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Low-temperature ageing of zirconia-toughened mullite composites

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Abstract

The change of mechanical properties of zirconia-toughened mullite composites, aged at low temperature in air, was investigated in this paper. The results indicated that the existence of microcracks, which were formed by the transformation of the zirconia tetragonal phase to the monoclinic during the cooling stage of processing was an important factor for the degradation of mechanical properties during subsequent ageing at 200–300°C. The increasing of flexural strength of the composites aged at 500–600°C was attributed to the relaxation of stress by reverse transformation of ZrO_2. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ageing; Composites; Mechanical properties; Mullite; ZrO_2

1. Introduction

Mullite ceramics have many unique properties, e.g. low thermal expansion and dielectric constant, high melting point, chemical resistance and creep resistance, which made it a potential candidate for several structural applications. However, the low mechanical properties at room temperature have hindered its applications. Therefore, various mullite-based composites have been investigated in order to improve the room temperature properties. Most attention has been paid to mullite matrix composites toughened by the addition of $ZrO_2(Y_2O_3)$ particles, and notable progress has been achieved.[1–4] The retention of the zirconia tetragonal phase in the mullite matrix at room temperature is essential for stress induced transformation of the tetragonal phase to the monoclinic one. However, it has been reported that the fracture toughness and strength of Y-TZP ceramics are greatly degraded by low–temperature ageing at 150–400°C in air or water-containing atmosphere. The loss of strength and toughness is believed to be caused by the tetragonal-to-monoclinic (t→m) phase transformation on the surface of sintered materials.[5–8] Because of the dispersion of tetragonal zirconia grains in the matrices, it is essential to know whether the zirconia-toughened mullite ceramics will also demonstrate similar degradation behavior when aged at low temperature.

The present work was undertaken to study the changes of mechanical properties of zirconia-toughened mullite, with composition 85% vol.% mullite — 15 vol.% zirconia, $ZTM_{15}(Y_2O_3)$, when aged at low temperature.

2. Experimental procedure

2.1. Raw material and sample preparation

The preparation method of ZrO_2 powders containing 2 mol% yttria was by coprecipitation. Fine mullite powder was prepared as in Ref. 9. Powders of ZTM_{15} (Y_2O_3) were milled with ZrO_2 media in alcohol for 4 h. The original powders with average particle size of ZrO_2 $D_{av}=$ 0.62 μm and $D_{av}=0.2$ μm were assigned as $ZTM_{15}(Y_2O_3)^*$ and ZTM_{15} $(Y_2O_3)^{\blacklozenge}$, respectively. The mixed powders were uniaxialy pressed at 50 MPa followed by cold-isostatic pressing at 200 MPa and sintered at 1570°C for 3 h.

2.2. Experimental methods

The pellets (2.5×5×25 mm) were placed in the sealed tubes and then into an electric furnace preheated to the desired temperature. The sealed tubes were removed from the furnace at regular time intervals and cooled to

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room temperature. Ageing temperatures of the polished specimens range from 200 to 600°C in air for a period of several hours to 800 h. The bulk density of the sintered ceramic was measured by the Archimedes method and the grain size was measured by the line intercept method from scanning electron micrographs of the polished surface. Monoclinic phase content was measured by an X-ray diffraction (XRD) technique (D/MAX-2500, CuK_α radiation) and calculated from the modified Garvie and Nichdon equation.[10] The polished samples were thermally etched (100°C lower than the sintering temperature) for 3 h and were examined using scanning electron microscopy (Model S-500).

The thermal expansion in air was determined for a number of specimens using precision dilatometry (LCP-1; heating rate of 10°C/min); the measurement was carried out up to 1000°C.

The strength was measured by three-point bending with a span of 20 mm. The fracture toughness was determined by the single-edged notched beam method. Every strength value reported was the average of at least five samples and every fracture toughness value was obtained from at least four bars.

