JOURNAL OF MATERIALS SCIENCE 21 (1986) 2277–2282

Influence of long-term ageing upon the mechanical properties of partially stabilized zirconia (Mg–PSZ) for heat-engine applications

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The influence of long-term ageing at 1000° C upon the mechanical strength of a commercial Mg–PSZ ceramic is investigated. The Weibull solution was used to measure the material reliability. The effects of sub-eutectoid ageing were related to the stability of the tetragonal phase. Grain boundaries are shown to often act as fracture origins, and to constitute a fracture-controlling population that is not significantly affected by high-temperature ageing.

1. Introduction
The fabrication of tough, strong ceramics, long a goal of ceramic scientists, has been difficult to achieve because of their inherent brittleness. Nevertheless such an old material as zirconia permits one to overcome this difficulty by way of transformation toughening.

The improved toughness of partially stabilized zirconia ceramics (stabilized with magnesia, yttria or calcia) results from a distribution of tetragonal and/or monoclinic precipitates in a cubic matrix. These tetragonal particles, when developed to an appropriate size by post-sintering treatment, will spontaneously transform into the room-temperature stable monoclinic form under the influence of the stress field about a propagating crack. The process zone is a source of stress and displacement disturbance that tends to shield the crack tip from the applied stress, in a manner analogous to a plastic zone. This martensitic transformation was first detected in 1929 by Ruff and Ebert [1]. Since then it has been intensively studied [2, 3].

PSZ ceramics are prone to exhibit remarkable properties and particularly enhanced strength and toughness. They are claimed to be candidates for important industrial applications involving high reliability. Unfortunately the ageing properties of PSZ ceramics become highly critical, and the mechanical properties may be greatly affected by high-temperature exposures. Various processes are reported in the literature:

1. At temperatures above the eutectoid (ranging between 1400 and 1500° C for Mg–PSZ), long-term exposures cause exaggerated coarsening of tetragonal particles (over-ageing). The precipitates lose coherency and transform to the stable monoclinic structure during cooling to room temperature. There are thus few precipitates remaining for a stress-induced transformation, which causes a tremendous drop in mechanical properties. The room-temperature bend strength of Mg–PSZ has been observed to decrease from between 700 and 800 MPa to 400 MPa after ageing at 1400° C for 64 h [4]. Similar bend-strength decreases have been measured with Ca–PSZ: from 400 to 200 MPa after ageing for 10 h at 1400° C or 50 h at 1300° C [5].

2. At temperatures below 1400° C, Mg–PSZ undergoes a sub-eutectoid decomposition reaction [6]. At such temperatures, little or no precipitate coarsening occurs [7, 8]. Instead, an ordering of the defect fluorite structure occurs, leading to considerable strain at the precipitate/matrix interface, and a decomposition of the matrix phase initiates at grain boundaries. The consequence of the increased strain is that after significant ageing time, depending upon the initial precipitate size, the precipitates transform to monoclinic zirconia on cooling, resulting in an important decay in mechanical properties. Marmach and Swain [4] thus found that the strength of Mg–PSZ decreased from 600 to 300 MPa after heat treatment at 1100° C for about 20 h.

3. The tetragonal to monoclinic transformation may also cause extensive microcracking [9] leading to a loss of mechanical integrity in components. Moreover, the stresses developed during the transformation of the pure ZrO_2 grains present at the grain boundaries may lead to separation and weakening of the grain boundaries, and consequent strength degradation [10, 11].

4. Reducing conditions may also cause grain-boundary weakening by decomposition of the grain-boundary phase [12] which contains a high amount of Mg–silica glass.

The intent of the present paper is to examine the influence of long-term mid-temperature treatments upon the mechanical properties of a commercial Mg–PSZ, with a view to evaluating the reliability of this material for usage in adiabatic diesel engines. The Weibull solution was used to assess the material

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TABLE I Properties of Mg–PSZ

Relative density	5.75
Porosity	1.5 vol %
Grain size	50 to 60 μm
Young's modulus	200 GPa
Flexural strength	$\simeq$ 600 MPa
K_{IC}	9 MPa m$^{1/2}$
Tetragonal phase	35 vol %
Cubic phase	34 vol %
Monoclinic phase	31 vol %

reliability [13]. The temperature of 1000° C was selected on the basis that it is close to the maximum conditions prevailing in combustion chambers. The effects of long-term ageing at 1000° C have been related to the stability of the tetragonal phase. Our investigation has also shown that grain boundaries often acted as fracture origins, and that this fracture-controlling population was not significantly affected by high-temperature ageing.

