JOURNAL OF MATERIALS SCIENCE 27 (1992) 3511–3518

Fracture toughness, strength and Vickers hardness of yttria–ceria-doped tetragonal zirconia/alumina composites fabricated by hot isostatic pressing

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Yttria–ceria-doped tetragonal zirconia ((Y, Ce)–TZP)/alumina (Al_2O_3) composites were fabricated by hot isostatic pressing (HIP) at 1400–1600 °C and 147 MPa for 30 min in Ar gas using fine powders prepared by hydrolysis of $ZrOCl_2$ solution. The mechanical properties of these ceramic composites were evaluated. The fracture toughness and bending strength of the composites consisting of 25 wt% Al_2O_3 and tetragonal zirconia with compositions 4 mol% $YO_{1.5}$–4 mol% CeO_2–ZrO_2, 2.5 mol% $YO_{1.5}$–4 mol% CeO_2–ZrO_2 and 2.5 mol% $YO_{1.5}$–5.5 mol% CeO_2–ZrO_2 fabricated by HIP at 1400 °C were 6–7 MPa m$^{1/2}$ and 1700–1800 MPa. Fracture toughness, strength and hardness of (Y, Ce)–TZP/Al_2O_3 composites were strongly dependent on HIP temperature. The fracture strength and hardness were increased, and grain growth of zirconia grains and phase transformation from the tetragonal to the monoclinic structure of (Y, Ce)–TZP during HIP in Ar at high temperature (1600 °C) were suppressed by the dispersion of Al_2O_3 into (Y, Ce)–TZP.

1. Introduction

It is well known that tetragonal ZrO_2 polycrystals (TZP) exhibit excellent mechanical properties with high values for strength and fracture toughness [1]. This enhancement of strength and toughness is believed to be due to stress-induced phase transformation of the tetragonal (t) ZrO_2 to the stable monoclinic (m) form in the vicinity of the crack front [2]. Although Y_2O_3 is a very effective stabilizer for t-ZrO_2, which exhibits high strength and fracture toughness at an optimum Y_2O_3 concentration of 2–3 mol% [3], it has been reported that Y–TZP is greatly reduced in strength by low temperature ageing at 200–300 °C [4, 5]. This degradation is due to the formation of microcracks accompanied by tetragonal-to-monoclinic phase transformation during ageing [6]. On the other hand, CeO_2 is also an effective stabilizer agent, and Tsukuma [7] and Sato and Shimada [8] reported that the Ce–TZP (12 mol % CeO_2–ZrO_2) showed high resistance to low temperature degradation. We fabricated the yttria–ceria-doped tetragonal ZrO_2 polycrystals ((Y, Ce)–TZP) using powders prepared by the hydrolysis technique, and reported they showed enhanced stability of tetragonal phase as compared with 3Y–TZP [9]. However, the fracture strength of Ce–TZP [7] and (Y, Ce)–TZP [10] are modest. Post-sintering hot isostatic pressing procedures are attractive for eliminating porosity and improving the fracture strength. It has been reported that the fracture strength of hot isostatically pressed Y–TZP can be enhanced by dispersing Al_2O_3 particles [11]. Although Ce–TZP and Ce–TZP/Al_2O_3 composites were fabricated by post-sintering hot isostatic pressing, their fracture strengths were lower than that of pressureless sintered Y–TZP [12].

In the present study, (Y, Ce)–TZP/Al_2O_3 composites were fabricated by hot isostatic pressing in Ar using fine powders prepared by the hydrolysis technique, and the effects of stabilizer composition of tetragonal zirconia, alumina content, and hot isostatic pressing conditions on the fracture toughness, strength and hardness of the composites ceramics were studied; at the same time, a comparative study has been made on 3Y–TZP/Al_2O_3 composites.

2. Experimental procedure

2.1. Powder and sample preparation

To produce a sol containing ultrafine monoclinic zirconia particles, 45 l of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) solution (0.2 mol l^{-1}) to which 500 ml of H_2O_2 (30 wt %) and 750 ml of NH_4OH (28 wt %) had been added, was boiled for 48 h and hydrolysed. The sol was uniformly mixed with cerium chloride ($CeCl_3 \cdot 7H_2O$) solution and yttrium chloride ($YCl_3 \cdot 6H_2O$) solution and added with stirring to dilute aqueous ammonia. The ZrO_2 particles precipitated together with $Ce(OH)_3$ and $Y(OH)_3$. The

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hydrolyzate was filtered, washed free from chloride, dried, pulverized, calcined and ball-milled with zirconia balls for 48 h in ethanol. In this way, fine powders with the compositions and specific surface areas listed in Table I were prepared.

The starting materials were as-synthesized Y_2O_3–CeO_2-doped zirconia powders, and Y_2O_3-doped zirconia powder and Al_2O_3 powder. The Al_2O_3 powder used had a particle size of 0.2 μm and a purity of 99.99%. These zirconia and Al_2O_3 powders were mixed by ball-milling with zirconia balls, followed by drying in air as listed in Table II. The powders were uniaxially cold-pressed at 19.6 MPa to form plates, and then isostatically cold-pressed at 196 MPa. The green compacts were sintered at 1350–1500 °C for 2 h in air to obtain the pre-sintered bodies, and then hot isostatically pressed at 1400–1600 °C and 147 MPa for 0.5 h using a graphite heater in Ar.

2.2. Characterization techniques

Specific surface areas of the as-synthesized zirconia powders were determined by the Brunauer-Emmett-Teller (BET) method. The bulk densities of sintered bodies were measured by water displacement. Fracture strength was measured by carrying out three-point bending tests at a span of 30 mm and a cross-head speed of 0.5 mm min^{-1} using an Instron testing machine with sample pieces measuring 3 × 4 × 40 mm. The tensile surface was finished with a 140 grit diamond wheel with the grinding passes parallel to the tensile axis. Phase identification was carried out by X-ray diffraction (XRD) analysis of the surface of the specimen. Scans of 2θ between 27 and 33° were conducted to determine the monoclinic to (tetragonal + cubic) zirconia ratio [13]. Fracture toughness was determined by the micro-indentation technique [14] (load = 294 N). Microhardness was measured by applying a load of 9.8 N using a diamond Vickers indentor. The microstructure of the samples was analysed by scanning electron microscopy (SEM).

