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Thermal Stability and Microstructural Development of Fine-grained (Y,Mg)–PSZ/MgAl$_2$O$_4$ Ceramics

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Abstract

Fine-grained (Y,Mg)–PSZ/MgAl$_2$O$_4$ ceramics are prepared using a processing method similar to that of conventional Mg–PSZ. This kind of material exhibits good thermal stability at 1100°C; the mechanical properties of the material improve gradually at 1100°C and the material possesses a strength of 640 MPa and a toughness of 14 MPam$^{1/2}$ even after ageing for 800 h. SEM results show that the spinel particles, produced during the sintering process, are homogenously distributed in the ZrO$_2$ ceramic matrix and hinder the growth of the c-ZrO$_2$ matrix grains. The development of the microstructure and phase composition has been examined with XRD and TEM. New eutectoid decomposition reactions occur, which are different from the traditional decomposition of commercial Mg-PSZ without Y$_2$O$_3$ addition. Furthermore, the t-ZrO$_2$ precipitates grow and the transformable content keeps increasing during the heat treatment, playing an important role in toughening the matrix. © 1998 Elsevier Science Limited. All right reserved

1 Introduction

With the rapid development of Mg–PSZ ceramics in the binary MgO–ZrO$_2$ system, more attention is being devoted to characterizing the PSZ alloys of ternary systems, such as Y$_2$O$_3$–MgO–ZrO$_2$,[1-3] CeO$_2$–MgO–ZrO$_2$,[4] CaO–MgO–ZrO$_2$[5] and TiO$_2$–MgO–ZrO$_2$[6] in terms of both mechanical behavior and microstructure. For Mg–PSZ, it is thought that the morphology and size of precipitates dispersed in cubic solid solution are controlled by the lattice misfit between the precipitate and matrix.[7]

Accordingly, Lee et al.[7] designed a zero misfit composition in the Y$_2$O$_3$–MgO–ZrO$_2$ system in terms of the radii of Mg and Y ions. They found that t-ZrO$_2$ precipitates in a particular (Mg,Y)–PSZ with an 8:5 molar ratio of Y$_2$O$_3$ to MgO developed with a tetrahedral shape and were composed of three variants; moreover, this precipitate morphology was quite stable against the martensitic transformation even in specimens which had been extensively annealed. However, there was no information about the mechanical behavior of this zero misfit alloy. Montross[8] investigated the toughness, Vicker's hardness and the corresponding phase composition at various ageing times and temperatures for one chemical composition (1.6 mol% Y$_2$O$_3$–8·75 mol%MgO–89·65 mol% ZrO$_2$). The composition chosen was found to be extremely stable for temperatures of 1100 to 1400°C and for times up to 5000 h, thus making it difficult to precipitate a transformable tetragonal phase. Furthermore, Dworak et al.[9] demonstrated that (Y,Mg)–PSZ alloy exhibited a superior thermal stability at 1250°C to that of traditional Mg–PSZ. It may be concluded that the Y ion in MgO–ZrO$_2$ alloys plays an important role in the development of microstructure and of mechanical properties.

The MgO/ZrO$_2$ molar ratio in most of the previous researches, especially in those focussed on the mechanical properties, was less than 10/90 and the Y$_2$O$_3$ content was less than 5 mol%. There was little investigation of the effect of MgO content, especially for MgO/ZrO$_2$ molar ratios larger than 10/90. In this paper, results are presented for a ternary alloy[10,11] where the MgO/ZrO$_2$ molar ratio is 14/86, corresponding to the eutectoid composition in the MgO–ZrO$_2$ binary system; the Y$_2$O$_3$/ZrO$_2$ molar ratio is 2/98. Additional α-Al$_2$O$_3$ and MgO powders with 1:1 molar ratio were added in order to form spinel particles during sintering;

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these not only inhibit the growth of ZrO_2 matrix grains but also enhance high temperature mechanical properties, since the t-ZrO_2 cannot toughen the alloy by stress induced martensitic transformation above 900°C. The researches in this selected system include the thermal stability at 1100°C and microstructural characteristics.

