Sub-eutectoid aged Mg–PSZ alloy with enhanced thermal up-shock resistance

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Mg–PSZ samples prepared in the as-fired condition were strong (550 to 600 MPa) but had poor thermal up-shock resistance in that they shattered during a standard test. However, ageing at 1100° C enabled 70% of their original strength to be retained after thermal up-shock damage. This marked improvement in thermal shock resistance was attributed to the conversion of tetragonal precipitates to the monoclinic state by a process other than particle growth. It is proposed that the precipitate/matrix interface which governs the crystal structure of a precipitate at room temperature was altered by a type of solid state reaction, not previously reported, which occurs during ageing at 1100° C.

1. Introduction

Although strong and tough ceramics have been prepared from both calcia– and magnesia–partially stabilized zirconia materials (Ca–PSZ, Mg–PSZ) their thermal up- and down-shock resistance is modest. For example, Ca–PSZ materials with moduli of rupture of about 600 MPa displayed unstable crack propagation when quenched from 300° C into water at 20° C [1]. Over-aged Ca–PSZ showed stable crack propagation in such tests but only with a considerable sacrifice of the initial strength (MOR ∼ 170 MPa) [2]. Schoenlein and Heuer [3] showed that transformation toughened Mg–PSZ materials had unstable crack propagation in thermal down-shock experiments.

Severe thermal up-shock is commonly encountered in industrial applications of ceramics. For example, ceramic dies made of Mg–PSZ materials, preheated to 450° C, are used to extrude metal billets heated in the range 800 to 1100° C. Conventional strong Ca– and Mg–PSZ materials disintegrated in a thermal up-shock test designed to simulate the thermal stresses generated in dies during extrusion. The purpose of this paper is to report a new type of strong Mg–PSZ material which has enhanced thermal up-shock resistance brought about by ageing the material at 1100° C [4].

Usually it is recommended that ageing Mg–PSZ materials in the range 1000 to 1400° C should be avoided, or is of no benefit, because of the eutectoid decomposition reaction [5, 6]. We observed that this reaction occurred either to a minor extent, or not at all, in the composition range 3.0 to 3.5 wt% MgO for the ageing temperatures and times required to produce strong and thermal shock resistant material. We report here for the Mg–PSZ systems, a solid-state reaction, which entails the nucleation of a new phase at the precipitate/matrix interface. The microstructure generated by this reaction during ageing at 1100° C allows stable crack propagation during severe thermal up-shock tests.

2. Experimental details
2.1. Materials

The zirconia powder used was a "glass quality" product made by the Ugine Kuhlman Co. The magnesia was analytical reagent grade MgO made by BDH Chemicals Ltd. The composition used in this work was 3.3 wt% MgO unless stated otherwise. The new materials were prepared by mixing and fabricating in a manner similar to that used for the conventional, strong Mg–PSZ ceramics which has been described elsewhere [7]. The major difference in the technique was that the new materials were aged at 1100° C, rather than 1420° C, as previously done.

Experiments show that the precipitates must have a minimum critical size (about 100 nm in their longest dimension) prior to ageing in order for the interfacial reaction to become significant. Mean precipitate size was controlled by the rate of cooling, subsequent to firing, in the temperature range 1700 to 1400° C. Details of the firing procedure and cooling rate have been published elsewhere [7].

2.2. Material characterization

The thermal shock properties of Mg–PSZ materials progressively aged at 1100° C were assessed by measuring the strength of test bars, 3 mm x 3 mm x 40 mm, before and after thermal up-shock tests. Details of the strength measurements are given elsewhere [7]. The thermal shock test consisted of up-quenching bars which had been preheated to 450° C into a bath of molten aluminium maintained at 900° C. As noted above, this test simulated the thermal stresses encountered during the hot extrusion of metals, a major application of the new ceramics.

The fine scale microstructure of foils prepared by ion beam machining of thin sections was studied by transmission electron microscopy (TEM).

