effects decreased rapidly in such a fashion that the difference increased to the maximum. However, it was surprising to note that in all the cases of ageing in a stream of humid air there is very little difference between the ageing degradation of the compositions with 10 and 12% 3Y-TZP. On the other hand, when they were exposed to ageing in the autoclave, the degree of transformation was found to be much higher with the materials containing 12 vol% 3Y-TZP. Figure 4 presents the effect of 3Y-TZP content on the phase transformation of different ZTA compositions under three different hydrothermal conditions in an autoclave, involving both temperature and pressure. It shows that phase transformation of ZTA compositions was maximum at 15 vol% 3Y-TZP content in each case and for all ageing conditions.

The results indicated that the rigid alumina matrix produced a constraint which restricted the volume expansion involved in the *t–m* phase transformation of ZrO_2. This constraint decreased with increasing ZrO_2 content, resulting in an increase in ageing effect. It may be noted that the ageing effect decreased from 15 to 20 vol% 3Y-TZP addition. Table 2 shows that as the 3Y-TZP content increases in the compositions the

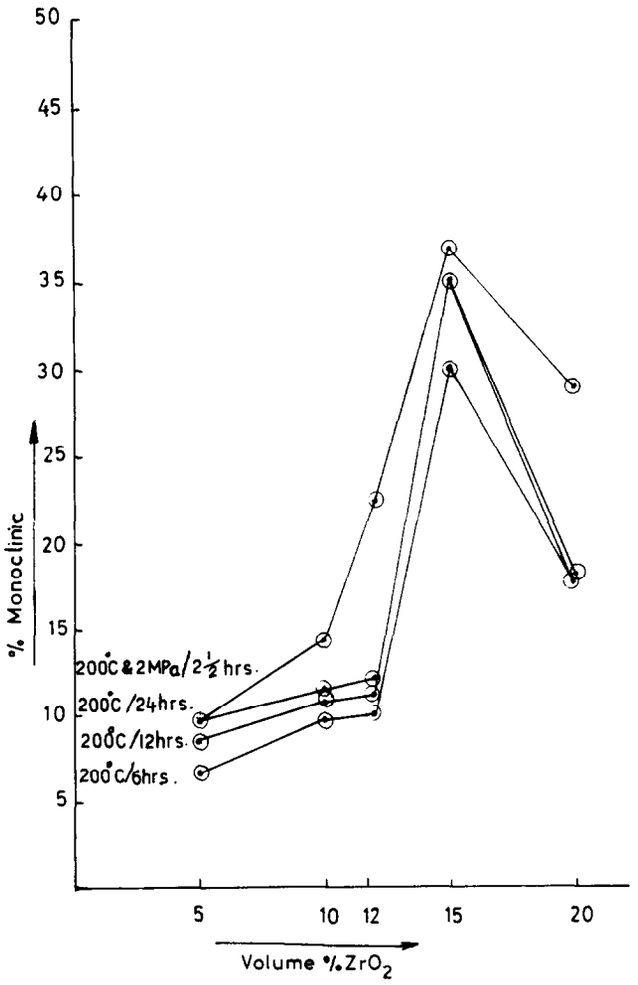

Fig. 2. Effect of ZrO_2 content on the phase transformation of different ZTA compositions when aged at 200°C in humid condition for up to 24 h and at 2 MPa pressure for 2·5 h.