TABLE I Compositions and specific surface areas of zirconia powders

Specimen	Composition (mol %)	Specific surface area of powder ($m^2 g^{-1}$)
Y	$3Y_2O_3 97ZrO_2$	18
XC	$4YO_{1.5} 4CeO_2 92ZrO_2$	21
IC	$4YO_{1.5} 4CeO_2 92ZrO_2$	27
IIC	$2.5YO_{1.5} 4CeO_2 93.5ZrO_2$	25
IIIC	$2.5YO_{1.5} 5.5CeO_2 92ZrO_2$	26

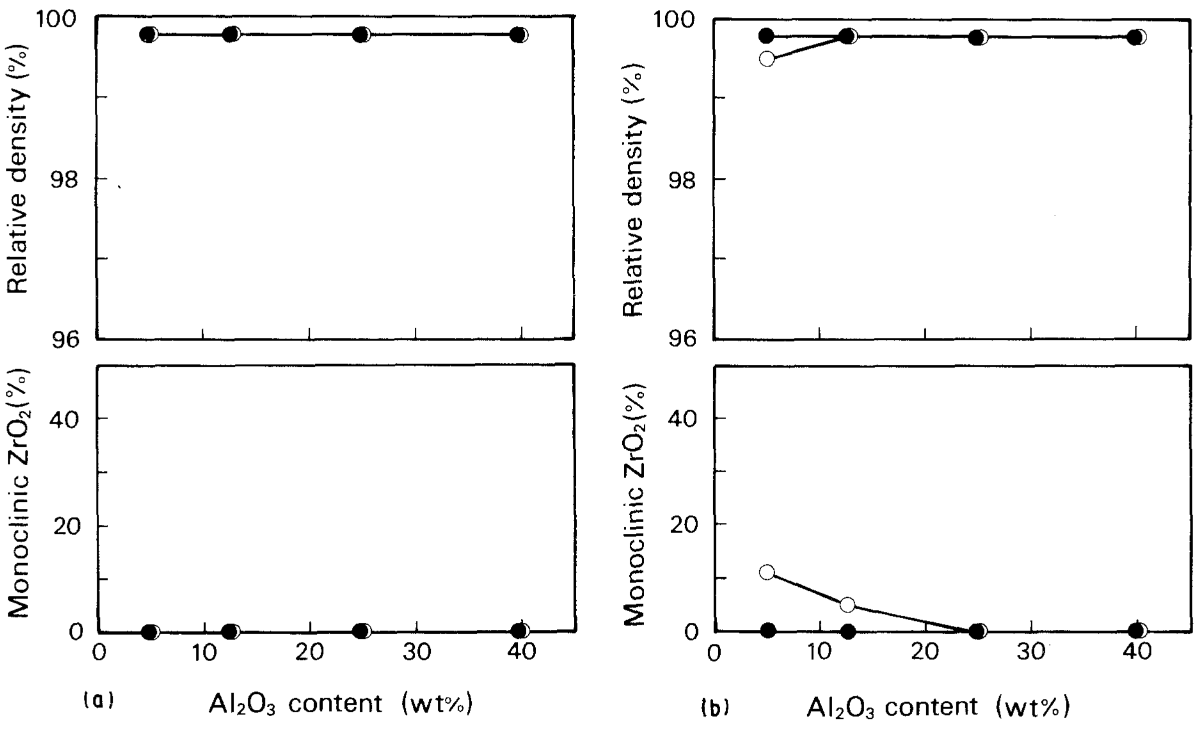
3. Results and discussion

3.1. Densification, phase and microstructure

The effects of the hot isostatic pressing temperature on the relative density and the monoclinic ZrO_2 phase content of (4Y, 4Ce)–TZP/Al_2O_3 and 3Y–TZP/Al_2O_3 composites hot isostatically pressed for 0.5 h in Ar are shown in Fig. 1. In the present study, the theoretical density of (Y, Ce)–TZP was determined from the lattice constants, which were calculated using the equation reported by Urabe *et al.* [15]. The relative density of the composites was calculated using 6.10 g cm^{-3}, 6.13 g cm^{-3}, 6.12 g cm^{-3}, 6.15 g cm^{-3}, and 3.98 g cm^{-3} as theoretical density of 3Y–TZP, (2.5Y, 4Ce)–TZP, (4Y, 4Ce)–TZP, (2.5Y, 5.5Ce)–TZP, and alumina, respectively. Both the relative density and the monoclinic phase content of (4Y, 4Ce)–TZP/Al_2O_3 and 3Y–TZP/Al_2O_3 composites hot isostatically pressed at 1400–1500 °C were almost constant at about 99.7% and 0% except for (4Y, 4Ce)–TZP/Al_2O_3 composites containing less than 12.5 wt % Al_2O_3. For (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1600 °C, the relative density was lower and the monoclinic phase content