Detailed analysis of the various forms of the monoclinic phase present on ground surfaces (GSM) and polished surfaces (PSM) was accomplished by X-ray diffraction and optical microscopy. Monoclinic material in the grain boundaries (GBM) was estimated using a line intercept analysis of optical micrographs.

The hardness of the material was measured on HF etched surfaces as a function of ageing time, using a Vickers indenter with 3 N loads. Care was taken to ensure that all the indentations measured were located entirely within the grains.

Finally the processes occurring at 1100° C were monitored by high temperature X-ray diffraction.

3. Results and discussion

The effect of ageing time at 1100° C on the strength and thermal shock resistance of Mg–PSZ is shown in Fig. 1. The initial strength of the bars was about 450 MPa which increased to a maximum value of 600 MPa after an ageing time of 3 h. This behaviour is in contrast to that observed by Porter and Heuer [6] who aged a Mg–PSZ material in the range 1200 to 1300° C. They observed the progressive development of the eutectoid decom-
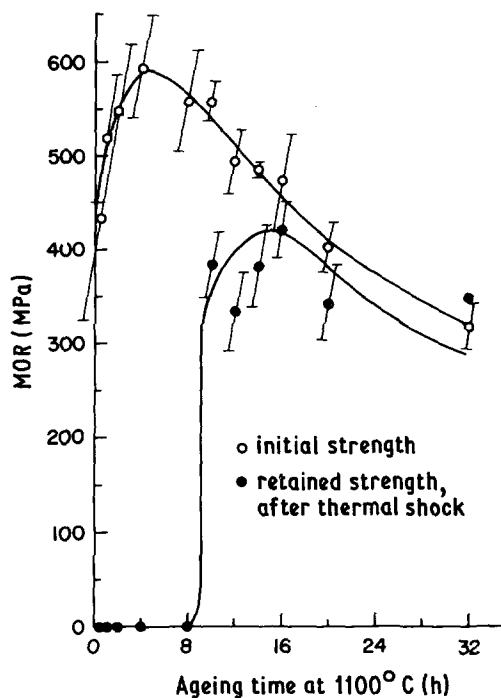
Figure 1 Original strength and strength retained after thermal up-shock damage of Mg–PSZ samples as a function of ageing time at 1100° C.

position reaction in the grain boundaries which caused a significant loss of strength. In the present work, with further ageing, the strength of the bars fell smoothly, attaining a value of about 310 MPa with 32 h ageing.

The thermal up-shock resistance of the material as a function of ageing time obeyed a step function. The test bars disintegrated during thermal shock for ageing times of 8 h or less. Surprisingly at about 9 h of ageing the retained strength increased suddenly to about 370 MPa and remained at this level for the remainder of the ageing run, up to about 32 h.

Values of retained strengths as high as 660 MPa were obtained when the mixed powder batch was calcined and then milled prior to cold pressing, as shown in Fig. 2. It is believed that the extra processing steps render the material more homogeneous which further enhances the thermochemical properties [4]. The incubation period of 1 h for the calcined batch (Fig. 2) is much less than the value observed for the uncalcined batch (Fig. 1). The reason for this difference is unknown. Further work on the higher performance material will be given in a future publication [8].

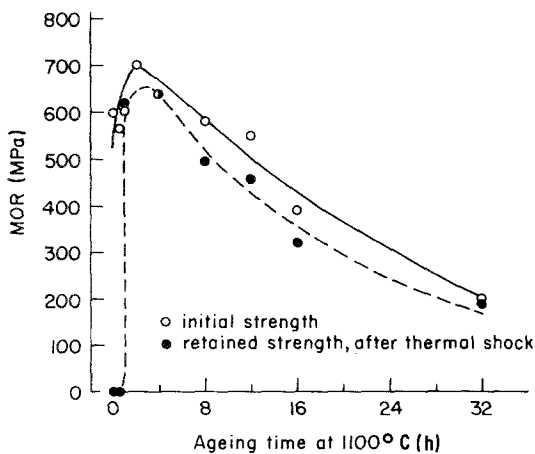The results of the TEM observations showed