2. Experimental procedure

The material used was a commercial 3.6 wt % Mg–PSZ (Feldmühle, Plochingen, West Germany) 35 vol % tetragonal phase. Other properties are given in Table I.

Bar samples were cut from a single plate. After machining, all the specimens were polished on one surface with 7 μm diamond paste to remove the monoclinic domains resulting from machining. The thickness of the removed surface layer was about 30 μm. The surfaces of the polished specimens were then analysed using X-ray diffractometry. They exhibited the same phase contents as the reference material.

The edges of specimens were bevelled for strength measurements. The final size of specimens was nominally 2 mm thick, 5 mm wide and 25 mm long.

The specimens were aged isothermally at 1000° C in air in an electrically heated furnace. A standard procedure was adopted to avoid thermal shocks (Fig. 1). The specimens were steadily heated from room temperature to 1000° C in 3 h. After ageing, they were cooled in the furnace at its natural rate. Two exposure times t_{exp} were selected for this study: 48 and

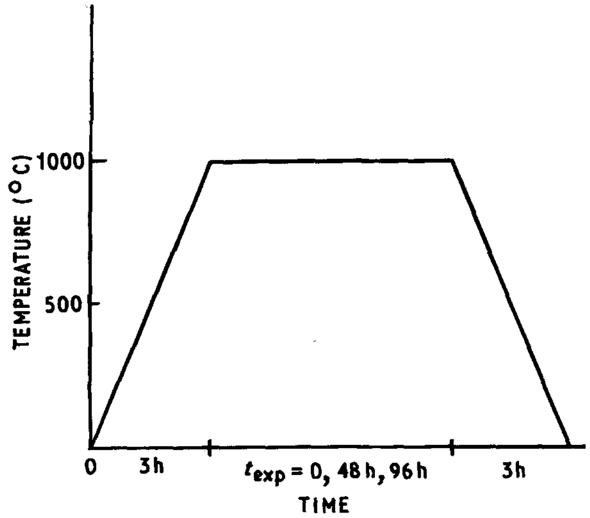

Figure 1 Schematic diagram of the ageing treatment programme.

96 h. Additional tests were performed to determine the influence of heating and cooling rates upon phase contents. For this purpose, the thermal treatments consisted of the heating and cooling steps exclusively (ageing time $t_{exp} = 0$).

Fracture strengths were measured at room temperature in three-point bending (span length = 17 mm) at a constant displacement rate of 0.2 mm min^{-1}. For simplicity the analysis of the strength distributions was performed using the Weibull function [13], which provides the same shape parameter for the tensile surface flaw populations as multiaxial approaches recently devised [14, 15].

The stress intensity factors were determined using Vickers-indented flexural specimens according to the equation

$$K_{Ic} = \eta \left(\frac{E}{H}\right)^{1/8} (\sigma_R P_i^{1/3})^{3/4} \quad (1)$$

where E is Young's Modulus, H the hardness, P_i the indentation load, σ_R the failure stress and η a constant ($\eta = 0.59$).

The fracture toughness was determined as the average from three specimens which were indented at a load of 100 N for producing a radial crack system.

The amounts of monoclinic ZrO_2 in reference and aged specimens were determined with Co$K\alpha$ X-radiation, by comparing the areas of selected diffractometer peaks. Despite its limitations the technique of Garvie and Nicholson [16] as modified by Porter and Heuer [17] was employed for estimating phase content changes with ageing. For the monoclinic structure factor, the measured value [18, 19] was used instead of the calculated value [17].

