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Methodology for analysing the degradation of Mg-PSZ

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For expanded applications and ease of manufacture, joining ceramics to other ceramic and metal components is a subject of intense interest, especially for heat engine applications. Magnesia partially stabilized zirconia (Mg-PSZ) is one possible material for various desired applications, due to its toughness and thermal and mechanical shock resistance. During processing of the join and during the lifetime of the ceramic component, thermal and chemical potential gradients are expected to cause complex reactions at the zirconia–metal interface. Particularly important reactions are the oxidation of the metal-joining agents and their diffusion/migration into the ceramic. Because of the small spatial scales of both the complex reactions and the interface, identifying mechanisms of degradation due to particular metals or metal oxides would be difficult. This research focuses on a methodology to identify whether the reaction of the metal oxides with Mg-PSZ would cause degradation. The methodology for investigating these reactions of Mg-PSZ to oxidized metals was developed by adapting a conventional metallurgical technique known as the temperature–time–transformation diagram. The metals selected for investigation were copper, tin and zinc (typical brazing agents), titanium and aluminium (reactive metals), and cobalt and nickel (super alloys and typical interlayer metals). To model the reaction at the interface layer, oxides of the metals were mixed with Mg-PSZ powder and its effect on precipitation analysed. All metal oxides accelerated the precipitation rate of the tetragonal phase, thereby shifting the nose of the temperature–time–transformation diagram to shorter times as compared to undoped Mg-PSZ. Additionally, these oxides enhanced growth of the monoclinic phase with increasing time at temperature.

1. Introduction

One important future commercial application of ceramics will be ceramic/metal components in heat engines. Zirconia-based ceramics are materials of choice for engine components because they are oxidation resistant, already being an oxide, and have a low thermal conductivity. In addition, zirconia ceramics have thermal expansion coefficients which match those of steels, making bonding easier. The fracture toughness of some zirconia materials is significantly greater than that of either SiC or Si_3N_4, and thus leads to improved resistance to mechanical and thermal shock. Mg-PSZ, with a toughness of $\sim 15\ \mathrm{MPa\,m^{1/2}}$, is particularly desirable for such applications.

Some techniques have been developed for analysing the various interactions in the manufacture of complex ceramic/metal components. Primary to good brazing and bonding is the wettability of the metal to the ceramic. Basic methods have been developed for studying the wettability of liquid metals to zirconia materials [1, 2]. It was found that the more reactive the metal is with oxygen, the greater the wettability of the metal to zirconia. This effect was also found for other oxides such as alumina, where the addition of a reactive metal introduced into the bond increased toughness and bond strength [3–7]. Macroscopic behaviour resulting from the reactions of the various zirconia and yttria–zirconia materials with bonding agents have also been investigated [9–12, 17]. It has been found that any thermal expansion mismatch between the metal and the zirconia material affects bond strength. A smaller mismatch results in a stronger bond, even though the wettability of the metal to the zirconia may be poor [2].

Another typical problem in this field is oxidation of the bonding agent which results in a loss of bond integrity. In a simple bonding of a titanium alloy piece to Y-TZP material with a copper–silver–titanium braze, Cu_2Ti_4O formed at the ceramic interface and the Y-TZP was reduced and partially transformed into monoclinic zirconia. In another case, where cubic stabilized zirconia was bonded to superalloys, the interlayer metals regularly used formed spinel and spinel-like phases at the expense of the interlayer [9–13]. Relatively short periods of less than 100 h, at temperatures of ~ 1000°C, were found sufficient for formation of these metal oxides within the metal interlayer [10–12]. Alternatively, diffusion of the bonding agent into the zirconia material can also influence the integrity of the host material. In some

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instances, interdiffusion of NiAlYTi into the zirconia layer causes the formation of non-transforming tetragonal phases, which results in a loss of strength and toughness [12]. The dissolution of a Ni_2AlTi layer into the zirconia layer produces coarsened tetragonal precipitates which are less resistant to tetragonal–monoclinic phase transformation [11].