2 Experimental Procedure

The mixed powders, 1·72 mol% Y_2O_3–13·76 mol% MgO–84·52 mol% ZrO_2 and additional 5·90 mol% α-Al_2O_3–MgO, were prepared with commercial grade ZrO_2, analysis pure Y_2O_3, chemical pure MgO and Al_2O_3 and ball milled in polymers jars with zirconia grinding media. Thereafter, they were dried in an oven at 80°C, screened through a 60 mesh screen, and calcined at 800°C for 1 h in order to remove the polymers. The calcined powder was ball milled again for a short time and granulated. Disc-shaped samples were formed by isostatic pressing under 200 MPa after uniaxal pressing. The green bodies were sintered and solution-treated at 1700°C for 4 h, then cooled at a rate of 150°C h^{-1} to 1000°C and furnace-cooled to room temperature thereafter.

The as-fired discs were ground to 5 mm thickness with a diamond wheel and cut to 2·5×5·0×30 mm³ test bars. Subsequently, the bars were buried in MgO powder and heat-treated at 1100°C for up to 800 h in an electric tube furnace.

The mechanical properties were tested with INSTRON 1341 (Instron Ltd, England). The strength was measured in three point bend with 20 mm span and 0·368 mm min^{-1} loading rate; the fracture toughness was measured by the SENB method with 20 mm span, 0·05 mm min^{-1} loading rate and 0·2 mm notch width. The test bars were not polished before the mechanical properties tests.

XRD was applied on polished surfaces and corresponding ground powders in order to determine both the phase composition and transformable t-precipitate volume in the annealed specimens. The volume percent of the transformable t-phase was calculated by measuring the volume fraction of the monoclinic phase on the polished surface and subtracting this value from the fraction found in the corresponding ground powder. The monoclinic contents were calculated with the formula suggested by Garvie and Nicholson.[12] The XRD examination was performed by Rigaku Dmax/-3B (Rigaku International Corporation, Japan). The diffraction peaks were measured using Cu K_α radiation, and the peak areas were calculated numerically after background subtraction.

Fracture surfaces of the as-fired samples were observed using secondary electron imaging with a KYKY-1000B SEM machine (Beijin Research and Development Center of Scientific Instrument, Chinese Academy of Sciences). The relation of the phases present in the aged material were examined with a JEM-200CX (JEOL Ltd, Japan). Before TEM observation, the samples were cut to 300 μm, mechanically polished, dimpled to a thickness of about 20 μm, and then thinned by Ar ion milling (Gatan 610DIF, Gatan Ltd, USA) before carbon coating.

3 Results

3.1 The microstructure of the as-fired body
In order to provide a strengthening mechanism and to restrict the grain size of the traditional c-ZrO_2 matrix, which is usually about 40–80 μm, 5·90 mol% spinel particles were dispersed in the selected alloy by the reaction of alumina particles with magnesia particles during firing. The as-fired sample contains a c-ZrO_2 matrix and spinel particles; no MgO, Al_2O_3 or Y_2O_3 were detected, as certified by XRD in Fig. 1. The XRD results indicate that Y_2O_3 can prevent the formation of m-ZrO_2 during cooling, and the additional MgO–Al_2O_3 mixture reacts fully to form $MgAl_2O_4$ particles, whose strongest XRD peak is present at 36·1°. The main purpose of adding spinel particles was to improve the high temperature mechanical properties because the transformation toughening mechanism is not effective at temperature higher than 900°C. Spinel is stable over a broad temperature range according to its phase diagram.[13] Figure 2 is the fractogragh of the as-fired alloy/particle composite. Most of the fine spinel particles (less than 1 μm) were well dispersed inside the zirconia alloy grains, and the others are located between the grains. Compared with the traditional Mg–PSZ or (Y,Mg)–PSZ, the grain size (less than 10 μm) is much smaller for the same firing conditions. It can be concluded that the spinel particles were effective in impending the growth of the zirconia grains.