For the determination of relative phase fractions in reference material, bulk specimens were ground to a powder. The problem of peak overlap (peaks from tetragonal precipitates with peaks from the cubic matrix) can thus be solved. During the grinding process, ZrO_2 transforms to monoclinic symmetry. Assuming that $V_c + V_m = 1$, X-ray diffractometry of the powder thus permitted deducing the cubic volume fraction V_c from the fraction of monoclinic phase V_m, determined from $(1\,1\,1)_m$ and $(1\,1\,\bar{1})_m$ peaks. The tetragonal phase fraction in the reference material could then be easily obtained from monoclinic phase analysis in a bulk specimen. Results are summarized in Table I.

This method may lead to errors if sample preparation (polishing, specimen grinding to a powder, etc.) is not rigorously controlled. The tetragonal phase content may be underestimated. In our experiments, the underestimation uncertainty may be reasonably considered as lower than 10%.

3. Results and discussion

The failure loads measured on flexure specimens were expressed in terms of the maximum tensile stress, and the resultant cumulative failure probabilities obtained as plotted in Fig. 2. The failure distribution of the reference material suggests that fracture is dictated by a bimodal flaw population. Fracture origins at the low-strength extreme could not be identified

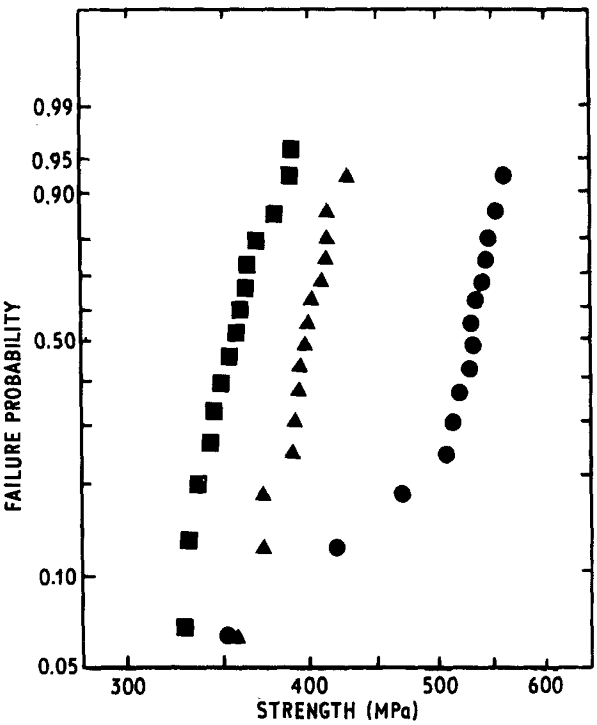

Figure 2 Strengths distributions for (●) reference Mg–PSZ and for specimens aged at 1000° C for (▲) 48 and (■) 96 h.

by fractographic examination. The shape parameter was determined from high-strength values. Low strengths were treated as censored data in the ranking of failure data.

Comparison of the strength distributions pertinent to aged and reference specimens revealed an important strength decrease with increasing ageing times (Fig. 2). The strength distributions exhibit comparable shape parameters, m (Table II), indicating that the fracture-inducing flaw population is not significantly affected by long-term ageing. As a consequence, the strength decrease mostly results from the K_{Ic} decrease (Table II).

Fractography of specimens showed predominantly transgranular fracture. Some differences were observed between fracture patterns. No fracture mirror could be detected in reference specimens. However, some typical patterns with associated extensive crack branching (Fig. 3) permitted the identification of fracture origins. Fracture-inducing defects thus appeared as located at the surface, except for the low-strength extreme where no success was had in detecting fracture origins.

For aged specimens the identification of fracture origins was generally easier, due to the presence of fracture mirrors (Fig. 4). Fracture origins were predominantly surface grain-boundary facets, as evidenced by Fig. 5. The pores that were observed along the grain-boundary facets (Fig. 6) are small in comparison with the defect sizes, and not of a sufficiently high density to clearly suggest the linking of several of them by cracks to form large flaws.

The predominance of grain boundaries in the fracture of PSZ was first noted by Rice *et al.* [10] who found that fractures originated predominantly from grain-boundary facets in as-received or oxidized heat-treated commercial Mg–PSZ (Zircoa 1027). This flaw population is probably created after sintering (on the cooling stage) and would result from the stresses developed at grain boundaries by the transformation of pure zirconia.

