

Hydrothermal corrosion of magnesia-partially-stabilized zirconia

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Changes in the phase compositions and microstructures of magnesia-partially-stabilized zirconia (Mg-PSZ) were studied in water at 80–300 °C, 1 M HCl solutions at 80–140 °C and 1 M CH₃COOH-CH₃COONa buffer solutions at pH 3 and 80–140 °C for 10–40 days. The tetragonal to monoclinic phase transformation and the degradation of the fracture strength occurred in water above 200 °C. On the other hand, although no noticeable tetragonal to monoclinic phase transformation proceeded in 1 M HCl solutions and 1 M CH₃COOH-CH₃COONa buffer solutions at pH 3 below 140 °C, the fracture strength of Mg-PSZ greatly degraded. The dissolution of Mg²⁺ ion was observed in water above 200 °C and in 1 M HCl solutions above 80 °C.

1. Introduction

Although yttria-doped tetragonal zirconia polycrystals (Y-TZP) show high fracture strength and toughness, the mechanical properties were sometimes greatly degraded by low-temperature annealing in air and/or in water due to the tetragonal to monoclinic phase transformation accompanied by the microcracking, which is enhanced by the chemical reaction between tetragonal zirconia polycrystals and water on the surface [1–3]. On the other hand, although the fracture strength of magnesia-partially-stabilized zirconia (Mg-PSZ) is not so high, Mg-PSZ shows excellent fracture toughness and thermal stability. Mg-PSZ possesses considerably different microstructure from the fine-grained Y-TZP materials. Mg-PSZ are characterized by a well-defined microstructure composing of large cubic (c) grains about 100 µm containing a second phase of finely dispersed submicrometre tetragonal (t) and possibly monoclinic (m) precipitates [4, 5], whereas the TZP materials often completely consist of metastable tetragonal grains. The maximum fracture strength of Mg-PSZ is only half that of Y-TZP whereas the fracture toughness is almost double. Because the metastable tetragonal zirconia of the Mg-PSZ is precipitated in the cubic zirconia matrix, it is well protected against attack by water. Therefore, Mg-PSZ shows high stability for low-temperature ageing in air. Recently, it was reported that Mg-PSZ showed the tetragonal to monoclinic phase transformation and the modest decrease in strength in a steam environment at high temperature and high pressure, such as 400 °C and 6 atm for 40 h [6]. However, no detailed information has been reported for the stability of Mg-PSZ in water. In the

present study, a series of tests were conducted to evaluate the chemical stability of Mg-PSZ in water and acidic solutions.

2. Experimental procedure

The samples tested were two commercially available grades of Mg-PSZ, a thermal shock-resistant grade (TS Mg-PSZ) and a maximum strength grade (MS Mg-PSZ). All samples were cut into rectangular coupons, 2 mm × 5 mm × 20 mm, and polished to mirror-like surface. In each experiment, the sample was placed in 20 ml sealed stainless steel tube or 20 ml sealed glass tube and then 5 ml distilled water, 5 ml 1 M HCl solution or 5 ml 1 M CH₃COOH-CH₃COONa buffer solution at pH 3 was added; the tube was sealed and then placed in a glycerol bath or electric furnace at 80–300 °C for 10–40 days. Pressure was set at the saturated vapour pressure of water at each temperature. The sealed tubes were removed from the bath or electric furnace at regular time intervals and quickly cooled to room temperature. The phases were identified by X-ray diffraction analysis of the flat surface by using nickel-filtered CuKα radiation. Scans of 2° between 27° and 33° were conducted to estimate the monoclinic to (tetragonal + cubic) ratio. Microstructures of the cross-section of samples were observed by scanning electron microscopy. The fracture strength of the sample was determined by three-point bending test with a crosshead speed of 0.5 mm min⁻¹ and span length of 10 mm. The amount of Mg²⁺ ion leached in the solution was determined by inductively coupled plasma spectroscopy.

3. Results and discussion

The amounts of m-ZrO₂ on the surface and the bending strength of the MS and TS grade Mg-PSZ samples annealed in water at 80–300 °C for 20 days are shown in Fig. 1. The tetragonal to monoclinic phase transformation proceeded noticeably above 140 °C. The amount of m-ZrO₂ formed increased with increasing temperature. On the other hand, the bending strength decreased with increasing temperature up to 200 °C, but the degree of degradation of the fracture strength at 250 and 300 °C was little. For comparison, similar experiments were carried out in air at 80–300 °C for 20 days, but no noticeable phase transformation and degradation of the bending strength was observed. Therefore, it might be concluded that the tetragonal to monoclinic phase transformation in Mg-PSZ by low-temperature ageing was enhanced by water.

