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Mechanical properties and microstructures of co-precipitation derived tetragonal Y_2O_3-ZrO_2–Al_2O_3 composites

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Y-TZP–Al_2O_3 specimens (2.5 mol% Y_2O_3-ZrO_2 and 5 to 30 wt% Al_2O_3) were prepared from coprecipitated powders and their mechanical properties were studied. The addition of alumina to Y–TZP improves the attainable density of the materials after sintering at 1500° C and reduces the degradation of their densities due to porosity formation when the materials are sintered above 1500° C. Near theoretical density could be achieved for most of the samples after HIPing at 1500° C for ½ h at 200 MPa pressure. The fracture strength of the HIPed specimens was in the range 2.0 to 2.4 GPa and the stress intensity factor was in the range 3.5 to 6.0 MPa $m^{1/2}$. The mechanical strength of the materials was not degraded seriously after autoclaving in water at 175° C for 24 h. The surface layer of transformed monoclinic zirconia was less than 70 μm thick even after autoclaving at 175° C for 5 days.

1. Introduction

It has been established that zirconia ceramics can display enhanced toughness and strength due to the stress-induced martensitic phase transformation from metastable tetragonal zirconia to the monoclinic form [1–4]. This transformation toughening has been used to improve the properties of a number of structural ceramics such as alumina, mullite and carbides [5–8].

Claussen [9] broadly classified the transformation toughened ceramics (TTC) into three main groups: (i) partially stabilized zirconia (PSZ), (ii) dispersed zirconia ceramics, and (iii) complex zirconia systems. Yttria-based tetragonal zirconia polycrystals (Y-TZP), is a type of PSZ. This ceramic has very high strength and moderate toughness because the grains are extremely fine and consist almost entirely of the active transformable phase.

It has been noticed frequently that addition of alumina to cubic stabilized zirconia influences the grain-boundary conductivity and also improves the density of the materials [10–12]. Lange [13] first indicated that considerable amounts of alumina may be introduced in Y-TZP to achieve optimum mechanical properties, and has also noted that the strength of alumina-rich composite materials may be improved by hot isostatic pressing (HIPing) [14]. Tsukuma and Ueda [15] used HIPing to improve the strength of Y-TZP and Y-TZP–Al_2O_3 composites and reported strengths near 2.4 GPa for Y-TZP containing $\geqslant$ 20 wt% alumina. According to them the improvement in strength of Y-TZP–Al_2O_3 composites is due to (i) elimination of flaws by HIPing, and (ii) suppression of crack initiation by alumina.

The use of improved processing techniques and production of ultrafine powder greatly reduce the sintering temperature of ceramics [16, 17]. Also it is an advantage to prepare fine ceramics from chemically homogeneous precursors [18], because it can be expected that better chemical homogeneity of different constituents and improved dispersion of co-existing phase may be achieved.

In view of these possible advantages, Y-TZP–Al_2O_3 composites were fabricated using a coprecipitation technique. The mechanical properties of these materials are reported in this paper.

2. Experimental procedure

Composite materials used in this study were all prepared from coprecipitated hydroxides. Stock solutions of yttria (prepared by dissolving 99.9% pure yttrium oxide in AR nitric acid), zirconia (Magnesium Elektron zirconium carbonate dissolved in nitric acid) and AR aluminium nitrate were mixed in appropriate proportions and the hydroxides precipitated with AR ammonia solution at a pH of 9.0 in a nitrogen atmosphere. The coprecipitates were calcined at 1000° C for 6 h to produce oxide powders.

The oxide powders were compressed isostatically into bars of 40 mm × 4 mm × 4 mm at 200 MPa and sintered conventionally in the temperature range 1400 to 1700° C in air for 2 h. Heating and cooling rates were fixed as 50 and 500° C h^{-1}, respectively. Hot isostatic pressing (HIPing) was carried out with the conventionally sintered materials at 1500° C for 30 min in an argon atmosphere at 200 MPa.

Bulk densities of the sintered bodies were determined by a mercury displacement method. Microstructures of the polished and thermally etched bodies were examined using a scanning electron microscope. The average grain size of the materials was determined by the linear intercept method.

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X-ray diffraction analysis was carried out on polished, ground and fractured surfaces of all the materials to identify phases and to estimate the proportions of tetragonal and monoclinic phases. The latter was done by using the procedure developed by Garvie and Nicholson [19].

Autoclave tests were carried out with sintered and HIPed bodies by immersing them in distilled water (20 ml) in an autoclave at 175° C.

Modulus of rupture (MOR) measurements were made using a three-point bend with 12.5 mm outer span and 0.05 mm min^{-1} cross-head speed. Fracture toughness was determined by the Vickers microindentation technique with 30 kg load, using the formula proposed by Anstis *et al.* [20].