3. Results and discussion

3.1. Grain size

The relative densities of the sintered bodies were above 97.8% of the theoretical density. On the polished surface of ZTM$_{15}$(2Y)* specimens and ZTM$_{15}$(2Y)◆ specimens sintered at 1570°C for 3 h, the average grain sizes of ZrO$_2$ in the mullite matrix were 1.2 and 1.8 μm, and the tetragonal phase contents were 52.3 and 18.9%, respectively. This indicated that monoclinic ZrO$_2$ was formed after cooling from the sintering temperature, accompanied by microcracks on the surface or within the bodies, especially in the ZTM$_{15}$(2Y)* samples, which have a relatively higher monoclinic ZrO$_2$ content.

Fig. 1a and b give the ageing behaviour for ZTM$_{15}$(2Y)* and ZTM$_{15}$(2Y)◆ when aged at 200, 250, 300, 400, 500 and 600°C, respectively. The amount of monoclinic phase reached the maximum after ageing 50 h, at a value of m-ZrO$_2$ 80.2% for ZTM$_{15}$(2Y)* when aged at 200°C. However, much less transformation to m-ZrO$_2$ was exhibited in the ZTM$_{15}$(2Y)◆ sample, even with prolonged ageing treatment for 800 h at the same temperature (200°C).

In comparison with Y-TZP ceramics, in ZTM(2Y)◆, apart from ageing temperature and grain size of t-ZrO$_2$, microcracks created by the transformation of t→m upon the cooling process after sintering appear to have a definite affect on the transformation during ageing. Because of the presence of microcracks along the grain boundaries in ZTM samples,[11–14] the microcracks opened up more space to accommodate the strains associated with the transformation of the adjacent grains, and was helpful in reducing the strain energy, which stabilized the tetragonal phase. Therefore, the transformation due to ageing occurred preferentially near existing microcracks and accompanied more microcrack formation. It can also explain why the amount of the monoclinic on ZTM$_{15}$(2Y)$*$ surface reached a maximum in a much shorter time than that of ZTM$_{15}$(2Y)◆. On the other hand, most ZrO$_2$ grains are located at the corner of mullite grains, where local tensile stress /strain concentration is easily generated because of thermal expansion coefficients (α) mismatch of t-ZrO$_2$ ($\alpha_a = 11.6\times 10^{-6}$/°C, $\alpha_c = 16.8\times 10^{-6}$/°C) and mullite ($\alpha_a = 4.5\times$