TABLE II Compositions of specimens

Material	Specimen	Composition		
		Synthesized zirconia		Al_2O_3
		Composition (mol %)	(wt %)	(wt %)
Y-TZP	YO	$3Y_2O_3 97ZrO_2$	100	0
(Y, Ce)-TZP	XCO	$4YO_{1.5} 4CeO_2 92ZrO_2$	100	0
Y-TZP/Al_2O_3	Y5	$3Y_2O_3 97ZrO_2$	95	5
	Y12.5	$3Y_2O_3 97ZrO_2$	87.5	12.5
	Y25	$3Y_2O_3 97ZrO_2$	75	25
	Y40	$3Y_2O_3 97ZrO_2$	60	40
(Y, Ce)-TZP/Al_2O_3	XC5	$4YO_{1.5} 4CeO_2 92ZrO_2$	95	5
	XC12.5	$4YO_{1.5} 4CeO_2 92ZrO_2$	87.5	12.5
	XC25	$4YO_{1.5} 4CeO_2 92ZrO_2$	75	25
	XC40	$4YO_{1.5} 4CeO_2 92ZrO_2$	60	40
	IC25	$4YO_{1.5} 4CeO_2 92ZrO_2$	75	25
	IIC25	$2.5YO_{1.5} 4CeO_2 93.5ZrO_2$	75	25
	IIIC25	$2.5YO_{1.5} 5.5CeO_2 92ZrO_2$	75	25



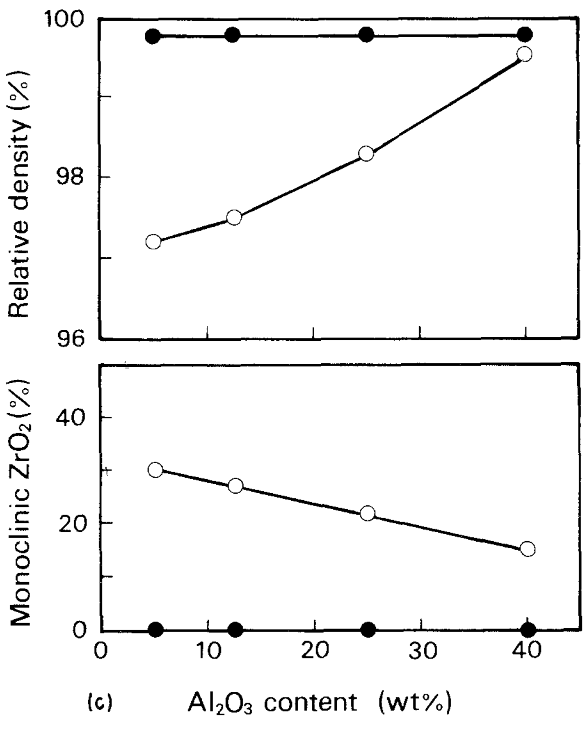


Figure 1 Relative density and fraction of monoclinic ZrO_2 as a function of Al_2O_3 content for (○) (4Y, 4Ce)-TZP/Al_2O_3 composites (XC specimen) and (●) 3Y-TZP/Al_2O_3 composites, hot isostatically pressed at: (a) 1400, (b) 1500 and (c) 1600 °C.

was higher than those of the composites hot isostatically pressed at 1400 and 1500 °C. From these results, the relative density and the monoclinic phase content of the (4Y, 4Ce)-TZP/Al_2O_3 composites depended on the hot isostatic pressing temperature. The relative density of (4Y, 4Ce)-TZP/Al_2O_3 composites hot isostatically pressed at 1600 °C increased and the monoclinic phase content of the composites decreased with increasing Al_2O_3 content. On the other hand, the relative densities and the monoclinic phase content of 3Y-TZP/Al_2O_3 composites were almost constant and were not dependent on the hot isostatic pressing temperature between 1400–1600 °C.

In the present study, hot isostatic pressing was performed using a graphite heater in Ar. The colour of (Y, Ce)-TZP/Al_2O_3 composites changed from yellowish-white after sintering to grey after post-sintering hot isostatic pressing in Ar. As shown in Fig. 1, phase transformation from the tetragonal to the monoclinic structure of (Y, Ce)-TZP was observed after hot isostatic pressing at high treating temperatures in Ar, which was considered to be caused by treating under a reducing gaseous atmosphere of (CO + Ar) that led to reduction of the CeO_2 dopant to Ce_2O_3. Fig. 1b and c indicate that the dispersion of Al_2O_3 into (4Y, 4Ce)-TZP was useful in suppressing the t → m phase transformation and increasing the relative density.

Scanning electron micrographs of (4Y, 4Ce)-TZP and (4Y, 4Ce)-TZP/Al_2O_3 composites are shown in Fig. 2. The grain size of zirconia in the specimens was decreased by the addition of Al_2O_3. Dispersion of Al_2O_3 was useful in suppressing the grain growth of zirconia grains.

3.2. Effect of Al_2O_3 content on the mechanical properties

The mechanical properties of specimens were examined by measuring the microhardness, K_{1c} value and bending strength. The effect of hot isostatic pressing temperature and alumina content on the Vickers hardness of the (4Y, 4Ce)-TZP/Al_2O_3 and 3Y-TZP/Al_2O_3 composites have been studied. Fig. 3 shows the relationship between Vickers hardness and hot isostatic pressing temperature. For (4Y, 4Ce)-TZP/Al_2O_3composites, the value of Vickers hardness was smaller than that for 3Y-TZP/Al_2O_3 composites. The Vickers hardness of both of the composites showed a