Figure 2 Original strength and strength retained after thermal up-shock damage of Mg–PSZ samples with improved processing as a function of ageing time at $1100°$ C. Mean standard deviations of unshocked and shocked samples = 8.8 and 7.4%, respectively.

that ageing at $1100°$ C resulted in four major microstructural changes, namely,

(1) the occurrence of an ordered anion vacancy phase (δ-phase, $Mg_2Zr_5O_{12}$) [9] in the cubic stabilized zirconia (CSZ) matrix,
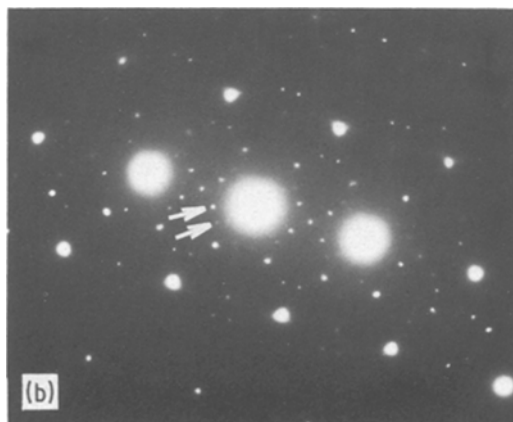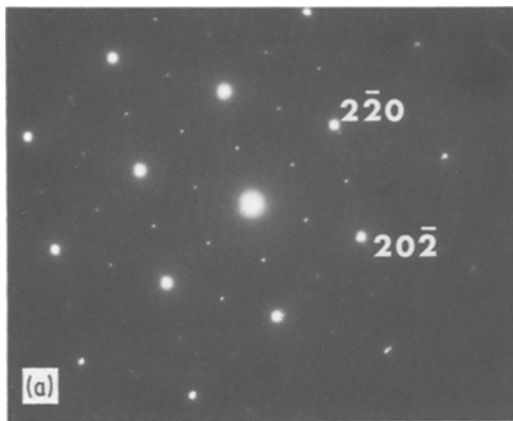

(2) development of a fine monoclinic structure within tetragonal precipitates,

(3) transformation of normally stable tetragonal precipitates to monoclinic, without significant particle growth, and

(4) growth of a decomposed region, originating in the grain boundary, containing monoclinic zirconia and magnesia-rich regions. The elucidation of the complete microstructural development is underway and will be reported at a later date. However, it is appropriate to describe the general features of these microstructural changes and their influence on the thermomechanical properties in the present work.

The microstructure of the as-fired material consisted of mainly tetragonal precipitates about 150 nm in their longest dimension distributed within grains of CSZ. This description is similar to that reported for near peak-aged Mg–PSZ materials except that the precipitate size of the latter was about 100 nm larger [7]. A typical selected area diffraction pattern (SAD) obtained from an as-fired material, showing a [1 1 1] cubic pole is presented in Fig. 3a. The intense $2\,2\,0$ reflections are due to the cubic fluorite matrix while the weaker half-order reflections are from the tetragonal precipitates. Tetragonal reflections also overlap the cubic spots and hence are not visible. Although some of the tetragonal precipitates in the as-fired material are metastable in that they will transform to monoclinic in the proximity of a crack, SAD illustrates the general absence of the monoclinic phase when the TEM specimens are carefully prepared.