However, Fig. 7 shows that high-temperature ageing may cause additional grain-boundary weakening in the same way as etching (Fig. 8). The defects created by this process pertain to the previous population of grain-boundary facets. Consequently, they do not exert any influence on the strength of specimens.

Table III shows that ageing at 1000° C induced a significant increase in the monoclinic fraction but no significant change in the PSZ composition. The monoclinic content increase did not result from the heating/cooling rates. As shown by Table III, no significant variations in the monoclinic fraction were detected on the samples which underwent heating/cooling steps exclusively.

In the sub-eutectoid conditions that prevail in ageing tests, Mg–PSZ undergoes a cubic phase decomposition to monoclinic ZrO_2 in accord with the reaction [8, 17]

$$(c)ZrO_2 \rightarrow (m)ZrO_2 + MgO$$

$$\text{at temperatures} < 1200^\circ\,C$$

Additionally, as a consequence of the considerable strain induced by the cubic decomposition at the precipitate/matrix interface, tetragonal particles transform on cooling at grain boundaries. The monoclinic fraction increase therefore results from both the decomposition of the cubic phase and the associated tetragonal to monoclinic transformation, rather than from the simple transformation of tetragonal precipitates. This means that all the precipitates did not transform and that precipitates remained in the metastable state at room temperature. This conclusion is consistent with the K_{IC} changes observed on aged specimens which exhibited a residual toughness ($\simeq 6.5\,MPa\,m^{1/2}$, Table II) lower than the reference material but much higher than the matrix plus transformed precipitates ($3\,MPa\,m^{1/2}$).

These points are supported by dilatometry, which is particularly useful for the detection of phase changes in these materials. Thermal expansion measurements were made from room temperature to 1200° C to determine if discontinuities, corresponding to phase transitions, occurred. Some dilatometer traces are shown in Fig. 9.

TABLE II Mechanical properties of specimens

Parameter	Reference specimens	Specimens aged 48 h	Specimens aged 96 h
$\sigma_R(P = 0.5)$* (MPa)	530	400	355
Shape parameter, m	26.7	21.6	19.7
Fracture toughness, K_{Ic} ($MPa\,m^{1/2}$)	9.0	6.7	6.4

*Strength at median failure probability.

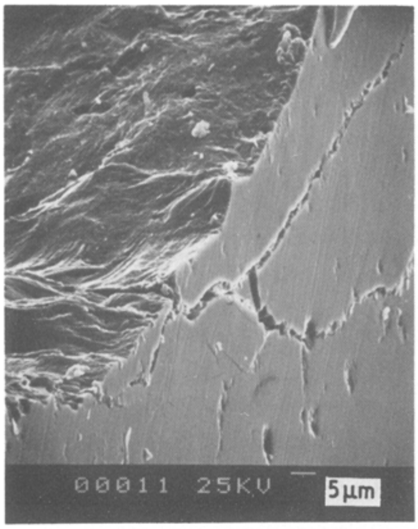

Figure 3 Scanning electron micrograph showing extensive crack branching in reference specimens of Mg–PSZ.

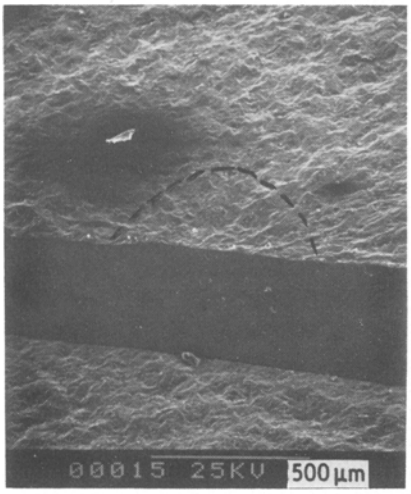

Figure 4 Scanning electron micrograph of fracture mirror in specimens aged for 48 h at 1000° C.