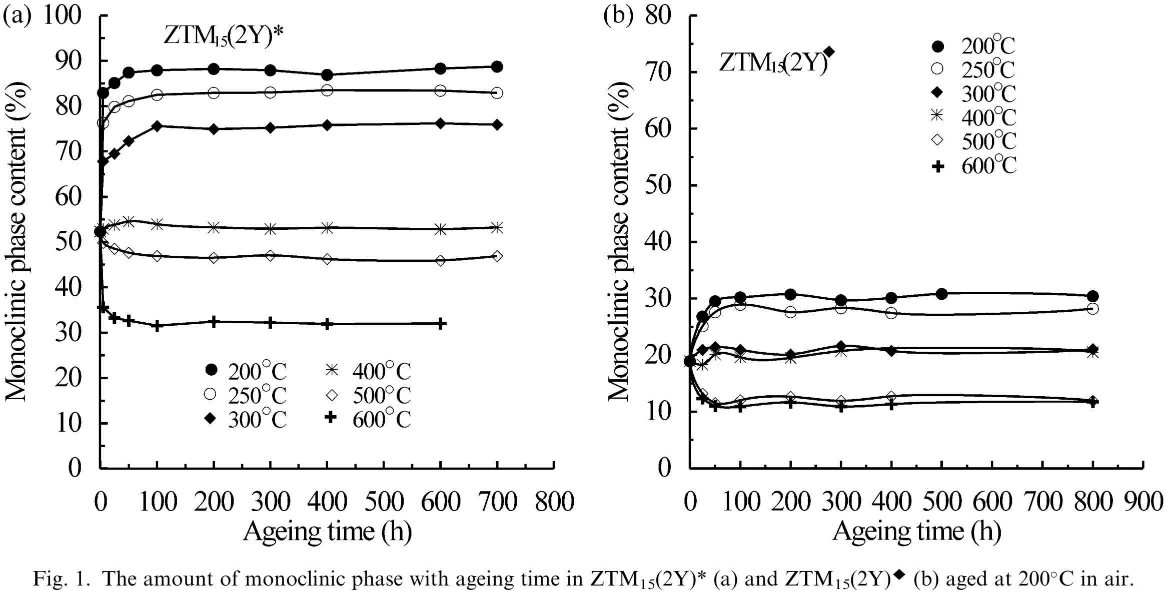

Fig. 1. The amount of monoclinic phase with ageing time in ZTM$_{15}$(2Y)* (a) and ZTM$_{15}$(2Y)◆ (b) aged at 200°C in air.

10^{-6}/°C, $\alpha_c = 5.7\times10^{-6}$/°C).[15] These local stress and strain concentrations could be expected to promote the martensitic transformation during ageing.[16,17]

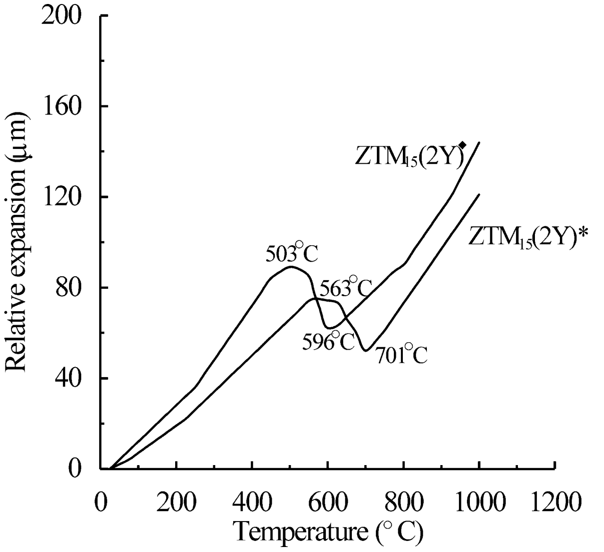

Fig. 2. Linear expansion as a function of temperature for ZTM$_{15}$(2Y)* and ZTM$_{15}$(2Y)$^{\blacklozenge}$.

As most ZrO_2 particles were homogeneously dispersed in mullite matrix, autocatalytic effects existed only in the local region in which t-ZrO_2 grain distribution appeared continuous or in an agglomerate. The transformation of these grains within granules proceeded rapidly by the autocatalytic effect and stopped at the grain boundary of mullite/zirconia. Therefore, the increase in the amount of m-ZrO_2 on the ZTM$_{15}$(2Y)* and ZTM$_{15}$(2Y)$^{\blacklozenge}$ surface was not proportional to the ageing time.

Fig. 2 exhibits thermal expansion behavior, which indicates that a phase transformation takes place upon heating. The increase of the amount of tetragonal phase above 500°C in ZTM$_{15}$ might be attributed to the reverse transformation. We found that the reverse transformation temperature ranges of ZrO_2 in ZTM$_{15}$(2Y)* and ZTM$_{15}$(2Y)$^{\blacklozenge}$ were 563–701°C and 503–596°C, respectively. As a result, in ZTM$_{15}$(2Y) samples, the extent of reverse transformation is believed to be associated with the grain size of ZrO_2 and the existence of microcracks. That is, the smaller the size of the ZrO_2 particles and the lower the volume fraction of the microcracks, the lower was the reverse transformation temperature and more reverse transformation tetragonal phase formed during ageing at 500–600°C.