Figure 3 Typical SAD patterns showing changes in a $[1\,1\,1]_c$ pole as a result of microstructural development due to ageing at $1100°$ C; (a) as-fired material, (b) ageing time 0.5 to 4 h, (c) ageing times > 4 h.
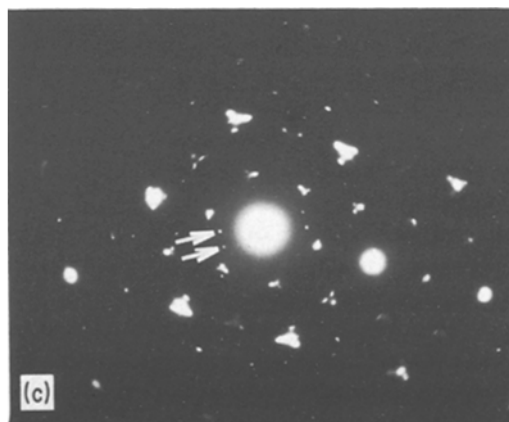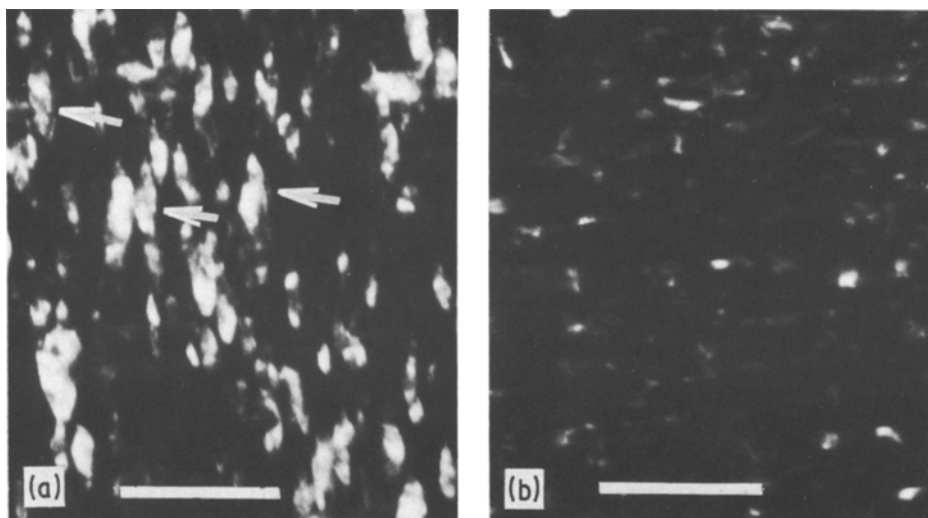
Figure 4 Dark-field transmission micrographs of Mg–PSZ samples aged at 1100° C for 16 h; (a) obtained with a split tetragonal/monoclinic lattice spot, (b) obtained with a δ-phase spot. The bar length equals 0.25 μm, beam direction near [3 1 0]$_c$.

The microstructural features outlined above, make their appearance with ageing at 1100° C. Ageing times greater than 30 min result in the formation of the ordered anion δ-phase. Nucleation of this phase occurs at the precipitate/matrix interface and grows to occupy the region of matrix between the precipitates. The occurrence of this phase is indicated by the presence of additional diffraction spots (arrowed) shown here in [1 1 1]$_c$, Fig. 3b. During the same ageing interval, there is a minor increase in the monoclinic content as shown by the splitting of some tetragonal and 2 2 0 cubic reflections (Fig. 3b). When the ageing time is increased to greater than 4 h there is a progressive increase in the amount of monoclinic phase, as can be seen in the SAD of Fig. 3c, which shows the splitting of the tetragonal diffraction spots in the different monoclinic variants (cf. Fig. 3b). The extra spots around the 2 2 0 cubic reflections are also a consequence of the tetragonal reflections splitting into monoclinic reflections. It is interesting to note that the δ-phase spots arising from the matrix in Fig. 3c are still quite sharp, showing no change.

The presence of considerable monoclinic material within the matrix grains, originating from formerly stable tetragonal precipitates is inconsistent with the TEM observation that precipitate size did not increase for ageing times as long as 32 h. The significance of these observations is that there must be a process other than growth whereby

precipitates can lose coherency and transform to the monoclinic structure during cooling. Prior to this study, growth of precipitates to their coherency limit was the only mechanism for generating the monoclinic phase within matrix grains [7].