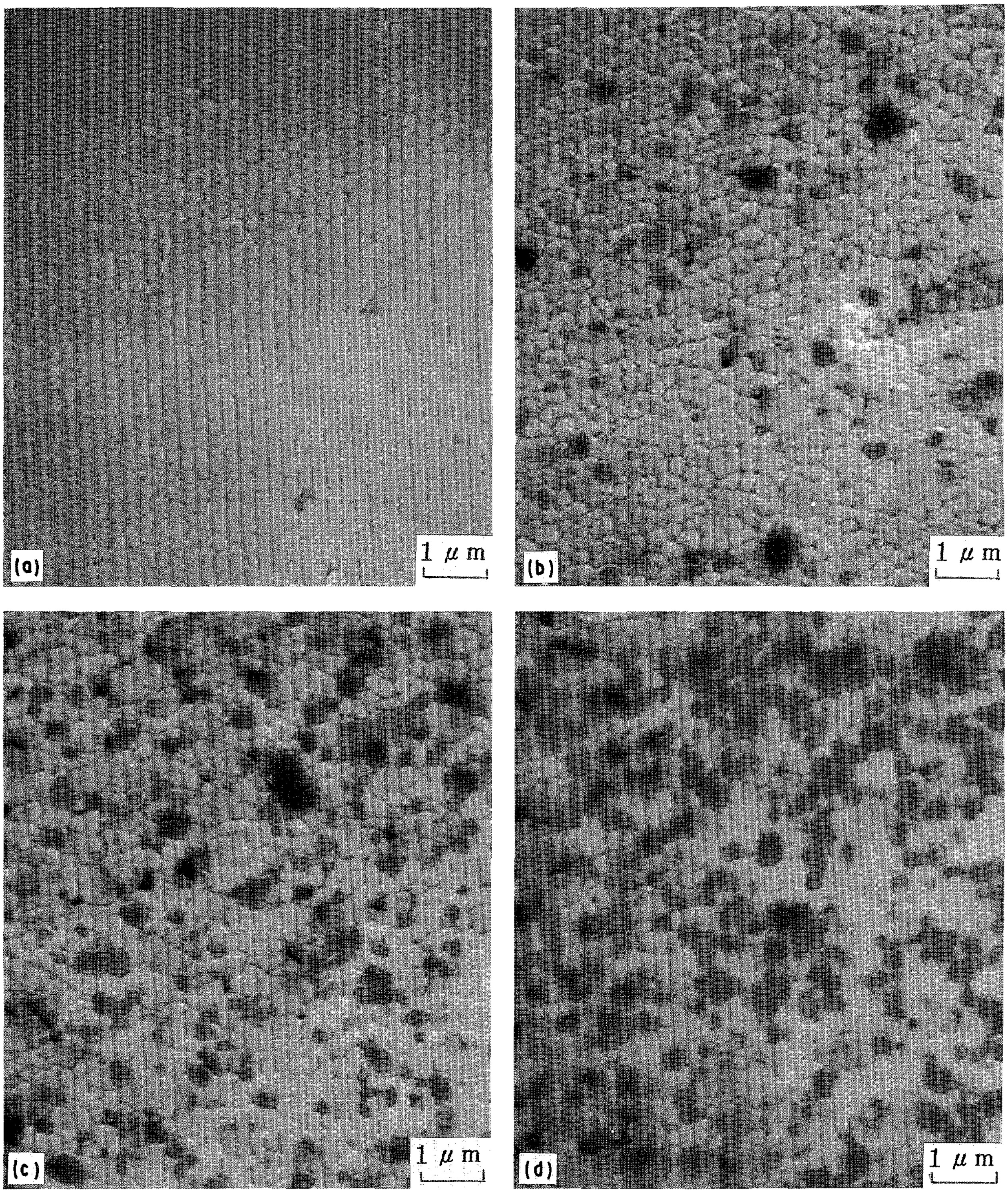


Figure 2 Scanning electron micrographs of the polished and thermally etched surface of (4Y, 4Ce)–TZP and (4Y, 4Ce)–TZP/Al_2O_3 composites (XC specimen) hot isostatically pressed at 1400 °C in Ar: (a) (4Y, 4Ce)–TZP; (b) (4Y, 4Ce)–TZP/5 wt % Al_2O_3 composites; (c) (4Y, 4Ce)–TZP/12. 5 wt % Al_2O_3 composites; (d) (4Y, 4Ce)–TZP/25 wt % Al_2O_3 composites.

tendency to decrease with an increase in hot isostatic pressing temperature. The over-all decrease in the Vickers hardness of the composites with increasing hot isostatic pressing temperature is due to the increase in grain size of the composites. It is noted that there is further decrease in the Vickers hardness of (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1600 °C in contrast with 3Y–TZP/Al_2O_3 composites. This significant decrease in Vickers hardness is due to the presence of considerable amount of monoclinic ZrO_2 phase and the decrease in relative density, which is shown in Fig. 1.

Fig. 4a and b show the dependence of the Vickers hardness on the amount of Al_2O_3 for (4Y, 4Ce)–TZP/Al_2O_3 and 3Y–TZP/Al_2O_3 composites hot isostatically pressed at 1400, 1500 and 1600 °C. The Vickers hardness of both of the composites increased with increasing amount of Al_2O_3. For 3Y–TZP/Al_2O_3 composites hot isostatically pressed at 1400–1600 °C and (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1400 °C, the Vickers hardness increased almost linearly with increasing amount of Al_2O_3. Whereas for the (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1500 and

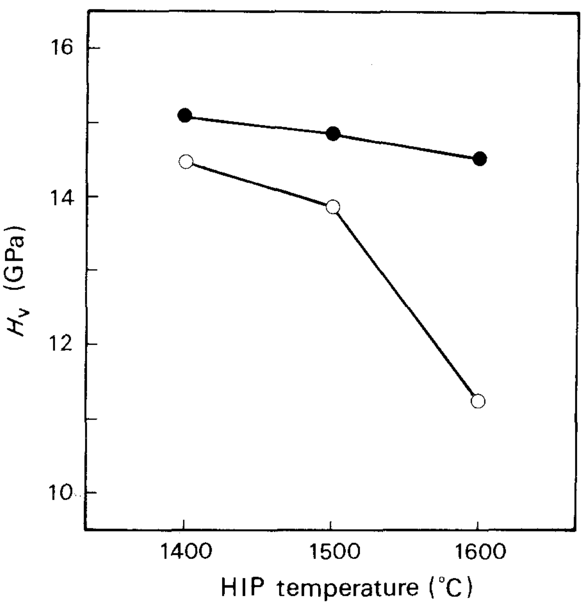


Figure 3 Vickers hardness as a function of hot isostatic pressing temperature for (○) (4Y, 4Ce)–TZP/Al_2O_3 composites (XC specimen) and (●) 3Y–TZP/Al_2O_3 composites.

