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The Role of Y_2O_3 in Fine-grained (Y,Mg)-PSZ/$MgAl_2O_4$ During Long Term Heat Treatment

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Abstract: Fine-grained (Y, Mg)-PSZ/$MgAl_2O_4$ ceramics are prepared by coating-coprecipitation technology. This kind of material exhibits very good thermal stability at 1100°C for it possesses strength values over 900 MPa and toughness over 15 MPam$^{1/2}$ even as the ageing time reaches 800 h. The microstructures and phase compositions are examined with XRD, SEM and TEM. The results show that the material derives from a new sub-eutectoid decomposition reaction: c-$ZrO_2 \rightarrow$ c′-ZrO_2 + t-ZrO_2 + MgO, which is different from the thermal decomposition of conventional Mg-PSZ without Y_2O_3 addition. Furthermore, two kinds of precipitations can be detected according to their stabilizer. It is found that the tweed-like and colony-like t-ZrO_2 phases in the ceramics, which are stabilized by Y_2O_3, can grow up and lead to an increase in volume of the transformable t-ZrO_2 with heat treatment. Only the transformable t-ZrO_2, originating from the eutectoid decomposition of Css, plays an important role in toughening the matrix. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

It is well known that the ZrO_2-based ceramics have gained much attention and yielded highly attractive results for a large number of investigations,[1–3] due to their series physical and chemical features, such as hardness, wear-resistance, high elastic modulus, chemical inertness, ionic and electrical properties, creep-resistance, poor thermal conductivity, high melting temperature, especially transformation toughening ability.[4] In these ZrO_2-based ceramics, Mg-PSZ is one of the most important ceramics which has stimulated much interest in research, and in applications. However, upon ageing above 1000°C, Mg-PSZ reveals high temperature degradation[5–7] because of the cubic phase thermal decomposition reaction,[7] so that only material that shows good thermal stability under 800°C is considered.[8]

Recently, progress has been achieved to improve the thermal stability of PSZ at comparatively high temperatures and widen its applications. Claussen *et al.*[9] have discovered that fine-grained PSZ had good thermal stability. This quality has been realized through the process of spontaneously stabilizing zirconia with MgO and Y_2O_3 and by adding appropriate amounts of Al_2O_3. Montross' investigation[10] indicated that the 1.6 mol% Y_2O_3 + 8.75 mol% MgO + 89.65 mol% ZrO_2 ternary compound exhibits toughness which increased constantly with the ageing time up to 5000 h in the temperature range 1000°C–1400°C. Dworak *et al.*[11] studied the thermal stability of (Y,Mg)-PSZ ceramics and concluded that this kind of PSZ can be used to 1250°C, although its bending strength is only about 450 MPa. More recently, Wu Houzheng *et al.*[12] showed that PSZ ceramics which have good mechanical properties and high temperature degradation resistance can be obtained by doping with a certain quantity of a rare-earth oxide, such as Y_2O_3 or CeO_2.

A previous study showed that a material whose composition lies within Y_2O_3–MgO–ZrO_2–Al_2O_3 system and ageing at 1100°C exhibited high temperature degradation resistance.[13] In this paper which represents a continuation of that earlier work, the effect of Y_2O_3 on the mechanical properties and thermal stability of fine-grained (Y,Mg)-PSZ is described, and the microstructure of this kind of PSZ is revealed. For this purpose, Al_2O_3 has been added to compositions for the ZrO_2–MgO–Y_2O_3 system to increase mechanical properties of the material.

2 EXPERIMENTAL PROCEDURE

In this work, the specimen was chosen with the 10/90 mol ratio of MgO/ZrO_2 and 2/98 mol ratio of Y_2O_3/ZrO_2, resulting in the composition of 1·8 mol% Y_2O_3–9.82 mol MgO–88.38 mol% ZrO_2. In addition, a 3.928 mol% Al_2O_3–MgO mixture was added with a 1:1 ratio to form $MgAl_2O_4$ particles during sintering.

The coating-precipitation of $ZrOCl_2$-·$8H_2O$, Y_2O_3, MgO and Al_2O_3 in aqueous solution with NH_4OH was used to prepare homogeneous and active powders. Green bodies were formed by isopressing from calcined, milled powders, and then sintered and solution-treated at 1600°C for 4 h and furnace-cooled to room temperature.

The sintered plates were ground to 5mm by using a diamond wheel and cut to 2.5 mm×5.0 mm ×30 mm test bars. Bars were then buried in MgO powder and heat treated at 1100°C from 20 to 1100 h.