Throughout this paper the nomenclature ZY*XX*Al_2O_3 has been used. ZY represents zirconia containing 2.5 mol % yttria and *XX* represents the weight per cent of alumina present in the specimens.

3. Results and discussion

3.1. Density measurements

Fig. 1 shows the bulk densities of the sintered and HIPed Y-TZP–Al_2O_3 composites. The densities of the sintered bodies varied from 83.0 to 99.4% theoretical and it can be seen in the figure that the maximum attainable density changes with alumina content in the materials. For example, the maximum density was more than 99% theoretical for ZY30Al_2O_3 whereas it was only about 93% for ZY5Al_2O_3. A sintering temperature between 1400 and 1450° C was optimum for ZY5Al_2O_3 and ZY10Al_2O_3 specimens: at higher sintering temperatures, the densities of these materials become smaller. However, for specimens of higher alumina content a sintering temperature of at least 1500° C was required, and such materials also displayed minimal degradation of density even after sintering at 1700° C.

X-ray photoelectron spectroscopic analysis of these sintered bodies showed the presence of graphitic carbon in amounts which decreased with increasing alumina content of the samples. Thus the evolution of carbon-containing gases at higher sintering temperatures could well be responsible for the degradation of the densities of these materials. HIPing improved the densities of all the materials and in most cases a theoretical density was achieved by HIPing the presintered bodies at 1500° C for $\frac{1}{2}$ h at 200 MPa pressure.

TABLE I Average grain size (μm) of HIPed Y-TZP–Al_2O_3 composites. Samples presintered at various temperatures for 2 h and HIPed at 1500° C for $\frac{1}{2}$ h at 200 MPa pressure

Samples	Presintering temperatures (° C)			
	1450	1500	1600	1700
ZY5Al_2O_3	0.75	0.82	1.30	–
ZY10Al_2O_3	0.70	0.76	1.16	3.28
ZY20Al_2O_3	0.60	0.65	1.09	2.60
ZY30Al_2O_3	0.52	0.59	1.01	2.41

3.2. Microstructural analysis

Scanning electron micrographs of the polished and thermally etched ZY*XX*Al_2O_3-1500° C specimens are given in Fig. 2 and the average grain size of the composites is given in Table I. The grain size gradually increases with increasing sintering temperature and no excessive grain growth was observed in any of the samples sintered to 1600° C. However, larger grains were observed in the 5 and 10 wt % alumina samples sintered at 1700° C. A gradual decrease of grain size was observed with increase in the alumina content and a grain-boundary pinning effect of alumina appears to be acting in reducing the grain size.

A single crack emanating from a Vicker's indentation was seen to travel in an intergranular way (Fig. 2). It is presumed that the compressive stress state within a transformed grain causes the crack to run around the grain boundary before progressing.

3.3. X-ray diffraction analysis of surfaces

Although X-ray diffractometry provides information only from the surface layer of the specimen, it is known that the surface of zirconia specimens that have been carefully polished is representative of the bulk. In the present cases, X-ray diffraction analysis of polished samples showed the presence of tetragonal zirconia and α-Al_2O_3 only.

The fractions of monoclinic zirconia in ground and fractured surfaces were determined by the procedure reported elsewhere [19]. The weight percentage of monoclinic zirconia phase in a ground surface (GSM)

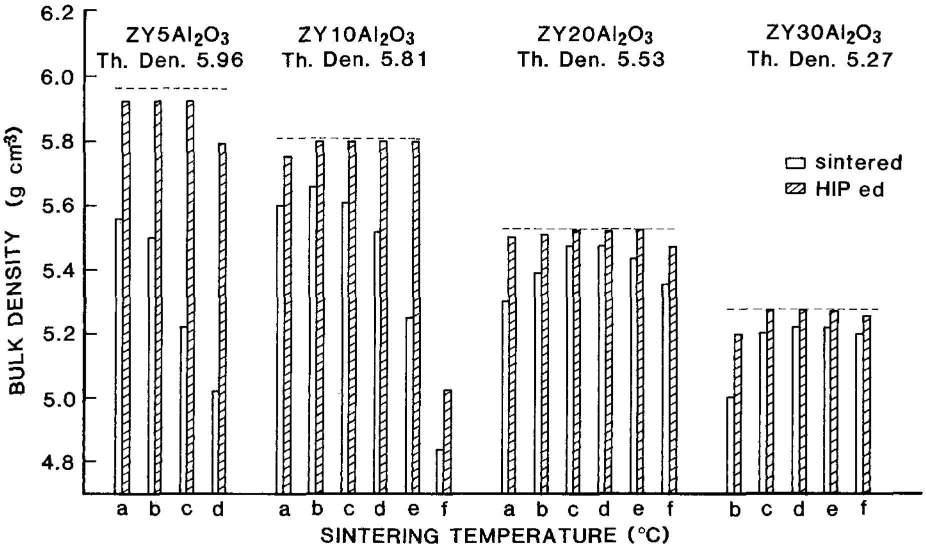

Figure 1 Bulk density (g cm^{-3}) of the ZY*XX*Al_2O_3 composites sintered at different temperatures; (a) 1400° C, (b) 1450° C, (c) 1500° C, (d) 1550° C, (e) 1600° C and (f) 1700° C.