3.2 Effect of ageing time on the bending strength and fracture toughness of the selected alloy
The ageing behavior is determined by holding the alloy at a certain temperature for different times and by measuring the corresponding mechanical properties. Figure 3 shows the ageing behavior at 1100°C. The bending strength and fracture toughness increase rapidly up to 145 h. The average strength and toughness at 145 h are 2·1 times and 5 times greater than at the outset, respectively. After 145 h at 1100°C, both strength and toughness

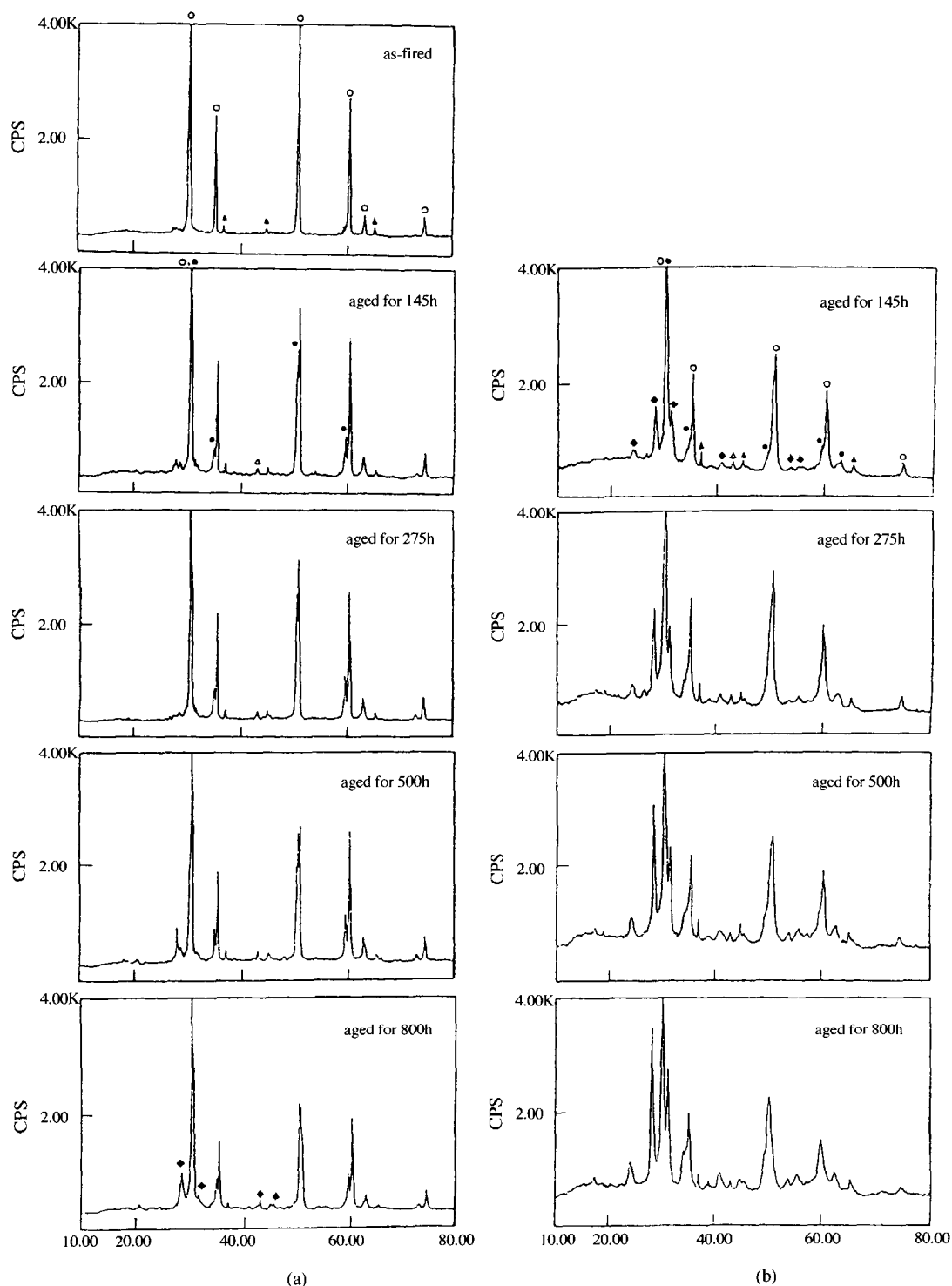**Fig. 1.** XRD patterns of (a) polished surfaces and (b) ground powders of as-fired sample and samples aged at 1100°C; $\bigcirc$ c-ZrO$_2$, $\bullet$ t-ZrO$_2$, $\blacklozenge$ m-ZrO$_2$, $\triangle$ MgO, $\blacktriangle$ MgAl$_2$O$_4$.

increase more slowly. At 800 h, the fracture toughness is 14·14 MPam$^{1/2}$ and the strength 640 MPa.