A methodology for analysing the degradation of zirconia ceramics by various metal oxides does not exist. A systematic method would be useful in screening metals and metal oxides used as bonding agents. To inquire into the effect of oxidized metals on a Mg-PSZ within a reasonable time, a known quantity of the selected metal oxide was alloyed with the starting materials of 9.5 mol % Mg-PSZ. The effect of the metal oxides on the precipitation behaviour was then investigated. The criteria for discriminating beneficial from deleterious metals are proposed as follows. If a selected metal oxide accelerated the precipitation rate, that metal would be considered deleterious for use in bonding. If a selected metal oxide did not affect or slow down the precipitation rate, then it would be considered beneficial for use in a bond. The metal alloys considered are copper, tin and zinc (typical brazing agents), titanium and aluminium (reactive metals), and cobalt and nickel (typical interlayer and super-alloy components). To identify the effect of these oxidized metals on the precipitation of the tetragonal phase in Mg-PSZ, a systematic method of comparison was needed. The method selected for comparison is the application of the temperature–time–transformation (TTT) behaviour curve to Mg-PSZ doped with these alloys.

Precipitation and growth of the metastable tetragonal phase has been shown via a temperature–time–transformation diagram in the work by Hughan and Hannink [13]. They developed curves to represent the volume of secondary precipitate growth which is equivalent to the volume of the stress-transformable tetragonal phase. Two curves developed were the start of secondary precipitate growth at 5 vol % and completion of the growth at 95 vol %. The behaviour of zones containing no secondary precipitates and the growth of the grain-boundary monoclinic phase have also been analysed [14]. As the transformable tetragonal phase content increases, the volume fraction of zones containing no secondary precipitates, or 'white spots', decreases to zero.

A temperature–time–transformation diagram, based on this previous work [13, 14], has been developed to allow ready comparison of the effect of the oxidized bonding metals on secondary precipitate growth. The peak in the volume fraction of the transformable tetragonal phase at 1400 and 1320 °C measured by X-ray diffraction (XRD) is used instead of metallographically determined secondary precipitate growth. Analysis of the transformable tetragonal phase by XRD provides a direct measure of the volume fraction of that phase. The metallographic technique provides only an indirect measure of the volume fraction and could be affected by the oxidized bonding metals.

The peak in the volume fraction of transformable tetragonal phase is expected to shift depending on how the alloys affect secondary precipitate growth with respect to undoped Mg-PSZ. If the oxidized bonding metals slow the secondary precipitate growth, the peaks in the tetragonal phase volume fraction would be shifted to longer times. If the secondary precipitate growth was accelerated with respect to undoped Mg-PSZ, the peaks would be shifted to shorter times. The accelerated precipitate growth would result in overaging with respect to undoped Mg-PSZ and a degradation of mechanical properties. The use of temperatures at 1320 and 1400 °C allows determination of the effect of the oxidized metal bonding on Mg-PSZ within a short time span, instead of several thousand hours at the expected use temperature. The use of one mol% additions of the metal oxides in this investigation is assumed to allow study of the resulting effects without overwhelming or underwhelming the secondary precipitation process.

2. Experimental procedure

Compositions were prepared with a baseline Mg-PSZ composition of 9.5 mol % MgO, 90.5 mol % ZrO_2. Six other compositions were prepared containing 1 mol % each of CuO, SnO_2, ZnO, [Al_2O_3 + TiO_2], CoO and NiO, the remainder 99 mol % Mg-PSZ. Metal oxides, 99.9% pure, were used along with high-purity ZrO_2 powder (Grade SF-Super, Z-Tech Pty Ltd, Melbourne, Australia). Batches were milled with zirconia grinding media and the resultant powders pressed into bars at 50 MPa. These bars were heated to 1700 °C and sintered for 2 h. The bars were furnace-cooled rapidly at $> 1000°C\,h^{-1}$ between 1700 and 1400 °C, and at $560\,°C\,h^{-1}$ between 1400 and 1200 °C. Samples were then heat treated for 1, 2, 5 and 10 h at 1400 and 1320 °C. The rapidly furnace-cooled samples were considered to have been heat-treated for 0.1 h at both 1400 and 1320 °C.