Time dependence of the amount of m-ZrO₂ on the surface and the bending strength of MS and TS grade Mg-PSZ annealed in water at 120–300 °C are shown in Fig. 2. As seen in Fig. 2, both MS and TS grade Mg-PSZ samples were stable in water below 120 °C, but the tetragonal to monoclinic phase transformation occurred above 200 °C. The amount of m-ZrO₂ on the surface increased with increasing temperature and reaction time. The final amounts of m-ZrO₂ on the surface of MS and TS grade Mg-PSZ corroded were 45.2 and 54.2 mol%, respectively. Fine *et al.* [7] reported that MS and TS grade Mg-PSZ originally consisted of approximately 65 vol %

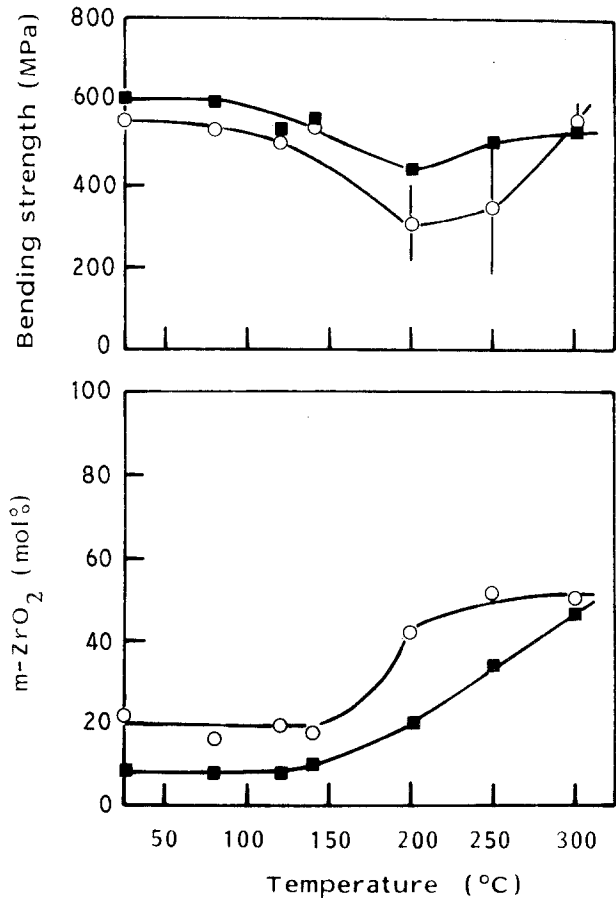


Figure 1 Bending strength and amounts of the monoclinic zirconia on the surface of (■) MS and (○) TS grade Mg-PSZ corroded in water at various temperatures.