3.3 The XRD results

For zirconia toughened ceramics, the relative content of the monoclinic, tetragonal and/or cubic phases is one of the key factors in determining the bulk mechanical properties. The change of monoclinic zirconia on the polished surface and in the ground powder with time at 1100°C, as determined by

XRD, is shown in Fig. 4. The middle curve on this figure is the difference between the monoclinic contents in the two states. The increase of monoclinic content with ageing time for both conditions is much slower found by Swain *et al.* for a MgO/ZrO$_2$ = 14/86 molar ratio alloy in the MgO–ZrO$_2$ binary system.[14] They found 90 vol% monoclinic phase on the polished surface. However, for the present alloy, 11 vol% monoclinic appears on the polished surface even after ageing for 800 h at
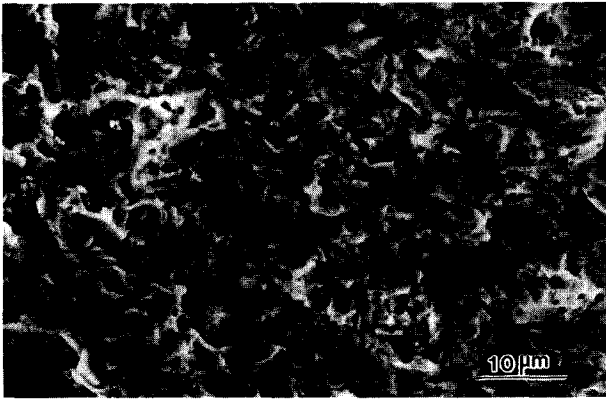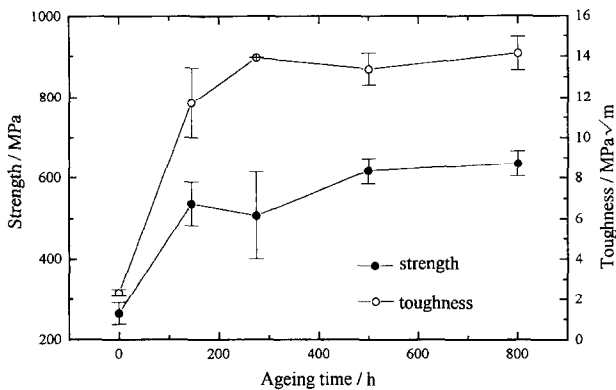
Fig. 2. Fracture surface of as-fired sample.

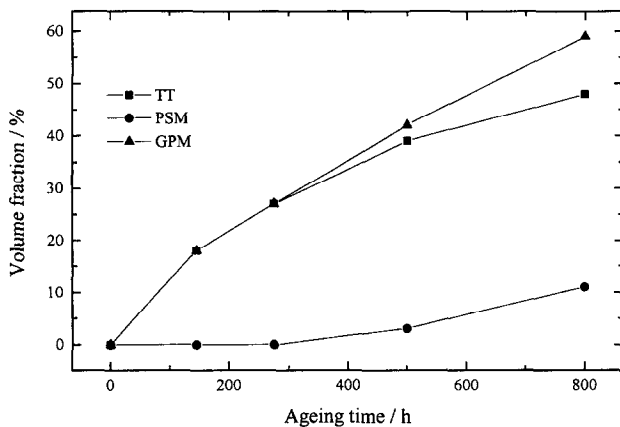**Fig. 3.** Mechanical properties as a function of ageing time at

Fig. 4. Polished surface and ground powder monoclinic contents, and transformable tetragonal phase content as a function of ageing time at 1100°C.