Each sample was machined with a 200 grit diamond surface grinder, and the volume fraction of the monoclinic phase from the ground surface was measured by XRD. CuK_α radiation was used with a single crystal graphite monochromometer on a computer-controlled Phillips horizontal diffractrometer. The areas of reflections for the 1 1 1 and $1 1 \bar{1}$ monoclinic peaks and the combined 1 1 1 peak for the tetragonal and cubic phases were numerically integrated from the diffractometer data. The ratio of combined area of the monoclinic peaks to the total peak areas of the $< 1 1 1 >$ reflections gave the volume fraction of the monoclinic phase. Samples were then polished from 600 grit through 1 μm diamond paste. The difference in the volume fraction monoclinic phase between ground and polished surfaces is deemed equivalent to the volume fraction of transformable tetragonal phase [15, 16].

3. Results

The transformable tetragonal phase content for undoped Mg-PSZ at 1400 and 1320 °C against time is plotted in Fig. 1. At 1400 °C, the maximum transformable tetragonal phase content occurs at 1 h, while

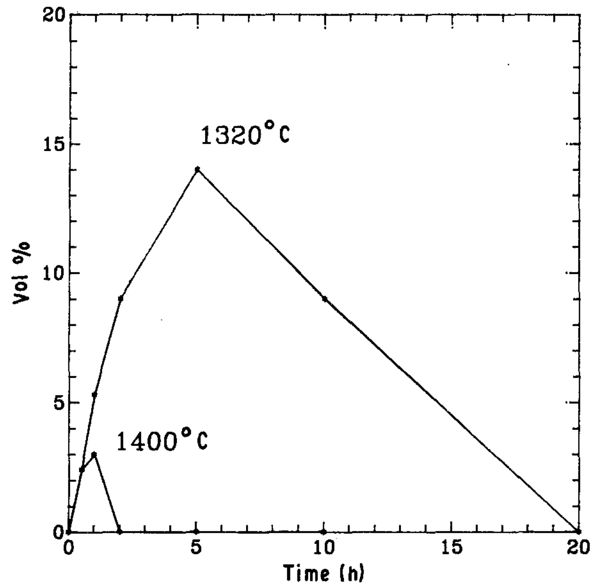

Figure 1 Consolidated transformable tetragonal phase content against time for undoped Mg-PSZ at 1400 and 1320 °C.

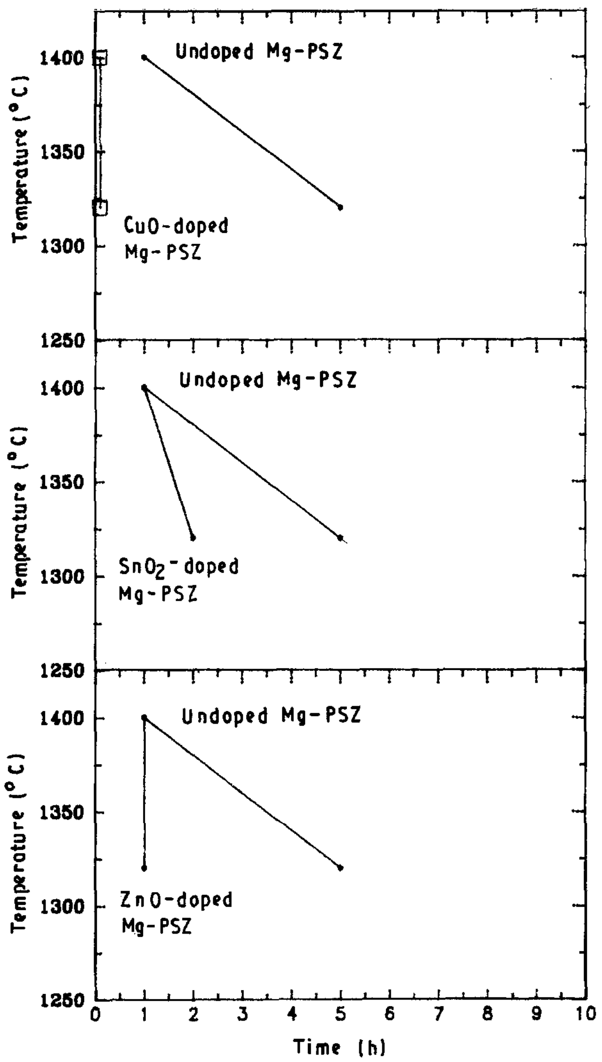

Figure 2 Modified T–T–T diagram for CuO-, SnO_2- and ZnO-doped Mg-PSZ against undoped Mg-PSZ.