The bending surfaces of the test bars were not polished before the bending test. The bending strength was measured in the three-point bending method with 20 mm span and 0.368 mm min^{-1} loading rate. The fracture toughness was measured in single edge notched beam (SENB) method with 20 mm span and 0.05 mm min^{-1} loading rate. The width of the notch was about 0.2 mm.

The volume densities of the sintered samples were measured by Archimedes' method and the relative densities were calculated. The phase compositions of the as-fired sample and polished and ground surfaces of the aged samples were analyzed by XRD. The monoclinic phase contents of polished and ground surfaces (PSM and GSM) were evaluated using the method proposed by Garvie and Nicholson,[14] and the transformable tetragonal contents (TT) were computered according to the following formula: %GSM-%PSM. Morphology of the as-fired sample etched by HF acid was analyzed by scanning electron microscopy. The microstructures of aged samples were examined by transmission electron microscopy using JEM-200CX. Before being examined, the samples were mechanically polished and dimpled to a thickness of about 20 μm, and then thinned by Ar ion milling (Gatan 610DIF).

3 RESULTS AND DISCUSSION

3.1 Characteristics of as-fired sample

The dense sample with a relative density of 99.6% is obtained after sintering at 1600°C for 4h.

X-ray analysis reveals that the sintered sample contains c-ZrO_2 phase and a small amount of $MgAl_2O_4$ spinel. Pure end members (alumina, magnesia or yttria) were not detectable. The XRD results indicate that Y_2O_3 can prevent the forming of m-ZrO_2 during cooling, and the additional MgO-Al_2O_3 mixture reacts fully to form $MgAl_2O_4$ particles. Therefore, the phase composition of Css is guaranteed in terms of the processing method and Y_2O_3-doping.

The microstructure of as-fired sample is determined by SEM, shown in Fig. 1. It demonstrates that the spinel particles distribute out over the c-ZrO_2 matrix and hinder the growth of c-ZrO_2. Thus, both the ultra-fine powders and the spinel particles play important roles in attaining fine-grained CSZ, and lead to grain sizes of about 4 μm in the c-ZrO_2 matrix.

3.2 Thermal stability and sub-eutectoid decomposition reaction at 1100°C

The effect of ageing time at 1100°C on the strength and toughness of the samples are shown in Fig. 2. The mean strength and toughness of the bar are about 221.52 MPa and 2.88 $MPam^{1/2}$ which increases to as high as 777 MPa and 13.57 $MPam^{1/2}$ after an ageing time of 800 h. To date, maximum values above 900 MPa and 15 $MPam^{1/2}$ have been

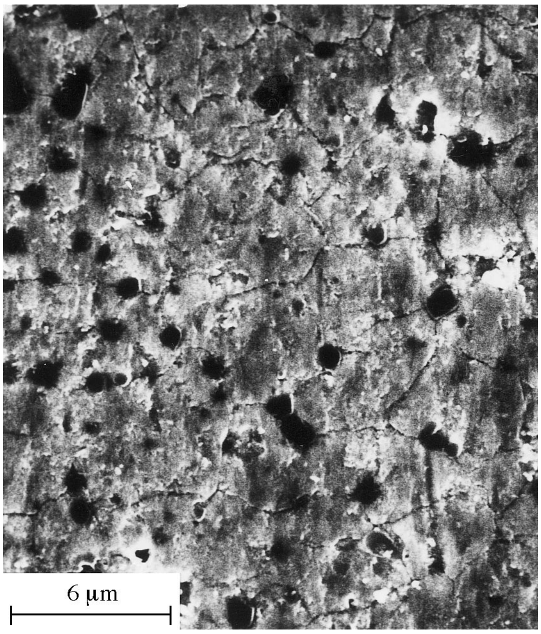

Fig. 1. Microstructure of as-fired sample etched by HF acid.

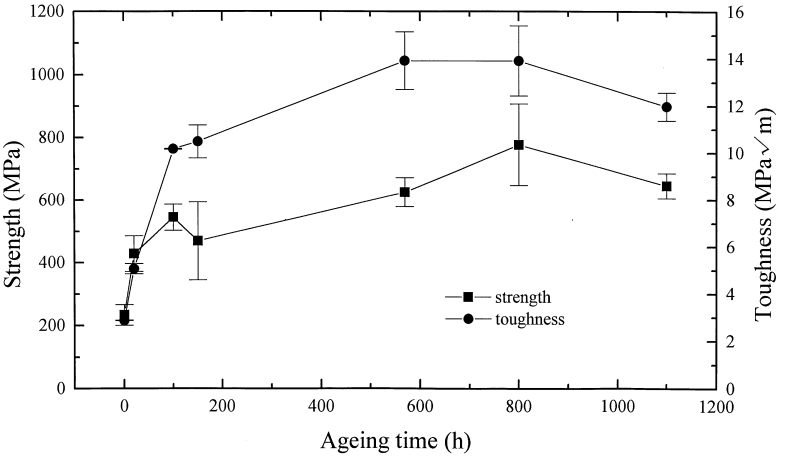

Fig. 2. Strength and toughness as a function of ageing time at 1100°C.

obtained. When compared with the conventional Mg-PSZ without Y_2O_3 addition, these specimens display improved thermal stability.