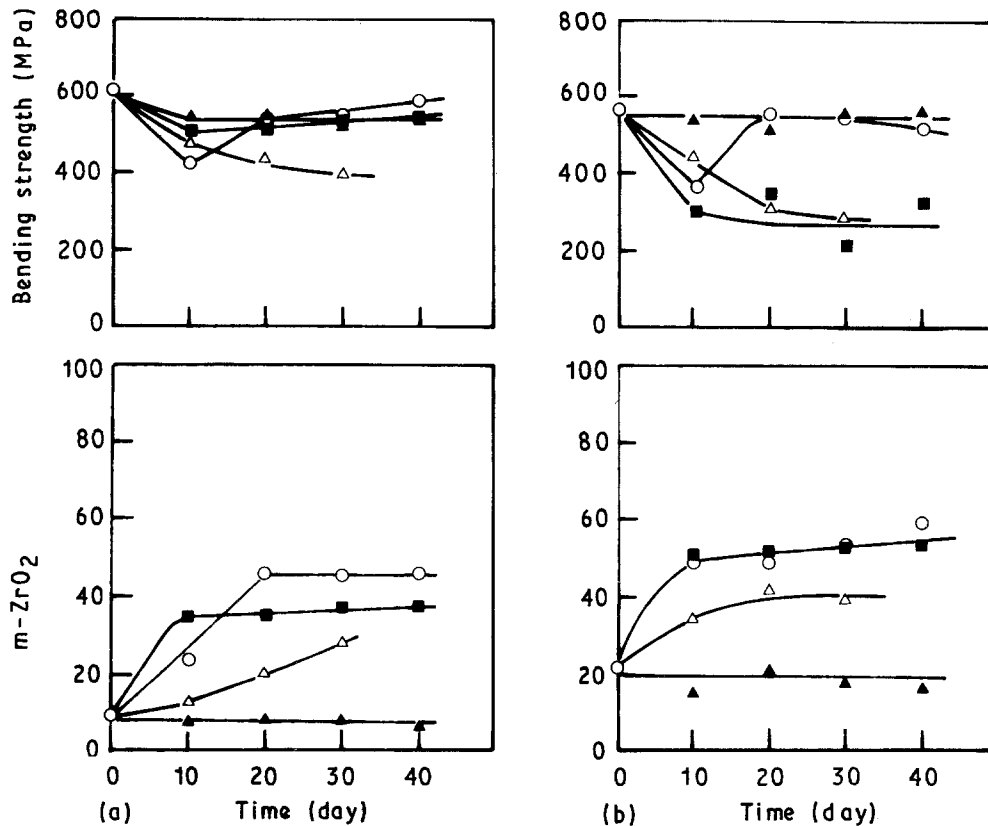


Figure 2 Time dependence of the bending strength and the amounts of the monoclinic zirconia on the surface of (a) MS and (b) TS grade Mg-PSZ corroded in water at (▲) 120 °C, (△) 200 °C, (■) 250 °C, (○) 300 °C.

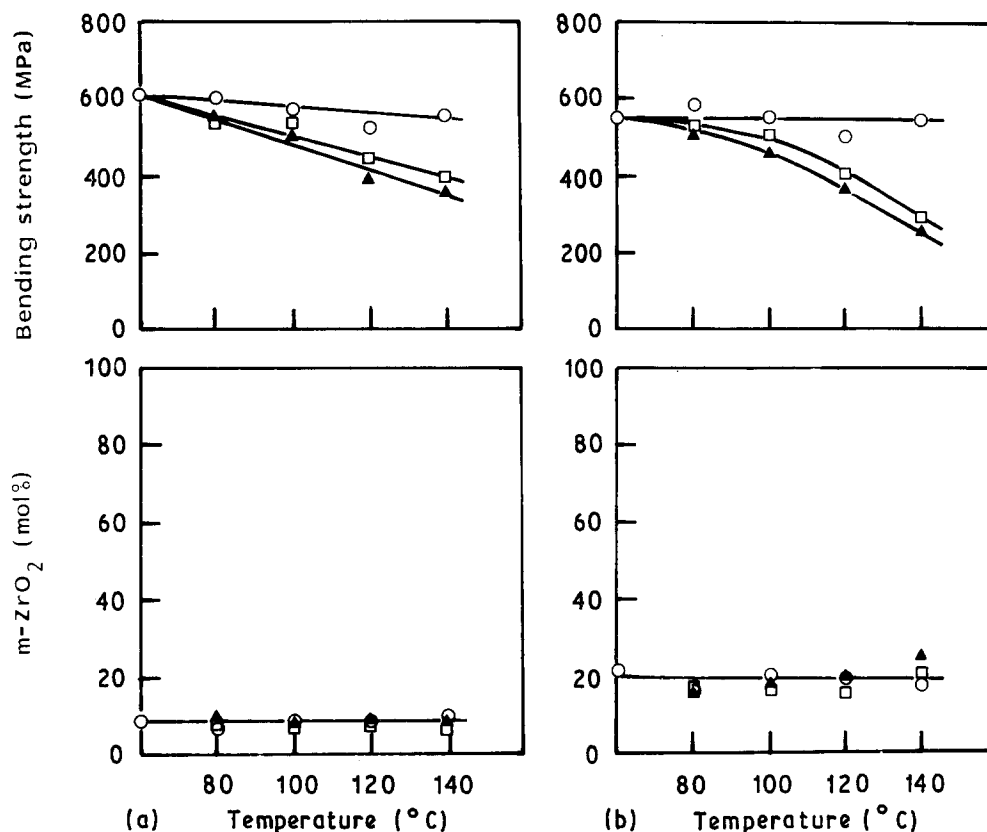


Figure 3 Bending strength and amounts of monoclinic zirconia on the surface of (a) MS and (b) TS grade Mg-PSZ corroded in (○) water, (□) 1 M HCl solution and (▲) 1 M CH₃COOH-CH₃COONa buffer solution at pH 3 as a function of temperature.