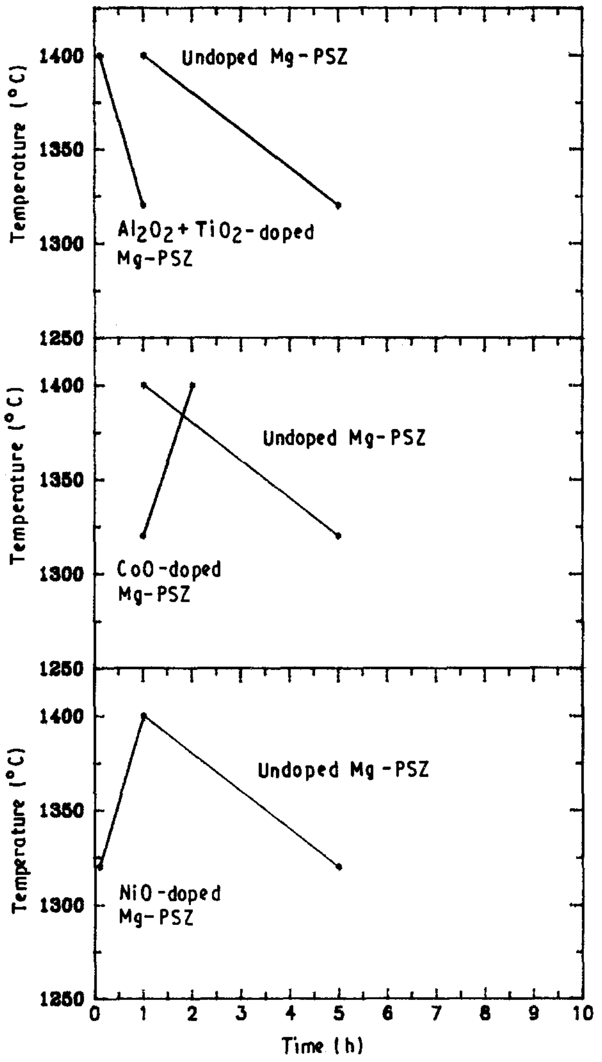

Figure 3 Modified T–T–T diagram for Al_2O_3 + TiO_2-, CoO- and NiO-doped Mg–PSZ against undoped Mg-PSZ.

at 1320 °C the maximum phase content occurs at 5 h. The result, when plotted on a graph of temperature against time, is a line sloping to longer times at lower temperatures. This is considered to be a temperature–time–transformation diagram modified to show how the secondary precipitate growth rates are affected. The peaks in the volume fraction of transformable tetragonal phase and the representative line are expected to shift, depending upon how the metal oxides affect the secondary precipitate growth with respect to undoped Mg-PSZ. If oxidized bonding metals slow secondary precipitate growth, the peaks in the tetragonal phase volume fraction and the respective line would be shifted to longer times. If the secondary precipitate growth was accelerated with respect to undoped Mg-PSZ, the line would be shifted to shorter times. For the doped Mg-PSZs, the times at which the maximum transformable tetragonal phase content occurs were also determined.

For CuO^-, SnO_2^-, ZnO-doped Mg-PSZ, the times for maximum tetragonal content are plotted against temperature in the modified TTT diagrams in Fig. 2. In CuO-doped Mg-PSZ against undoped Mg-PSZ, the maximum tetragonal content occurs only for the rapidly furnace cooled sample. In the SnO_2- and ZnO-doped Mg-PSZs against undoped Mg-PSZ diagrams, both SnO_2 and ZnO cause an increase in the tetragonal precipitation rate at 1320 °C. Plotted in Fig. 3, are the data for Al_2O_3 + TiO_2-, CoO- and NiO-doped Mg-PSZ against undoped Mg-PSZ. In this figure, $Al_2O_3 + TiO_2$ has accelerated the precipitation rate for the doped Mg-PSZ at both 1400 and 1320 °C. Both CoO and NiO increase the precipitation rate at 1320 °C similar to SnO_2- and ZnO-doped Mg-PSZ, while NiO shifts the TTT curve the most. Comparing Figs 2 and 3, CuO accelerates the transformable tetragonal precipitation rate the most, with $Al_2O_3 + TiO_2$ similar in behaviour for the degradation of Mg-PSZ.