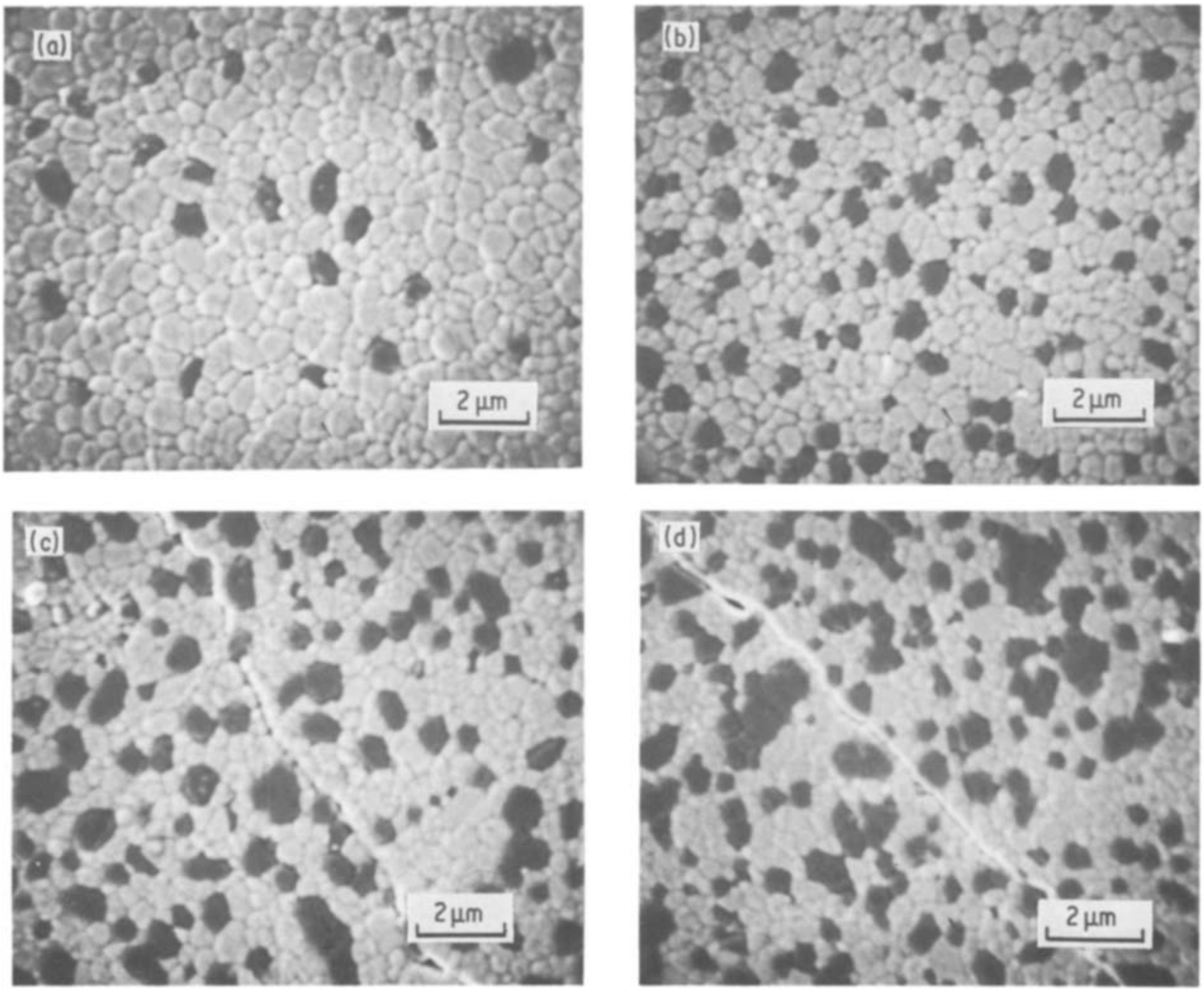

Figure 2 Scanning electron micrographs of polished and thermally etched ZY*XX*Al_2O_3-1500° C composites, (a) ZY5Al_2O_3, (b) ZY10Al_2O_3, (c) ZY20Al_2O_3 and (d) ZY30Al_2O_3. In (c) and (d), a crack emanating from a Vickers intent can be seen.