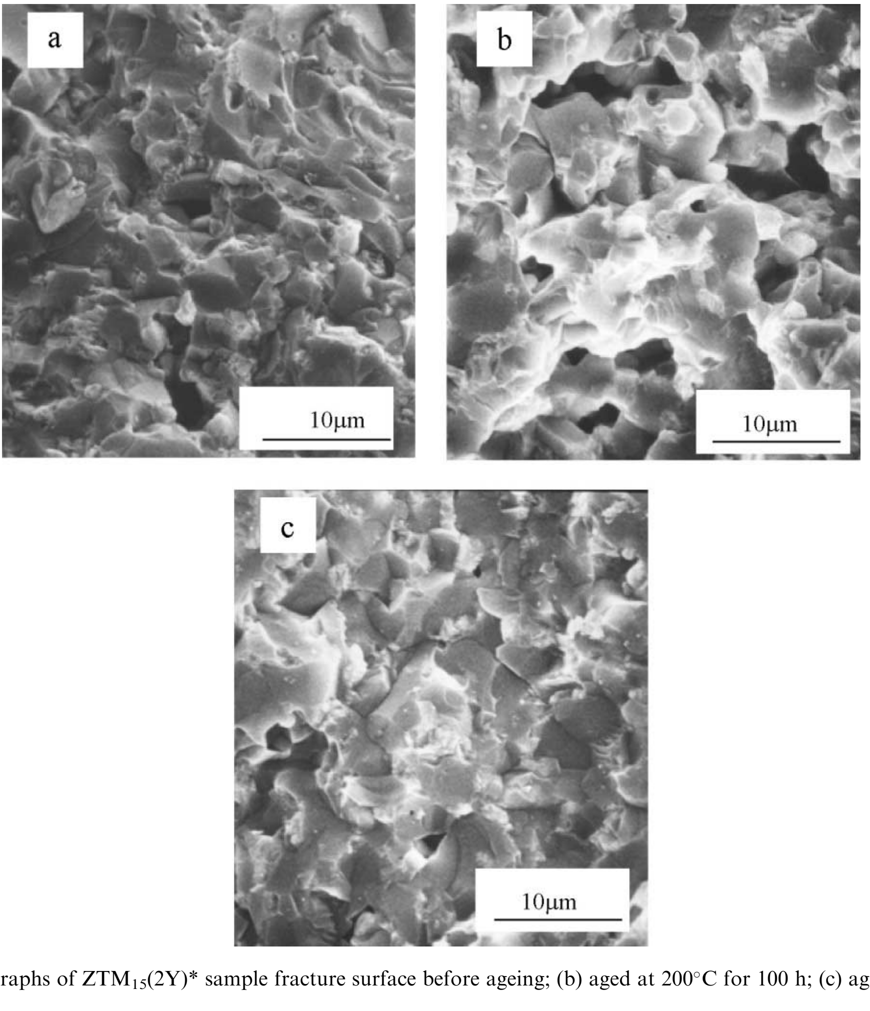

Fig. 3. (a) SEM micrographs of ZTM$_{15}$(2Y)* sample fracture surface before ageing; (b) aged at 200°C for 100 h; (c) aged at 600° C for 300 h.