1600 °C, the Vickers hardness had smaller values and showed non-linear increase with increasing amount of Al_2O_3, which is thought to be due to the presence of monoclinic ZrO_2 phase and to be related to its content and relative density of the composites as shown in Fig. 1b and c.

Fig. 5 shows the indentation load dependence of the fracture toughness of (4Y, 4Ce)–TZP and (4Y, 4Ce)–TZP/25 wt %Al_2O_3 composites hot isostatically pressed at 1500 °C, determined using an indentation load of 98–490 N. It can be seen from Fig. 5 that the value of the fracture toughness of both of the materials decreases gradually with increasing indentation load. We evaluated the fracture toughness of the materials using an indentation load of 294 N in this study.

Fracture toughness of (4Y, 4Ce)–TZP/Al_2O_3 composites and 3Y–TZP/Al_2O_3 composites hot isostatically pressed at 1400, 1500 and 1600 °C are shown in Fig. 6a–c. It is found from Fig. 6a that the fracture toughness of (4Y, 4Ce)–TZP/Al_2O_3 composites and 3Y–TZP/Al_2O_3 composites hot isostatically pressed at 1400 °C is almost independent of the amount of Al_2O_3. (4Y, 4Ce)–TZP hot isostatically pressed at 1500 °C showed high fracture toughness as compared with 3Y–TZP as shown in Fig. 6b. The fracture toughness of 3Y–TZP/Al_2O_3 composites hot isostatically pressed at 1500 °C showed a tendency to increase slightly with increasing Al_2O_3 content. On the other hand, the fracture toughness of (4Y, 4Ce)–TZP was greatly decreased by the addition of 5 wt % Al_2O_3, and showed a similar tendency to that of 3Y–TZP/Al_2O_3 composites with increasing Al_2O_3 content. For (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1600 °C, the fracture toughness increased gradually with increasing Al_2O_3 content.

The variation of the fracture toughness with hot isostatic pressing temperature is shown in Fig. 7. The fracture toughness of 3Y–TZP/Al_2O_3 composites increased slightly with increasing hot isostatic pressing temperature within the range of the experimental design, whereas the fracture toughness of (4Y, 4Ce)–TZP/Al_2O_3 composites (XC specimen) reached a maximum value at 1500 °C. Fig. 8 shows the dependence of the fracture strength on the amount of Al_2O_3 for (4Y, 4Ce)–TZP/Al_2O_3 composites fabricated by hot isostatic pressing. The fracture strength increased gradually with increasing amounts of Al_2O_3.

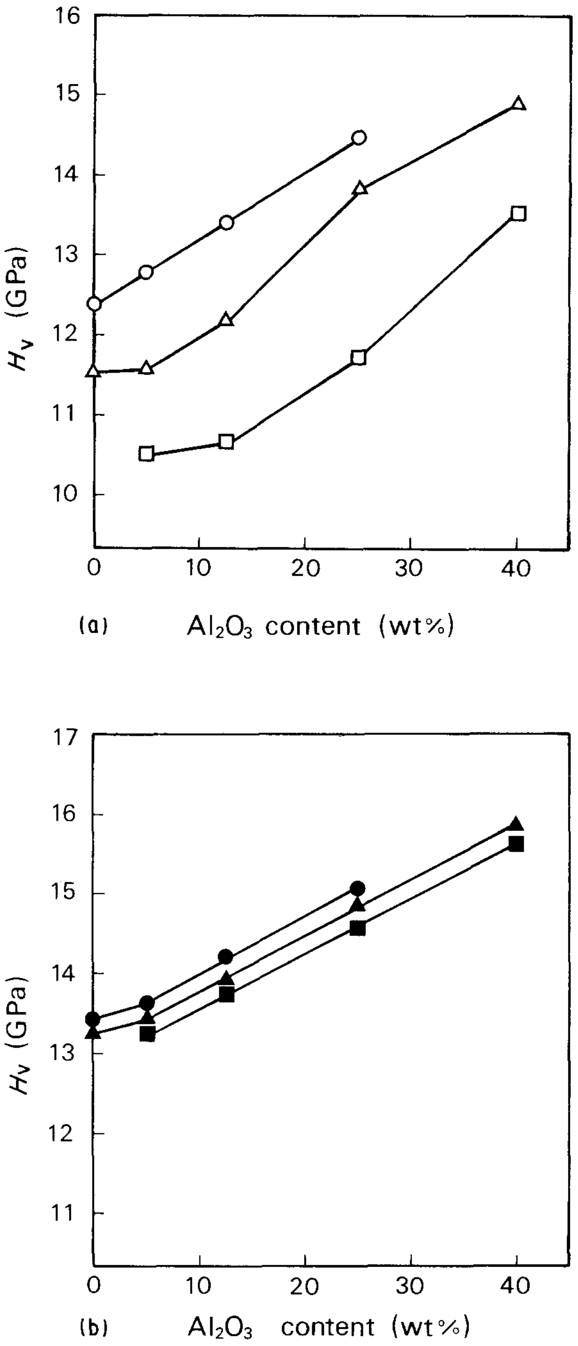


Figure 4 Vickers hardness as a function of Al_2O_3 content for: (a) (4Y, 4Ce)–TZP/Al_2O_3 composites (XC specimen) and (b) 3Y–TZP/Al_2O_3 composites hot isostatically pressed at: (○) 1400, (△) 1500, and (□) 1600 °C.