Many of the precipitates have a fine structure so that they appear to be polycrystalline. The effect is best seen in a dark-field TEM image (Fig. 4a) obtained with a split tetragonal monoclinic diffraction spot such as shown in Fig. 3c. It is observed that at a certain stage of development, the precipitates have a hybrid structure consisting of the simultaneous existence of both the tetragonal and monoclinic phases. The localized white regions within the precipitates (some typical examples are arrowed in Fig. 4a), having the appearance of sub-grains, are ascribed to monoclinic intergrowth within the tetragonal precipitates. Fig. 4b is a dark-field TEM micrograph which illustrates the presence of the δ-phase in the matrix areas between the precipitates. The final major microstructural change is the growth of a decomposed region which nucleates in the grain boundaries. This phase is similar to the one reported by Porter and Heuer [6] and results from the decomposition reaction of the cubic matrix into the original monoclinic zirconia and magnesia reactants. The grain boundary phase only affects the room temperature bend strength significantly after sufficient monoclinic phase has been formed and the monoclinic grains have

grown to the critical size at which stresses arising from their anisotropic thermal expansion introduce cracking in the grain boundaries. A significant decrease in strength by this mechanism occurs with ageing times > 8 h, depending on the fabrication conditions.

The TEM observations imply that the remarkable onset of thermal shock resistance is the result of the subtle process occurring during ageing at 1100° C. The observations of this study allow the construction of the following model. As-fired material contains a population of mainly stable tetragonal precipitates distributed about a mean size. The size distribution has not been determined in the present work but the precipitate size in a Ca–PSZ alloy aged at 1300° C obeyed a log normal distribution [10]. During ageing at 1100° C the coherent interface, which we believe controls the structure of the precipitate at room temperature, becomes incoherent as a result of the solid-state reaction at the interface. We speculate on the nature of this reaction. Whilst cooling from firing, coherent tetragonal precipitates are nucleated and grow to 150 nm in a matrix of CSZ. During ageing at 1100° C, CSZ transforms and grows to large particles of ordered δ-phase, as a result of MgO diffusion. Consequently the lattice parameter of the δ-phase is sufficiently diminished compared to the original CS2 value that interfacial strains are generated which destroy coherency and allow some of the precipitates to transform to the monoclinic structure during cooling from the firing temperature whilst decreasing the stability of others.

This process has the following consequences. Formerly coherent, stable tetragonal precipitates (type 1) become semi-coherent and unstable (type 2) in the presence of a crack. The increase in the number of type 2 precipitates enhances the transformation toughening mechanism and is responsible for the increase in strength of the material during the early stages of ageing as noted in Fig. 1. Former type 2 precipitates become incoherent and transform to the monoclinic structure (type 3) when the material is cooled to room temperature. It is believed that it is these latter type 3 precipitates which impart thermal shock resistance and enhanced fracture toughness to the material, as discussed by Swain [11].

The working hypothesis is consistent with a detailed analysis of the monoclinic content of the material as a function of ageing time, shown in
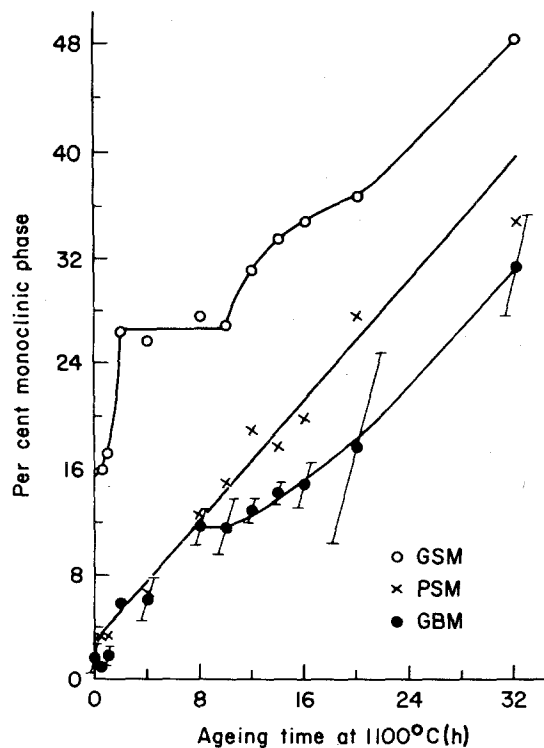

Figure 5 Analysis of the various monoclinic phases present in Mg–PSZ materials, as a function of ageing time, by X-ray diffraction and optical microscopy.