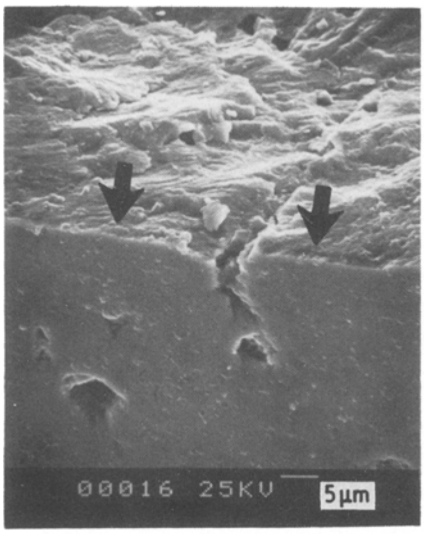

Figure 5 Scanning electron micrograph of a fracture-initiating grain-boundary facet (shown by arrows) in aged Mg–PSZ.

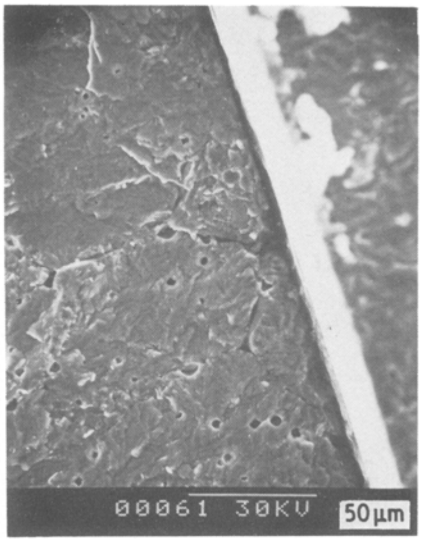

Figure 6 Scanning electron micrograph showing intergranular and intragranular porosities in the fracture surface of an aged Mg–PSZ specimen.

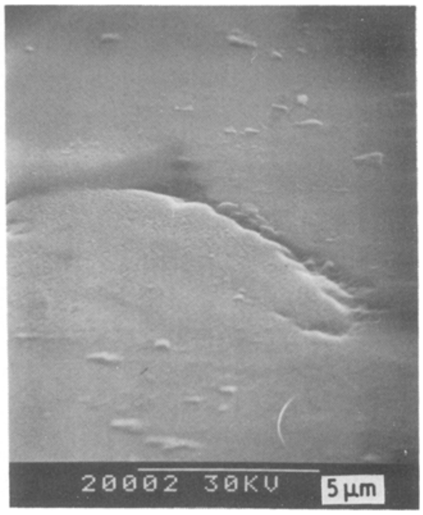

Figure 7 Grain-boundary weakening on the surface of an Mg–PSZ specimen aged for 15 h at 1000° C.

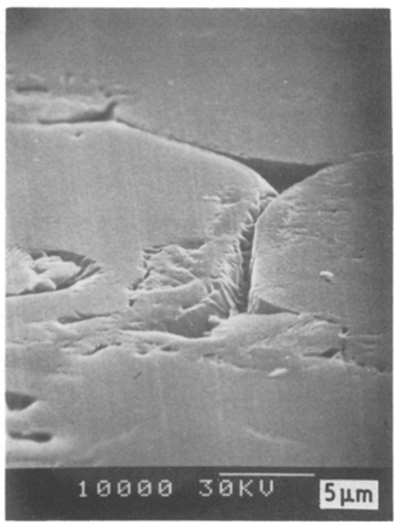

Figure 8 Grain-boundary weakening produced by etching using boiling NH_4F acid.

TABLE III Results of X-ray diffraction and electron microprobe analyses of specimens

Material	Reference specimens	$t_{exp} = 0$ h	$t_{exp} = 48$ h	$t_{exp} = 96$ h
Monoclinic phase (vol %)	31	32	64	65
Tetragonal phase (at constant V_c) (vol %)	34	34		
MgO (wt %)	3.2	3.2	3.4	4
SiO_2(wt %)	0.13	0.13	0.23	0.25
ZrO_2(wt %)	95.5	95.5	95.2	95.2
HfO_2(wt %)	1.0	1.0	1.2	0.35

These curves reflect a change in the volume fraction of zirconia after ageing (increase in the height of the hysteresis, *H*) indicating that tetragonal particles did transform.

They additionally show that the reverse transformation temperature did not experience a significant decrease ($\simeq 750°$ C), indicating that little or no particle coarsening occurred. The particle transformation is thus caused by the matrix decomposition exclusively. The reverse transformation decrease also indicates that the 48 and 96 h ageing times developed a similar microstructure, i.e. tetragonal particles up to a constant limiting size remained in the metastable state at room temperature.