The amount of transformable tetragonal phase, the polished surface monoclinic content and the MgO intensity are measured at 1100°C for times to 1100 h. Results of these measurements are plotted in Fig. 3. During experimentation, it is found that, except c + t-ZrO_2, MgO and $MgAl_2O_4$, no polished surface monoclinic(PSM) content is detected even to the time of 800 h, and after reaching 1100 h, only 4% PSM is found. In the meantime, the amount of transformable t-ZrO_2 develops progressively with the increase of ground surface monoclinic content and obtains a highest value of 56% at 800 h, then degrades slowly. Obviously, the tendency of both strength and toughness depends on the TT situation. Thus the improving TT mainly contributes to the enhancing of mechanical properties; and furthermore, is the reason why these samples have high temperature degradation resistance.

The XRD results show that this material aged at 1100°C exhibits a new sub-eutectiod decomposition reaction and decomposes to MgO, t-ZrO_2 precipitation and destablized c-ZrO_2 (shown by c′):

$$c - ZrO_2 \rightarrow c' - ZrO_2 + t - ZrO_2 + MgO$$

which is different from the traditional thermal decomposition of commercial Mg-PSZ,[7] and is the same phase compositions as reported by Jin Zhenpeng *et al.*[15] It is the t-ZrO_2, which forms constantly with the decomposition reaction, that leads to the development of TT, and thereby influences the properties.

The MgO intensity as a function of the heat treatment is also shown in Fig. 3. It gets its high level about 535CPS between 150 h and 569 h ageing at 1100°C and then maintains the height, which indicates that the sub-eutectiod decomposition reaction has finished before 569 h. Comparison of the MgO intensity with the amount of transformable t-ZrO_2 indicates that the t-ZrO_2 grow continuously even after the sub-eutectoid decomposition reaction has finished. In contrast to the thought that the t-ZrO_2 precipitates of conventional Mg-PSZ don't

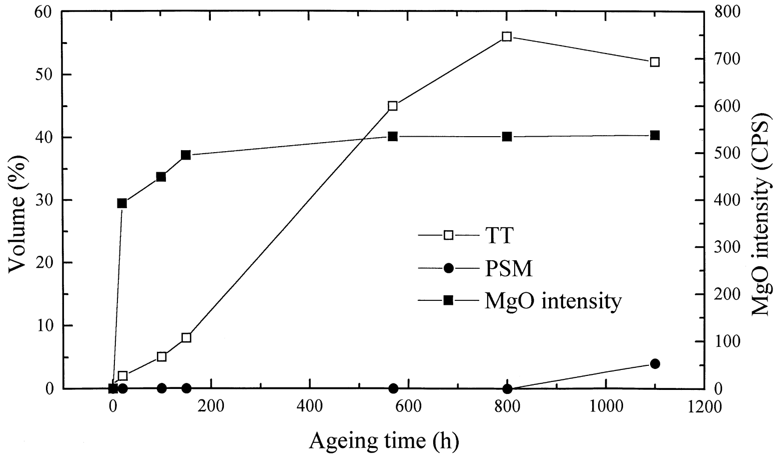

Fig. 3. Transformable tetragonal, polished surface monoclinic content and MgO intensity as a function of ageing time at 1100°C.

Fig. 4. Typical microstructure including c-, t- and m-ZrO_2, MgO pipes and $MgAl_2O_4$ particles.

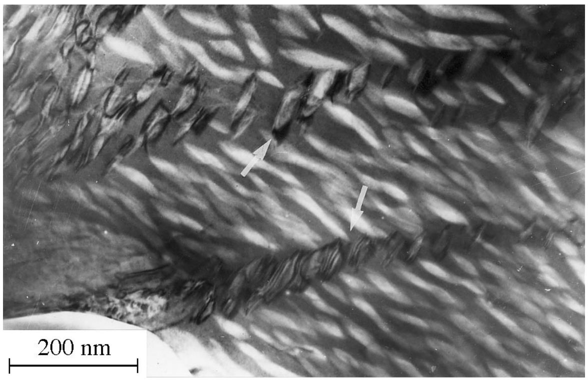

Fig. 5. Morphology of t-phase precipitations: colony-like precipitates (arrowed) in lense-shaped precipitates.

grow up, the precipitates in this work actually swell. So some small precipitates can transform into m-ZrO_2 under the stress condition when they grow up during the heat treatment and raise the TT amount. Others exceeding the critical size transform spontaneously to m-ZrO_2 and lose the ability to significantly toughen the material after the sub-eutectoid decomposition reaction. Just this fraction of precipitations causes the 4% PSM when aged to 1100 h. Therefore, it can be considered that the characteristic of precipitates in this work is obviously distinct from those in traditional Mg-PSZ.