Fig. 5. Monoclinic material at room temperature can form as a result of (a) stressing metastable tetragonal precipitates, (b) cooling of incoherent tetragonal precipitates whose transformation temperature is greater than room temperature or (c) the eutectoid decomposition reaction which occurs at the grain boundaries. The GSM curve in Fig. 5 gives the total of all three types of monoclinic, (a), (b) and (c). The PSM curve is a measure of (b) and (c) type monoclinic, whilst the GBM curve gives only the (c) type monoclinic content.

During the ageing interval, 0 to 3 h, the GSM value rises rapidly from about 15 to 25% due to formerly stable tetragonal precipitates (type 1) becoming unstable (type 2) in the presence of a crack. This is a consequence of the proposed interfacial reaction. The PSM and GBM curves coincide approximately and increase linearly from about 2 to 6%. Thus the only monoclinic material formed (in the absence of stresses) is in the boundaries due to the decomposition reaction. The difference between the GSM and PSM curves is a measure of the number of precipitates which can be transformed by stresses. This number is a

maximum at about 3 h of ageing which coincides with the time required to obtain the maximum initial strength observed in Fig. 1.

With ageing in the interval 3 to 8 h, the GSM value remains constant at 26%, whilst the PSM and GBM curves continue to coincide and to increase linearly to about 12%. The constant value of the GSM curve implies that the number of metastable tetragonal precipitates decreases in this interval. This fact is reflected in the decrease in the initial strength of the material observed in Fig. 1. When ageing is increased beyond 8 h, the GSM curve increases linearly, as does the PSM curve. However, now the GBM curve diverges from the PSM curve, increasing at a slower and non-linear rate, as a function of ageing time. The difference between the PSM and GBM curves must be due to monoclinic material primarily within the grains and presumably, is due to formerly metastable tetragonal precipitates (type 2) transforming to monoclinic during cooling of the material to room temperature. Because of the precise coincidence of the occurrence of the two phenomena it seems most likely that it is the formation of these monoclinic precipitates which imparts thermal up-shock resistance to the material.

Apparently Porter and Heuer [6] did not observe the phenomena we report here in their ageing studies of Mg–PSZ. There appears to be two reasons for this. Firstly, their initial precipitate size of 5 nm was too small. We find that the precipitates must be of the order of 100 nm after firing to observe the phenomena described in this work. Second, those authors aged the material in the range 1200 to 1300° C and also at 1000° C. In the former range the destructive effect of the rapid eutectoid decomposition reaction masks any beneficial effect of the particle/matrix interfacial reaction, while, at 1000° C, the interfacial reaction is too slow to be observed at practical ageing times [4]. Ageing at or about 1000° C is much more favourable to the development of the special microstructure discussed in this work; at this temperature the decomposition reaction is slow enough so that the amount of GBM phase formed does not affect the mechanical properties in the ageing time required to develop thermal shock resistance. The alternative way of developing monoclinic precipitates within the grains by over-ageing Mg–PSZ materials at 1400° C and above [7] is much less satisfactory than ageing at 1100° C because over-ageing at the higher ageing
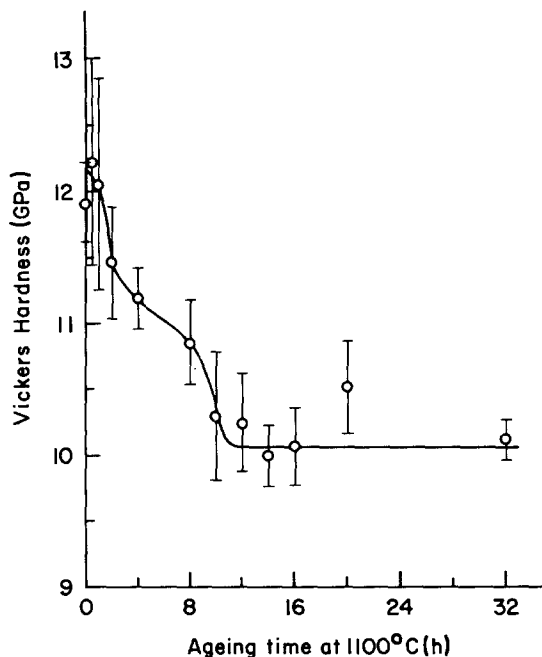