c-ZrO₂, 26 vol % t-ZrO₂ and 9 vol % m-ZrO₂ and 50–64 vol % c-ZrO₂, 20–22 vol % t-ZrO₂ and 16–28 vol % m-ZrO₂. Therefore, it was found that the final amounts of m-ZrO₂ on the surface of both Mg-PSZ hydrothermally corroded were approximately equal to the total amounts of m-ZrO₂ and t-ZrO₂ in original Mg-PSZ samples. These results indicated that only the tetragonal precipitates in original Mg-PSZ transformed to the monoclinic phase by the present hydrothermal conditions. The relationship between the amount of m-ZrO₂ formed and the bending strength of the sample was not simple. The bending strength of both Mg-PSZ decreased with reaction time at 200 °C. On the other hand, significant decrease in the bending strength of both Mg-PSZ was observed after annealing for 10 days at 300 °C, but then the bending strength recovered to almost the same value of original samples after annealing for 20 days at 300 °C. The recovery of the bending strength by annealing more than 20 days at 300 °C seemed to be due to the surface compressive stress accompanied by the tetragonal to monoclinic phase transformation on the surface. Therefore, it can be suspected that the hydrothermal corrosion of Mg-PSZ resulted in the formation of surface flaws, which decrease the fracture strength and in the induction of surface compressive stress by the tetragonal to monoclinic phase transformation, which thus increases the bending strength.

The amount of m-ZrO₂ on the surface and the bending strength of both MS and TS grade Mg-PSZ corroded in water, 1 M HCl solutions and 1 M CH₃COOH-CH₃COONa buffer solutions at pH 3 at 80–140 °C for 20 days are shown in Fig. 3. It was

noticeable that although no phase transformation was observed in the present experimental conditions, significant degradation of the bending strength was observed for the samples corroded in 1 M HCl and 1 M acetate buffer solutions. These results indicated that the surface flaws, which decrease the bending strength of Mg-PSZ annealed in aqueous solution, were formed not only by the tetragonal to monoclinic phase transformation but also by the corrosive attack without phase transformation. Because the degree of the degradation of the bending strength increased with

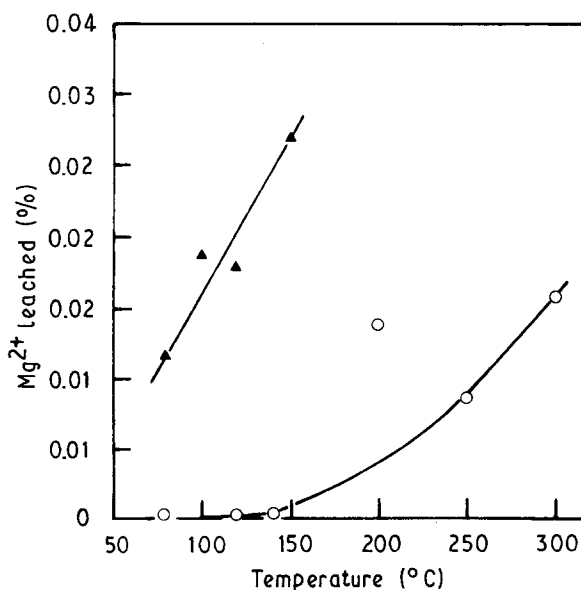


Figure 4 Amounts of Mg²⁺ ion leached in (○) water and (▲) 1 M HCl solutions at various temperatures for 20 days.

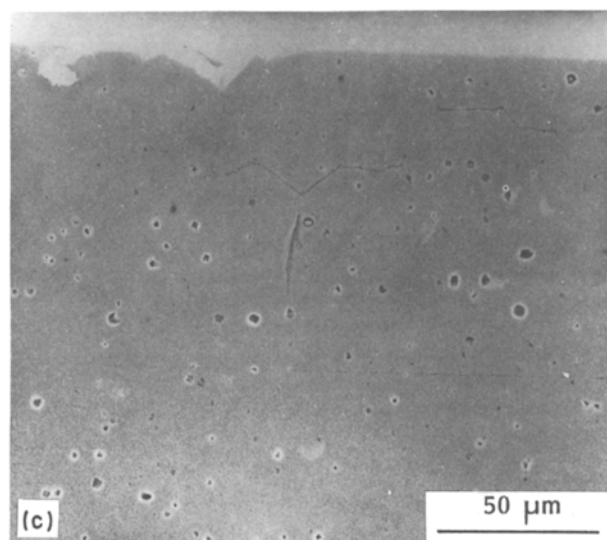
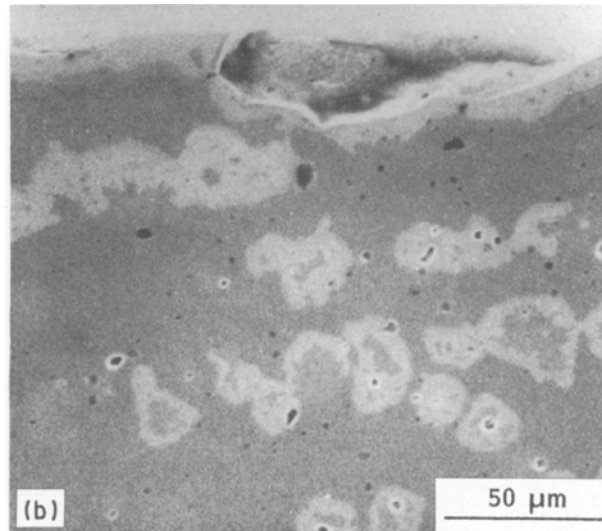
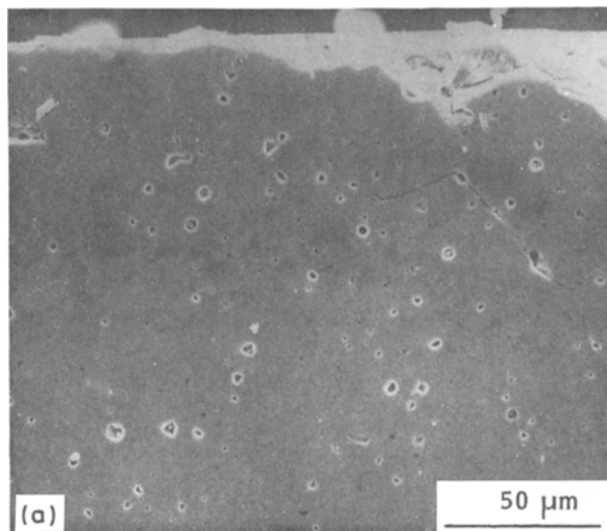