3.3. Effect of stabilizer composition on the mechanical properties

The effect of stabilizer composition of (Y, Ce)–TZP on the fracture toughness and strength of the composites

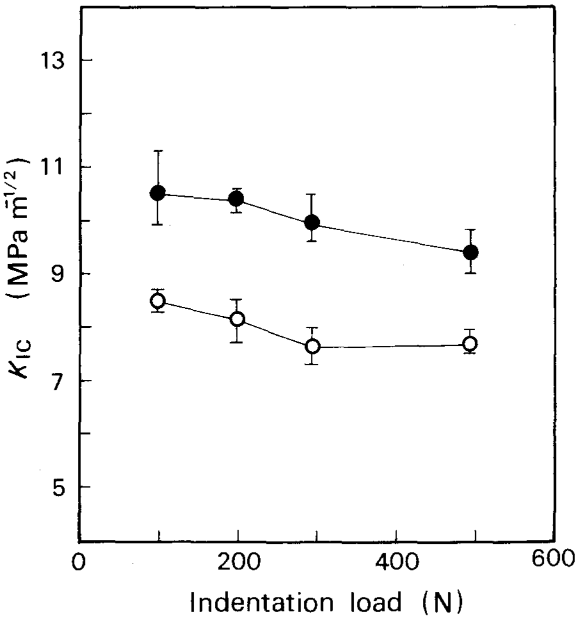
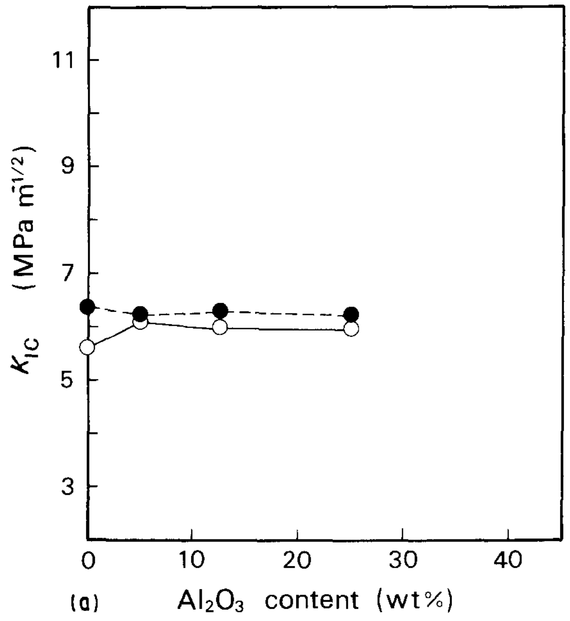


Figure 5 Indentation load dependence of fracture toughness of (●) (4Y, 4Ce)–TZP and (○) (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1500 °C.

was investigated. The fracture toughness and strength of three kinds of (Y, Ce)–TZP/Al_2O_3 composites were shown in Figs 9 and 10. The fracture toughness of the composites hot isostatically pressed at 1400 °C were a similar value for (2.5Y, 4Ce)–TZP/Al_2O_3, (4Y, 4Ce)–TZP/Al_2O_3 and (2.5Y, 5.5Ce)–TZP/Al_2O_3 composites. The change of fracture toughness as a function of hot isostatic pressing temperature was similar for (4Y, 4Ce)–TZP/Al_2O_3 and (2.5Y, 5.5Ce)–TZP/Al_2O_3 composites, increasing slightly with increasing hot isostatic pressing temperature. For (2.5Y, 4Ce)–TZP/Al_2O_3 composites, however, the increase in fracture toughness of the composites hot isostatically pressed at 1500 °C was much larger than that for (4Y, 4Ce)–TZP/Al_2O_3 and (2.5Y, 5.5Ce)–TZP/Al_2O_3 composites.

The effect of composition of tetragonal zirconia, alumina content, hot isostatic pressing temperature and atmosphere of hot isostatic pressing on fracture toughness in transformation-toughened composites ceramics is a complex issue. An increase in grain size which is a result of hot isostatic pressing at higher temperature gives an increase in the transformability (i.e. tetragonal to monoclinic), therefore increasing toughness. The fracture toughness of the composites hot isostatically pressed at 1400 °C is almost independent on the amount of Al_2O_3, whereas the fracture toughness of (4Y, 4Ce)–TZP/Al_2O_3 composites hot isostatically pressed at higher temperature increased gradually with increasing amounts of Al_2O_3. This increase in fracture toughness was considered to be due to the decrease in the amount of monoclinic phase as a consequence of suppression of the t → m phase transformation during hot isostatic pressing in Ar by increasing the amount of Al_2O_3.

The fracture strength and bulk density decreased with an increase in hot isostatic pressing temperature.