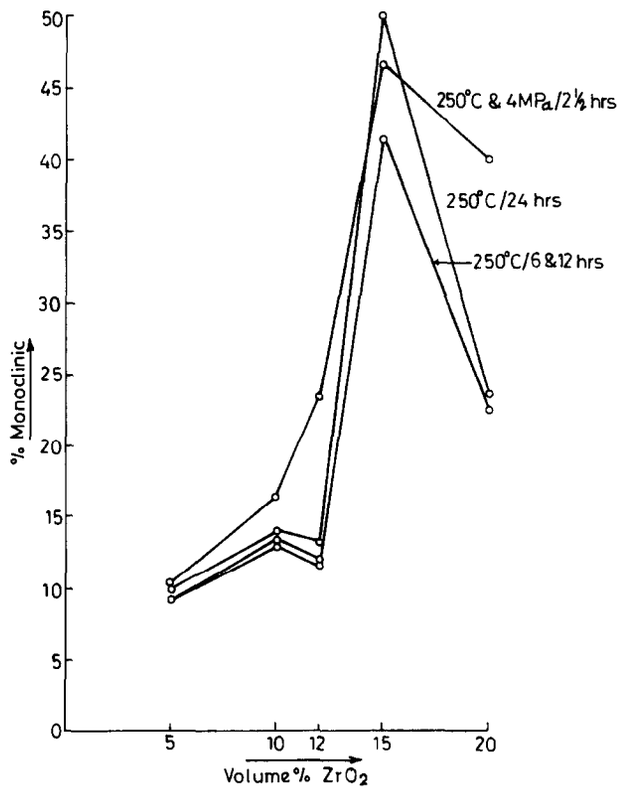

Fig. 3. Effect of ZrO_2 content on the phase transformation of different ZTA compositions when aged at 250°C in humid condition for up to 24 h and at 4 MPa pressure for 2·5 h.

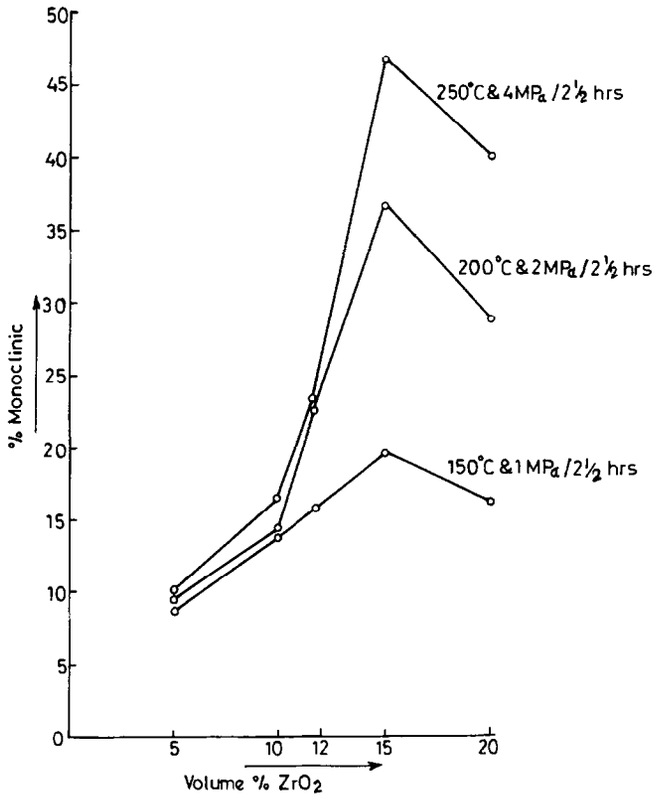

Fig. 4. Effect of ZrO_2 content on the phase transformation of different ZTA compositions under three different hydrothermal conditions: (1) 150°C/ 1 MPa, (2) 200°C/ 2 MPa, (3) 250°C/ 4 MPa.