In Figure 4, the polished monoclinic content at both 1400 and 1320 °C is plotted against time for undoped Mg-PSZ and CuO-, SnO_2- and ZnO-doped Mg-PSZ. For undoped Mg-PSZ, at 10 h the monoclinic content reaches 30–35 vol % for both 1400 and 1320 °C. The monoclinic content at 1400 °C reaches an equilibrium value of ~ 30 vol %, while the 1320 °C data slowly increase to that value. In CuO doped Mg-PSZ, the monoclinic content for both 1400 and 1320 °C rapidly increases to 40–50 vol % after 2 h and continues to increase to 60–80 vol % by 10 h. Both SnO_2- and ZnO-doped Mg-PSZ behave similarly to the undoped Mg-PSZ reaching approximately 40 vol % monoclinic content by 10 h. The monoclinic content for the 1320 °C temperature has a more rapid increase for the SnO_2- and ZnO-doped samples than the undoped Mg-PSZ.

Fig. 5 shows the polished monoclinic content at both 1400 and 1320 °C against time of undoped Mg-PSZ for comparison with $Al_2O_3 + TiO_2$-, CoO- and NiO-doped Mg-PSZ. The $Al_2O_3 + TiO_2$-doped Mg-PSZ behaves similarly to CuO-doped Mg-PSZ, with a

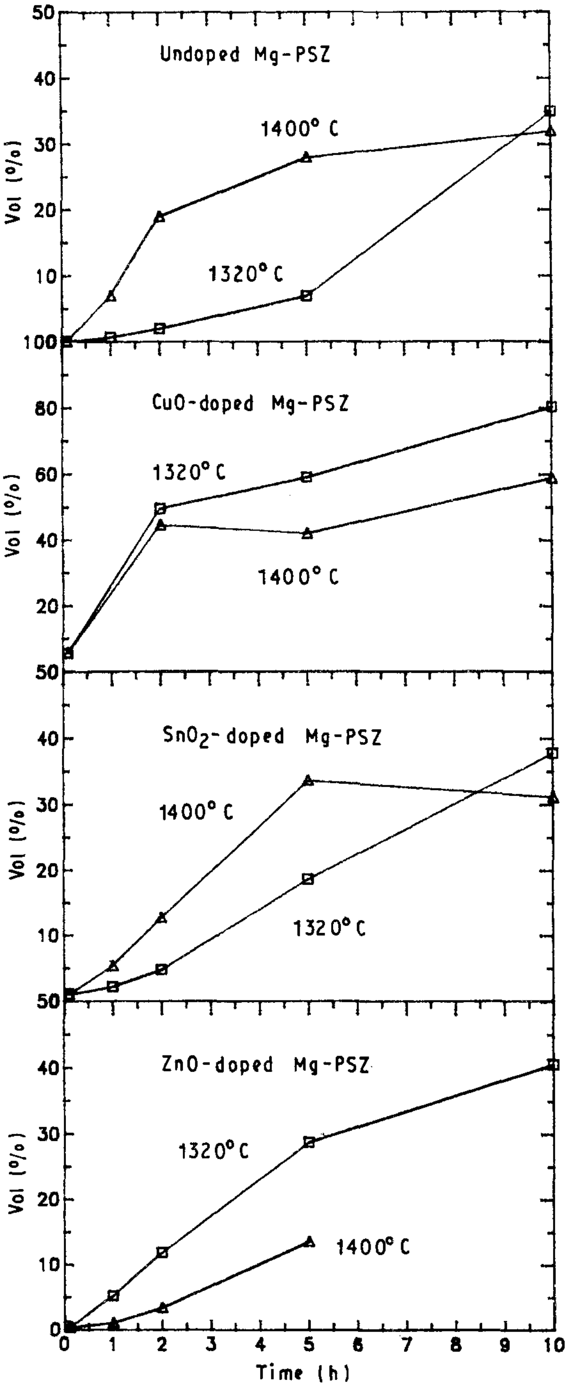

Figure 4 Polished monoclinic phase content at 1400 and 1320 °C for undoped Mg-PSZ and CuO-, SnO_2- and ZnO-doped Mg-PSZ.

