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 decomposition 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 thermo-chemical 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