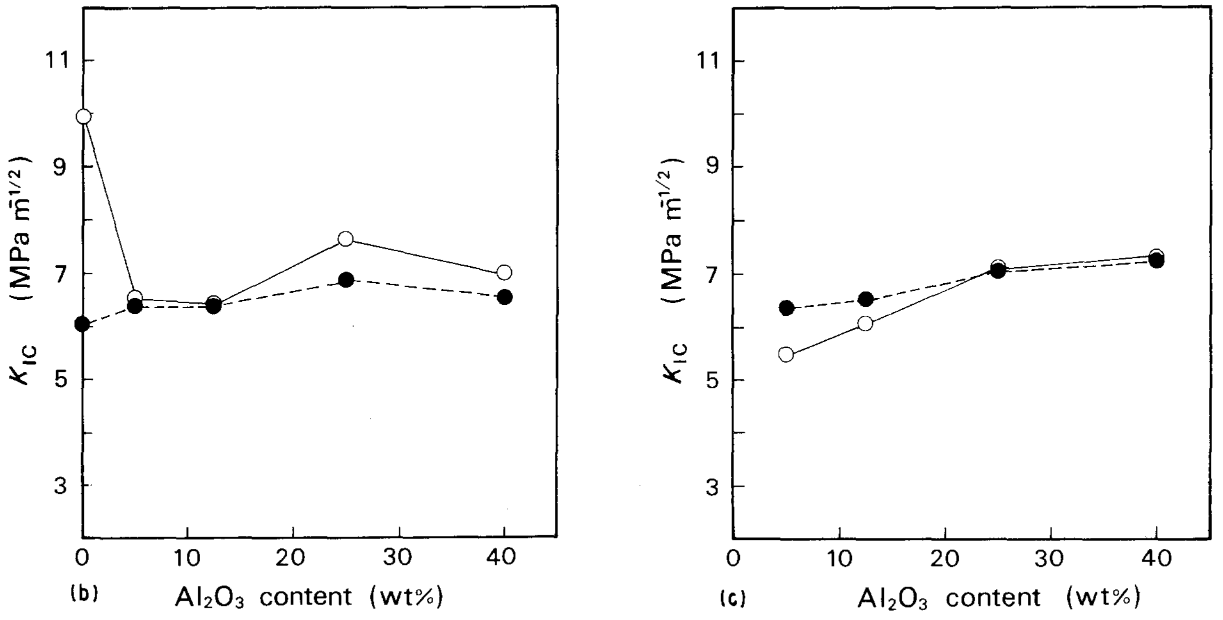


Figure 6 Fracture toughness as a function of Al_2O_3 content for (○) (4Y, 4Ce)–TZP/Al_2O_3 composites (XC specimen) and (●) 3Y–TZP/Al_2O_3 composites, hot isostatically pressed at: (a) 1400, (b) 1500 and (c) 1600 °C.

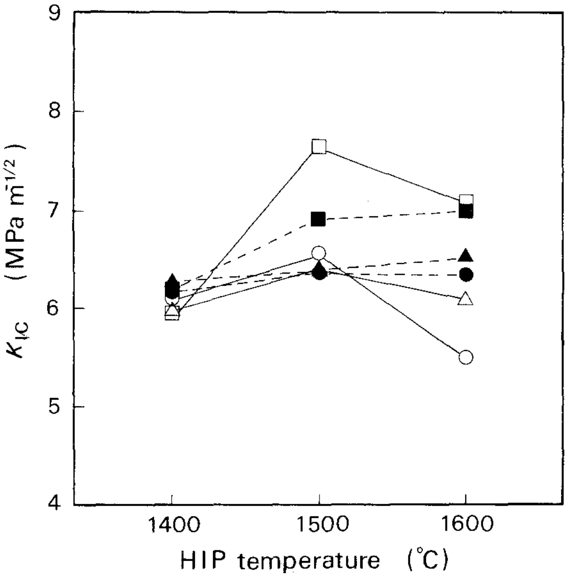


Figure 7 Fracture toughness as a function of hot isostatic pressing temperature for (i) (4Y, 4Ce)-TZP/Al_2O_3 composites (XC specimen), (○) 5 wt % Al_2O_3, (△) 12.5 wt % Al_2O_3, (□) 25 wt % Al_2O_3 and (ii) 3Y-TZP/Al_2O_3 composites (●) 5 wt % Al_2O_3, (▲) 12.5 wt % Al_2O_3, (■) 25 wt % Al_2O_3.

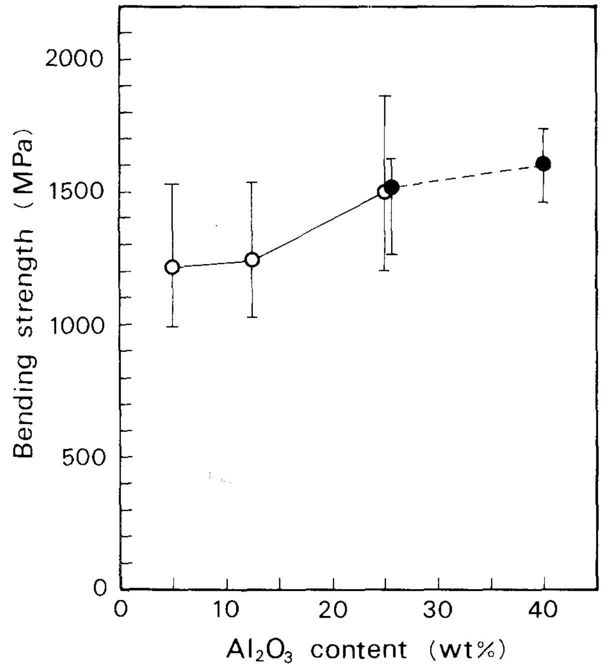


Figure 8 Relation between alumina content and bending strength of (4Y, 4Ce)-TZP/Al_2O_3 composites (XC specimen): (○) pre-sintered at 1400 °C, then hot isostatically pressed at 1400 °C; (●) pre-sintered at 1500 °C, then hot isostatically pressed at 1500 °C.

The fracture strength of the composites consisting of three kinds of (Y, Ce)-TZP and 25 wt % Al_2O_3 hot isostatically pressed at 1400 °C were 1700–1800 MPa. As the fracture strengths of (4Y, 4Ce)-TZP/25 wt % Al_2O_3, (2.5Y, 4Ce)-TZP/25 wt % Al_2O_3 and (2.5Y, 5.5Ce)-TZP/25 wt % Al_2O_3 composites fabricated by pressureless sintering at 1500 °C for 1 h were 1000–1100 MPa [16], it can be seen that the enhancement in fracture strength was achieved by hot isostatic pressing. On the other hand, the specimens hot isostatically pressed at 1600 °C were greatly reduced in strength, which was considered to be due to the phase transformation from the tetragonal to the monoclinic structure of yttria–ceria-doped tetragonal zirconia, the decrease in bulk density and the microcracks observed after post-sintering hot isostatic pressing. As hot isostatic pressing was performed using a