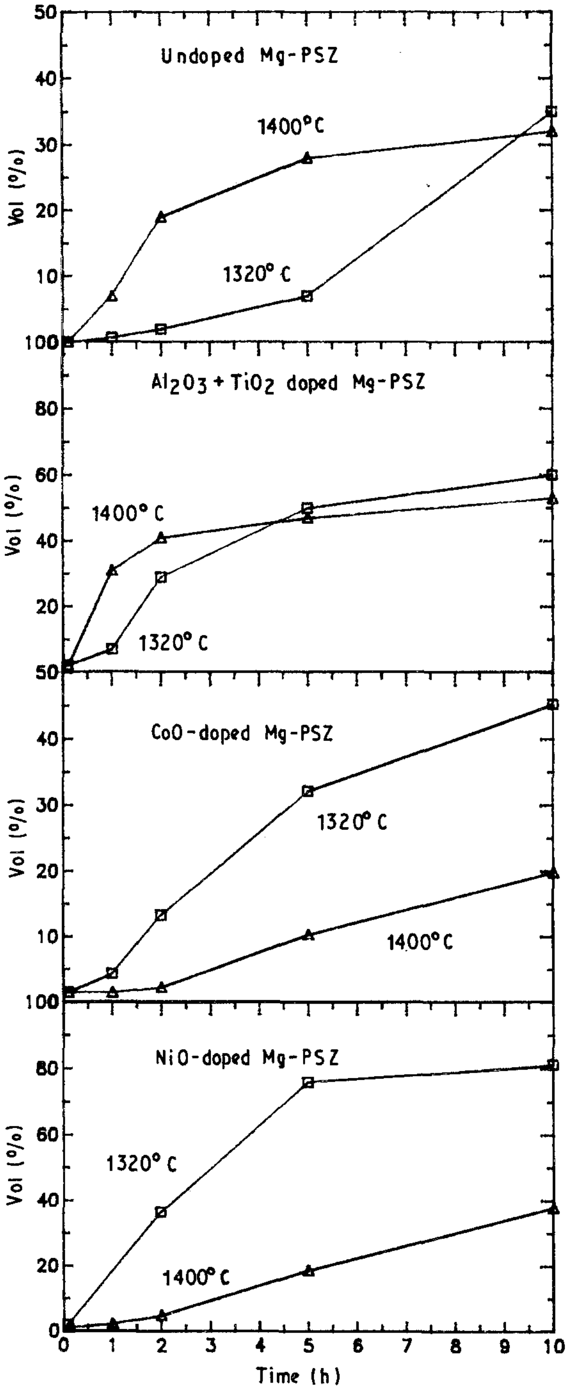

Figure 5 Polished monoclinic phase content at 1400 and 1320 °C for undoped Mg-PSZ and $Al_2O_3 + TiO_2$-, CoO- and NiO-doped Mg-PSZ.

rapid rise in monoclinic content to about 40 vol % and continuing to increase to approximately 60 vol %. CoO- and NiO-doped Mg-PSZ exhibit the same behaviour with the 1320 °C monoclinic content accelerated, and at 1400 °C the monoclinic content is depressed. This is the opposite in behaviour to the undoped Mg-PSZ. CoO depresses the formation of the monoclinic phase at 1400 °C when compared with undoped Mg-PSZ, reaching only 20 vol % at 10 h. NiO, however, accelerates the formation of the monoclinic phase at 1320 °C with 80 vol% being reached by 10 h.

4. Conclusions

The modified temperature–time–transformation curve was used to identify the effect of selected oxidized metals on Mg-PSZ. It was found that copper, tin, zinc, titanium, aluminium, cobalt and nickel oxides shifted the precipitation to shorter times and accelerated the formation of the monoclinic phase. The methodology presented, the modified temperature–time–transformation curve, will be useful for preliminary filtering and identification of metals and metal oxides that would not cause degradation of Mg-PSZ.

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