Figure 6 Vickers hardness data of Mg–PSZ samples as a function of ageing time.

temperature causes a considerable reduction in the room temperature strength whilst imparting only relatively modest thermal up-shock resistance to the material.

Vickers hardness data as a function of the ageing time are given in Fig. 6. These data can be correlated with changes in the precipitate/matrix interface and precipitate structure as follows. The hardness decreases rapidly in the interval 0 to 3 h. The slope has its maximum value in this interval which coincides with the rapid increase in type 2 precipitates (semi-coherent, tetragonal) noted in Fig. 5. The decrease in hardness is attributed to the loss of coherency of many of the precipitates. The curve goes through an inflection point at about 3 h, with a reduced value of the slope maintained until about 8 h of ageing. This behaviour reflects a lower rate of formation of type 2 precipitates. At about 8 h of ageing, the curve again passes through an inflection point and the slope increases; this increase coincides with the formation of type 3 (monoclinic) precipitates. It is known that the monoclinic phase is considerably softer than the CSZ phase [12, 13]. After about 12 h the hardness attains a low constant value even though the matrix monoclinic phase continues to increase; apparently the influence of the mono-clinic (type 3) precipitates on the hardness of the system is saturated at about 12 h of ageing.
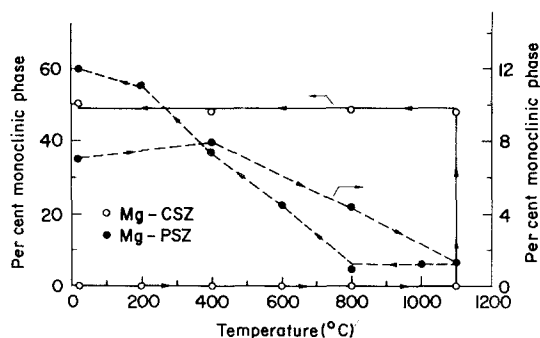
Figure 7 Monoclinic phase content of Mg–PSZ and Mg–CSZ samples as a function of temperature and ageing time at 1100° C as measured by high temperature X-ray diffraction analysis.

Data obtained from a high temperature X-ray diffraction study at 1100° C of Mg–CSZ containing about 5 wt% MgO (~ the eutectoid composition) and also of Mg–PSZ are presented in Fig. 7; the Mg–PSZ material was made from a different batch of powder than the material discussed earlier in this work. The PSM value of the Mg–CSZ sample was zero when it was first heated to 1100° C. After 3 h the PSM content increased to about 50% and remained at this value during cooling of the material to room temperature. The PSM value of the Mg–PSZ sample was 7% initially which decreased to about 1% at 1100° C. The temperature dependence of the PSM is due to the presence of monoclinic precipitates of varying size and hence varying transformation temperature [14]. After 9 h of ageing there was no change in the PSM content indicating that very little grain boundary (eutectoid) decomposition had occurred. However, when the sample was cooled, the PSM increased smoothly to about 12% at room temperature, therefore, there has been an increase in the number of precipitates having the monoclinic structure at room temperature. It is reasonable to conclude that the increase in PSM content observed in the Mg–CSZ and Mg–PSZ samples occurs by different mechanisms. The behaviour of the latter material is consistent with the proposed interfacial reaction discussed above.

4. Conclusions
(a) Ageing Mg–PSZ materials at 1100° C trans-forms initially tetragonal zirconia precipitates to the monoclinic structure by a process other than particle growth.

(b) The formation of monoclinic precipitates in Mg–PSZ by ageing at 1100° C greatly improves the thermal up-shock resistance as well as fracture toughness of the material.

Acknowledgements

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