Finally, the widening in the transformation temperature range (Fig. 9) reflects a bimodal particle-size distribution. Smaller particles are able to transform after ageing. This effect must be attributed to the destabilization of the tetragonal particles associated with matrix decomposition.

4. Conclusions

Typical fractography clearly showed that grain boundaries are often fracture origins in Mg–PSZ. This flaw population is probably created during the cooling stage after sintering, and is not significantly affected by ageing treatments at 1000° C. Ageing may also promote grain-boundary weakening. However, the defects thus created pertain to the initial population of grain boundaries and are not limiting factors for strength.

The tremendous strength decreases caused by ageing treatments at 1000° C are directly attributable to changes in toughness (K_{IC}). The associated increase in the monoclinic phase fraction must be attributed to the decomposition of the cubic matrix and to the associated transformation of tetragonal particles. However, the toughness of aged specimens of Mg–PSZ remains important when compared with the toughness of the cubic matrix and with that of several structural ceramics. This residual toughening can essentially be attributed to the presence of precipitates that remained in the metastable state at room temperature.

Finally, it may be concluded that Mg–PSZ ceramics exhibit residual transformation toughening after long-term ageing at 1000° C. Unfortunately, the strength appears to be extremely limited.

Acknowledgements

The authors wish to thank Renault Co. (Regienov Division) for support and for permission to publish this paper. In addition the help of D. Couratin and G. Desplanches (from Direction des Affaires Scientifiques

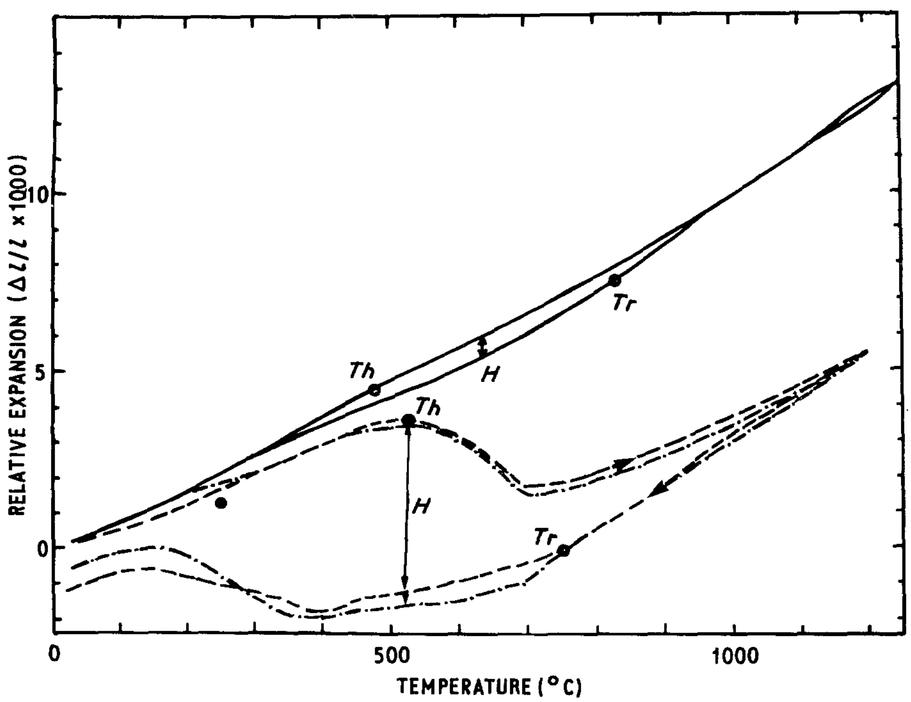

Figure 9 Typical dilatometer traces obtained for (—) reference Mg–PSZ and for specimens aged at 1000° C for (– –) 48 and (– · –) 96 h (*Tr* = reverse transformation temperature, *Th* = transformation temperature on heating, *H* = height of hysteresis).

et Techniques, Lab. Divisions) with the X-ray diffraction and dilatometry work is gratefully acknowledged.

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Received 14 January
and accepted 11 September 1985