Figure 5 Scanning electron micrographs of the cross-sections of MS grade Mg-PSZ corroded in water at (a) 200 °C, (b) 300 °C and (c) 1 M HCl solution at 140 °C for 30 days.

increasing acidity of the solutions, surface flaws might be introduced by the dissolution of the samples.

Under the present experimental conditions, the dissolution of ZrO_2 matrix was negligible, but a noticeable amount of Mg^{2+} ion was leached in the solution. The amounts of Mg^{2+} ion leached in the solution by annealing MS grade Mg-PSZ samples in water at 80–300 °C and in 1 M HCl solutions at 80–140 °C for 20 days are shown in Fig. 4. The dissolution of Mg^{2+} ion was significant above 80 and 200 °C in 1 M HCl solutions and water, respectively. The amounts of Mg^{2+} ion dissolved in 1 M HCl solution at 80–140 °C were almost the same as those dissolved in water at 200–300 °C. Therefore, it might be concluded that the dissolution of Mg^{2+} ion played a significant role not in introducing the tetragonal to monoclinic phase transformation, but in the formation of the surface flaws.

Scanning electron micrographs of the cross-section of the MS grade Mg-PSZ samples corroded in water at 200 and 300 °C for 20 days and in 1 M HCl solution at 140 °C for 20 days are shown in Fig. 5. The volumetric dilation accompanied by the tetragonal to

monoclinic phase transformation was detected on the surface of the samples corroded in water at 200 and 300 °C. As seen in Fig. 5, the microstructural changes accompanied by the tetragonal to monoclinic phase transformation were observed only around the original surface of the sample corroded at 200 °C, but they were observed in both parts around the original surface and pores located far from the original surface of the sample corroded at 300 °C. On the other hand, large intergranular cracks were observed in the cross-section of the samples corroded in water at 200 °C and in 1 M HCl solution at 140 °C. Therefore, it was suspected that the dissolution of Mg^{2+} ion resulted in the degradation of the bending strength by the cracks at the grain boundary of Mg-PSZ. As the transformation zone in the sample corroded in water at 300 °C was much larger than that at 200 °C, the strengthening effect by the compressive stress due to the tetragonal to monoclinic phase transformation became more significant in the former sample than in the latter sample, as shown in Fig. 2. These results indicated that the bending strength of the hydrothermally corroded Mg-PSZ depended on both the amounts of Mg^{2+} ion dissolved and the tetragonal to monoclinic phase transformation zone size.

4. Conclusions

1. The tetragonal to monoclinic phase transformation and the degradation of the bending strength occurred noticeably in water above 200 °C.

2. Although no tetragonal to monoclinic phase transformation proceeded in 1 M HCl solutions and in 1 M $CH_3COOH-CH_3COONa$ buffer solutions at pH 3 in the temperature range 80–140 °C, the bending strength of Mg-PSZ greatly degraded.

3. The dissolution of ZrO_2 matrix was negligible under the present experimental conditions, but Mg^{2+}

ion was noticeably leached in water and in 1 M HCl solutions above 200 and 80 °C, respectively.

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