3.3 Microstructure of aged samples

The microstructural features are outlined above. Besides the spinel particles, the typical microstructure, shown in Fig. 4, there still exist MgO-rich pipes and precipitates within MgO-rich pipes, but the phases among these pipes are quite different from the conventional Mg-PSZ. In conventional Mg-PSZ, the phase among the pipes is mainly m-ZrO_2. In this experiment, the phases among the pipes are cubic and tetragonal ZrO_2 obviously, and the lens plate-like t-ZrO_2 precipitates are revealed clearly in this BF image. It also can be concluded that the less the amount of Y_2O_3, the more unstable the t-ZrO_2 precipitates. Moreover, the microstructure in Fig. 5 confirmed the sub-eutectoid decomposition reaction judged by XRD.

The more detailed microstructure of t-ZrO_2 precipitates can be detected by TEM. There exist three characteristic shapes of t-ZrO_2 precipitation textures in this work, namely: (1) the lense plate-shape t-precipitates mainly stabilized by MgO, as shown in Figs 4 and 5; (2) the tweed-like precipitates stabilized by Y_2O_3, whilst TEM/EDAX indicated the chemical composition of this kind of precipitate;[16] and (3) the colony-like precipitates stabilized by Y_2O_3 as well, arrowed and shown in Fig. 5.

The tweed-like precipitates occurs because the phase composition is in the c + t two-phase field, which has been proved by XRD, at the heat treatment temperature of 1100°C. According to Heuer *et al.*,[17] precipitating such a tweed texture involves two basic conditions: (a) alloys with Y_2O_3 content in the c + t two-phase field which are cooled slowly from high temperatures (generally above 1400°C), and (b) precipitates nucleated with a low Y_2O_3 composition (<4 wt% Y_2O_3) in a Y_2O_3-rich c-matrix (≈ 12 wt% Y_2O_3). However, in this experiment, there is no evidence to indicate that the two conditions are satisfied, though the Y_2O_3 composition in tweed-like precipitates was less than 4 wt% Y_2O_3. The reason for cultivating the tweed-like precipitates may be due to the MgO content in the material and the precipitates form in the area in which MgO has precipitated or MgO content of matrix is lower. In the absence of other dynamic and/or thermodynamic reasons to explain these phenomena at present, there comes the only conclusion that these phases are precipitated during a long time process of heat treatment at 1100°C.

The colony-like precipitates are obtained from tweed textures, and they enlarge further afterwards until they can be transformed to m-phase after exceeding their critical size, which is the root cause of the so-called over-aged condition.

In this work, it is the tweed-like and colony-like precipitates that can grow up gradually during the ageing process and cause the phenomenon in Fig. 3. Therefore, the Y-PSZ structure plays an important role in toughening the material and leading to the high temperature degradation resistance.

4 SUMMARY AND CONCLUSIONS

At 1600°C for 4h, the material is sintered fully, with a relative density of 99·6%. Its phase compositions are c-ZrO_2 and a small amount of $MgAl_2O_4$; no free alumina, magnesia or yttria is detected. The microstructure of as-fired samples indicates that the spinel particles are distributed on grain boundaries of the c-ZrO_2 and restrain the growth of the c-ZrO_2, which leads to grain sizes of about 4 μm in the c-ZrO_2 matrix.

The strength and toughness of the samples aged at 1100°C improve gradually with time, attaining the maximum strength value over 900 MPa and toughness $\approx$15 MPa $m^{1/2}$ when aged to 800 h. So the material shows high temperature degradation resistance.

During the process of heat treatment at 1100°C, the material undergoes a new sub-eutectoid decomposition reaction: c-$ZrO_2 \rightarrow$c$'$-ZrO_2 + t-ZrO_2 + MgO. The resultant t-ZrO_2 causes the increase of transformable t-ZrO_2 and provides good thermal stability.

In the material, two kinds of t-ZrO_2 precipitates dependent upon different stabilizers are found: one form is stabilized by MgO and the other is stabilized by Y_2O_3. These findings show that the tweed-like and colony-like t-ZrO_2 phases, which are Y_2O_3 rich, can develop and cause increase in transformable t-ZrO_2 during heat treatment. It is, of course, transformable t-ZrO_2 that plays an important role in toughening the material.

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