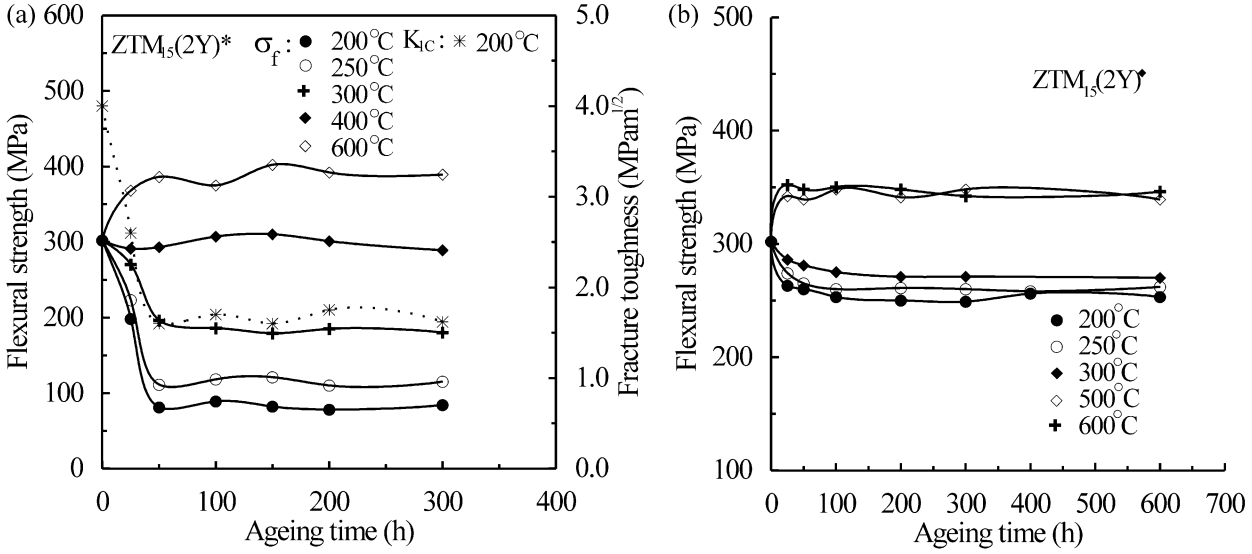

Fig. 4. Mechanical properties of $ZTM_{15}(2Y)^*$ (a) and $ZTM_{15}(2Y)^◆$ samples; (b) aged at different temperatures.

3.2. Microstructure development

The microstructural change of $ZTM_{15}(2Y)^*$ which appeared during isothermal phase transformation due to ageing at 200°C is shown in Fig. 3b. SEM of the fracture surface indicates that there are more pores existing in the matrix after ageing for 100 h. It also indicated that the transformation of t→m proceeded both on the surface and in the body. However, the fracture surface of $ZTM_{15}(2Y)^◆$ aged at the same temperature showed no obvious changes. Therefore, we can conclude that the existence of microcracks in the mullite before ageing is an important factor to induce the transformation of t→m during ageing.

As shown in Fig. 3c, the fracture surface of ZTM_{15} $(2Y)^*$ aged at 600°C for 600 h was similar to the as-sintered samples (Fig. 3a).

3.3. Mechanical properties

For samples of $ZTM_{15}(2Y)^*$ aged at 200 and 250°C, Fig. 4a showed that the mechanical properties decreased sharply, and then kept almost the same with the increase in ageing time. The flexural strength and fracture toughness of as-sintered $ZTM_{15}(2Y)^*$ were 302 MPa and 4.0 MPa $m^{1/2}$, respectively. When samples were subjected to ageing treatment at 200°C for 50 h, the mechanical properties degraded to the minimum K_{1C} of 1.6 MPa $m^{1/2}$ and σ_f of 81 MPa. This coincided with the maximum m-ZrO_2 content as shown in Fig. 1a. However, the mechanical properties of sample $ZTM_{15}(2Y)^◆$ decreased quite slowly. This suggests that the microcracks created by transformation upon cooling would change the transformation conditions of the adjacent tetragonal grains, such as strain energy and strain force between the grains, etc., and consequently accelerate the transformation of tetragonal phase to monoclinic during ageing, generating microcracks and macrocracks on the transformed surface owing to volume expansion upon transformation, and leading to the severe degradation of mechanical properties. However, the flexural strength of $ZTM_{15}(2Y)$ increased when aged at 500–600°C. This might be attributed to the relaxation of stress due to volume shrinkage by reverse transformation.

4. Conclusion

1. Degradation phenomena of mechanical properties occurred in $ZTM_{15}(2Y)$ composites after ageing at 200–300°C. The grain size of the ZrO_2 particles in the mullite matrix and the microcracks formed by transformation of t?m during cooling from sintering temperature have a definite effect on the degradation behavior of $ZTM_{15}(2Y)$.
2. The transformation of tetragonal phase to monoclinic one during ageing proceeded both on the surface and in the body, and an autocatalytic effect existed only in local regions where t-ZrO_2 grain distribution appeared continuous.
3. The increase of flexural strength of $ZTM_{15}(2Y)$ composites aged above 500°C was considered to be achieved by stress relaxation due to volume shrinkage caused by reverse transformation, thereby closing inherent cracks.

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