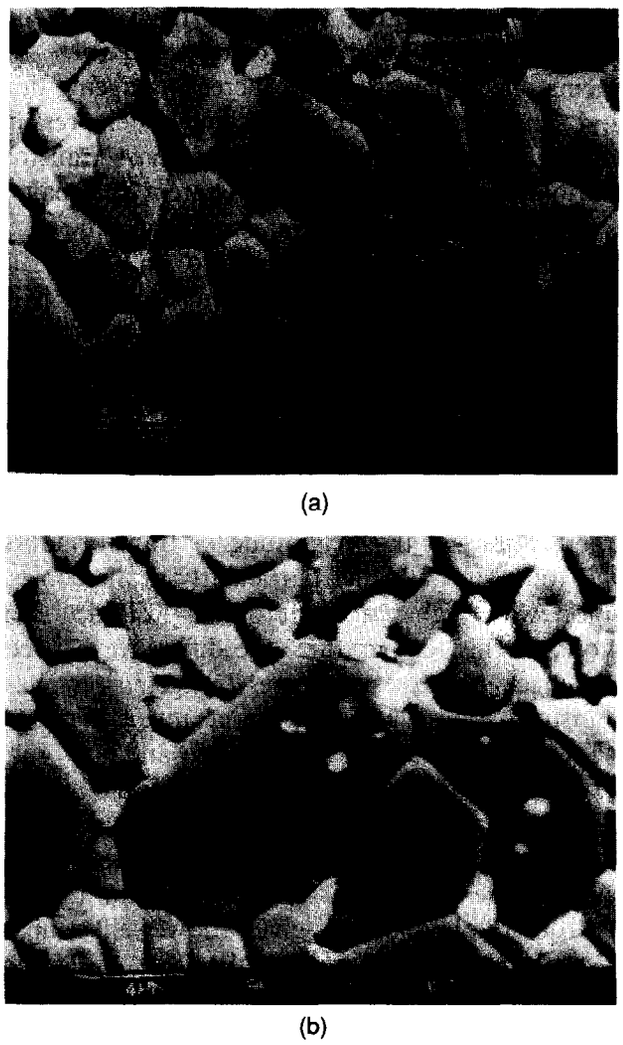

Fig. 5. Scanning electron micrographs of two sintered ZTA compositions: (a) 5 vol% ZrO_2, (b) 15 vol% ZrO_2.

average grain size of ZrO_2 decreases, and as the grain size approaches the critical value (which is between 0·2 and 0·6 μm according to Lange *et al.*[16]) the probability of the stress-induced transformation of the ZrO_2 grains is reduced. This is also reflected in the fracture toughness data of these materials: the fracture toughness decreased after attaining the maximum value at 15 vol% 3Y-TZP addition, thus indicating the reduction in transformability of the zirconia grains due to decrease in grain size. This suggests that lowering the grain size has a more dominant effect than the dilation strain. Further, the results revealed that the effect of pressure was more detrimental in most of the cases although the additional pressure should have restricted this phase change involving volume expansion. It has been hypothesized by Lange *et al.*[16] that water vapour reacts with yttrium in the zirconia to produce clustures of small α -$Y(OH)_3$ crystallites, resulting in a monoclinic nucleus on the surface of an exposed tetragonal grain. The additional pressure within the autoclave probably generated micro- and macrocracks which exposed the subsurface tetragonal grains to the ageing phenomenon, resulting in catastrophic degradation.

Figure 5 represents photomicrographs of two sintered ZTA compositions containing different amounts of 3Y-TZP. Both microstructures exhibited well-dispersed ZrO_2 grains in inter- and intragranular mode in the alumina matrix, and the average size of both the alumina and the zirconia grains was found to decrease with higher 3Y-TZP additions.

4 Conclusions

The tetragonal phase of 3Y-TZP undergoes a phase change during low temperature ageing in humid atmosphere. The degree of phase transformation in all the individual ZTA compositions increased with ageing temperature, duration and pressure. This transformability increased with 3Y-TZP content in the system up to a peak at 15 vol%. Thereafter the smaller grain size of the zirconia led to a greater stability of the tetragonal phase.

The exposure to the pressure of superheated water in the autoclave for 2·5 h greatly increased the ageing kinetics for all the compositions, and the ageing effect was found to be much greater than that of ageing in a stream of humid air even

for 24 h. However, the composition with 15 vol% zirconia addition did not show this behaviour during ageing at 250°C.

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