1100°C. It can be concluded that the added yttria has impeded the formation of the monoclinic phase. There was little t-ZrO_2 phase in the MgO–ZrO_2 binary alloy with the eutectoid MgO/ZrO_2 molar ratio without Y_2O_3.

4 Discussion

For this (Y,Mg)–PSZ/$MgAl_2O_4$ composite in which the MgO/ZrO_2 molar ratio was 14/86

(excepting the magnesia in the spinel particles), both its strength and toughness increased simultaneously with the ageing time. There was a superior degradation resistance at 1100°C since the strength and toughness were sustained even after the ageing time reached 800 h.
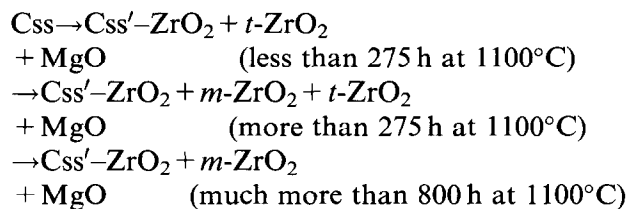
The mechanical properties are tightly correlated with the formation of tetragonal and monoclinic phase, as determined by the addition of yttria to the MgO–ZrO_2 system.[15] If we compare the changes of XRD diffraction patterns at different ageing durations carefully and correlate these with the TEM results, then the microstructure development can be outlined. The XRD patterns in Figs 1(a) and (b) are from the polished surface and the ground powder. Before the alloy was aged, there were no phases other than the spinel and cubic zirconia. Once the composite was aged at 1100°C, a magnesia peak appeared at 43°(2θ). According to the ageing behavior of MgO–ZrO_2 binary alloy at a temperature of less than 1400°C,[16] Mg segregates from the zirconia lattice to form a magnesia phase. This phase is clearly found in the composite aged at 1100°C for 275 h. The pipe-like or plate magnesia is quite similar to that formed by sub-eutectoid decomposition in Mg–PSZ alloy after ageing at 1100°C.[17,18] The phase found between the magnesia regions is, in contrast, completely different from that found in undoped Mg–PSZ alloys. Phase regions retain the cubic phase, with precipitated tetragonal phase inclusions, as shown in Fig. 5. In MgO–ZrO_2 binary alloy without Y_2O_3, the phase between the MgO is monoclinic. When the ageing time at 1100°C increased from 145 h, the intensity of the MgO peak in the XRD pattern remained constant, as noticed in Fig. 1. This means that the segregation of Mg from the zirconia lattice is completed after 145 h. This process in MgO–ZrO_2 binary alloys is completed in a very short time at 1100°C with the zirconia solid solution decomposed to monoclinic zirconia and magnesia or a metastable intermediate product $Mg_2Zr_5O_{12}$.[19,20] From 145 h to 800 h, the monoclinic phase began to

Fig. 5. Microstructure of sample aged at 1100°C for 145 h.

appear after 275 h and steadily increased with the time; there is a loss of stability of the tetragonal precipitates due to their size exceeding the critical size.

The following formula can be used to describe the decomposition process in this system:

$$Css \rightarrow Css'-ZrO_2 + t\text{-}ZrO_2$$
$$+ MgO \qquad \text{(less than 275 h at 1100°C)}$$
$$\rightarrow Css'-ZrO_2 + m\text{-}ZrO_2 + t\text{-}ZrO_2$$
$$+ MgO \qquad \text{(more than 275 h at 1100°C)}$$
$$\rightarrow Css'-ZrO_2 + m\text{-}ZrO_2$$
$$+ MgO \qquad \text{(much more than 800 h at 1100°C)}$$

where the Css and Css' stand for the cubic alloys with different stabilizers. The yttria in the MgO–ZrO₂ binary system makes the intermediate phases more stable.

5 Summary and Conclusions

A fine-grained (Y,Mg)–PSZ/MgAl₂O₄ composite has been prepared. The material exhibits superior thermal stability at 1100°C, with the mechanical properties increasing gradually even after an ageing time of 800 h.

In terms of the microstructure and phase compositions as studied by XRD, SEM and TEM, a series of eutectoid decomposition reactions are suggested. The transformable t-ZrO₂ plays a key role in toughening the matrix.

Acknowledgements

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