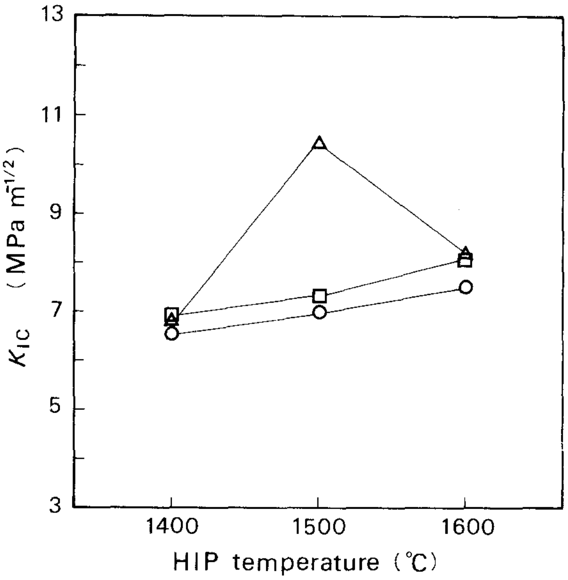


Figure 9 Fracture toughness as a function of hot isostatic pressing temperature for (○) (4Y, 4Ce)-TZP/Al_2O_3 composites (I C25 specimen); (△) (2.5Y, 4Ce)-TZP/Al_2O_3 composites (II C25 specimen), and (□) (2.5Y, 5.5Ce)-TZP/Al_2O_3 composites (III C25 specimen).

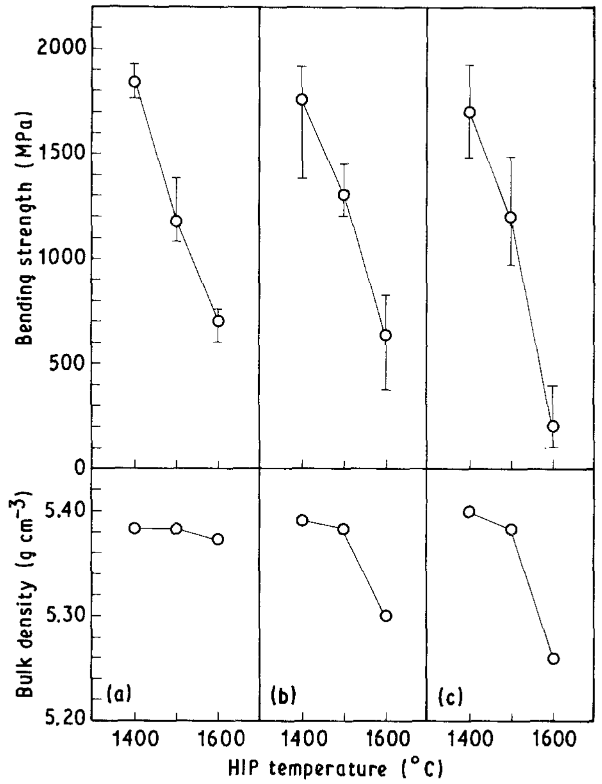


Figure 10 Bending strength and bulk density of (a) (4Y, 4Ce)-TZP/Al_2O_3 composites (I C25 specimen); (b) (2.5Y, 4Ce)-TZP/Al_2O_3 composites (II C25 specimen); and (c) (2.5Y, 5.5Ce)-TZP/Al_2O_3 composites (III C25 specimen) presintered at 1400 °C for 2 h, then hot isostatically pressed at various temperatures for 0.5 h.

graphite heater in Ar in this study, it was considered that the t → m phase transformation and the decrease in fracture strength and toughness in the (Y, Ce)–TZP system were caused by treating under a reducing gaseous atmosphere of (CO + Ar) that led to reduction of CeO_2 dopant to Ce_2O_3.

From these results, (Y, Ce)–TZP/Al_2O_3 composites fabricated by hot isostatic pressing at relatively low treating temperature (1400 °C) showed high fracture strength. It is considered that the enhancement in strength is due to the following effects: microstructures consisting of small grains, elimination of defects such as pores, densities with almost theoretical value and increasing the elastic modulus by the addition of Al_2O_3. Heussner and Claussen [17] reported that sintering of Ce–TZP in nitrogen or even hot isostatic pressing of presintered material in a reducing environment using a graphite heating element was not possible since the t phase was completely destabilized and transformed to m symmetry on cooling. For (Y, Ce)–TZP/Al_2O_3 composites, it was shown in the present study that the post-sintering hot isostatic pressing using a graphite heating element was possible by treating at lower temperature.

4. Conclusions

The effect of stabilizer composition of tetragonal zirconia, alumina content and hot isostatic pressing temperature on the fracture toughness, strength and hardness of (Y, Ce)–TZP/Al_2O_3 composites fabricated by hot isostatic pressing in Ar using the fine powders prepared by a hydrolysis technique were evaluated.

1. Fracture toughness, strength and hardness of (Y, Ce)–TZP/Al_2O_3 composites were strongly dependent on hot isostatic pressing temperature.
2. (Y, Ce)–TZP/Al_2O_3 composites hot isostatically pressed at 1600 °C showed degradation in strength and fracture toughness, whereas a bending strength of 1700–1800 MPa and a fracture toughness of 6–7 MPa $m^{1/2}$ were obtained for (4Y, 4Ce)–TZP/25 wt % Al_2O_3, (2.5Y, 4Ce)–TZP/25 wt % Al_2O_3 and (2.5Y, 5.5Ce)–TZP/25 wt % Al_2O_3 composites hot isostatically pressed at 1400 °C.
3. Dispersion of Al_2O_3 into (Y, Ce)–TZP was useful to suppress the phase transformation from the tetragonal to the monoclinic structure of yttria–ceria-doped tetragonal zirconia during hot isostatic pressing in Ar at higher temperature.
4. The fracture strength and hardness were increased and the grain growth of zirconia grains was suppressed by an increase in the amount of Al_2O_3.

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Received 18 February
and accepted 20 June 1991