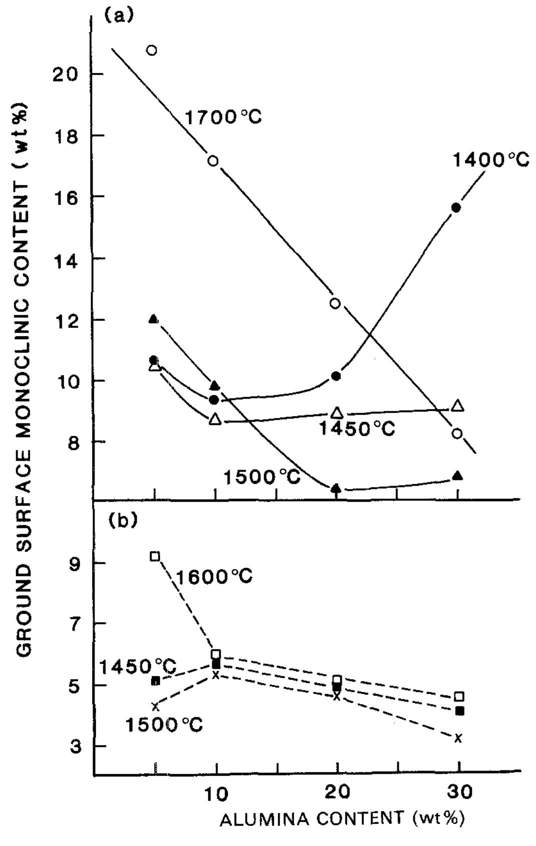

Figure 3 Change in ground surface monoclinic percentage with alumina concentration in the materials; (a) sintered and (b) HIPed.

has been plotted against the weight per cent of alumina in Fig. 3. The GSM fraction of the sintered samples (Fig. 3a) changes both with the alumina content and the sintering temperature. An almost linear variation of GSM fraction with alumina content can be noted for the ZY*XX*Al_2O_3-1700° C samples. The GSM fractions of the HIPed materials (Fig. 3b) are much lower than those of the sintered samples. Also there is little change of GSM fraction with changes of the sintering temperature or of alumina content in those samples. The GSM fractions of the materials are inversely related to the densities (Fig. 1), which in turn are dependent on the alumina contents, as shown above. This is in accord with the fact that retention of the tetragonal zirconia phase in a grain depends on the constraint imposed by neighbouring grains. According to Lange [21], porosity lowers the elastic modulus and introduces free surfaces. The effect of both of these factors would reduce the strain energy associated with the transformation and allow more tetragonal grains to transform to the monoclinic form. Also, it is expected that elastic modulus of the composite will increase with increasing alumina content as the Young's modulus of alumina is almost twice that of zirconia. Recent observations of Y-TZP and Ce-TZP materials indicate that although grinding appears inefficient in nucleating the transformation, there is evidence that some reverse transformation

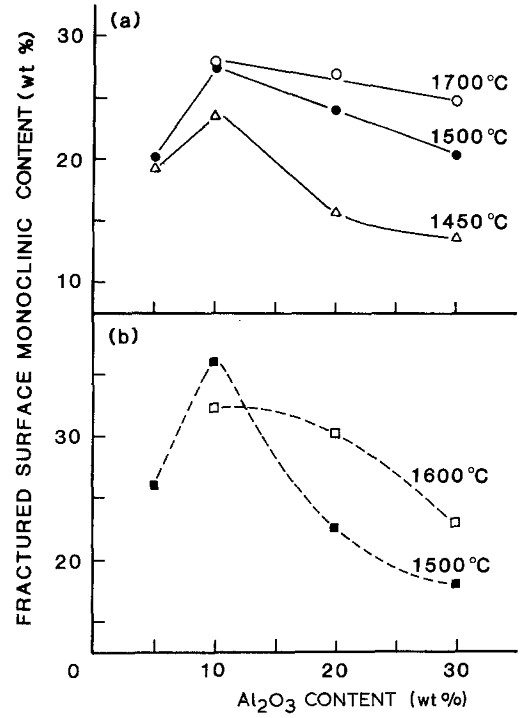

Figure 4 Change in fractured surface monoclinic percentage with alumina content in the materials, (a) sintered and (b) HIPed.

takes place because of the heat generated during grinding [22].

The fractured surface monoclinic (FSM) fractions of the sintered and HIPed bodies are plotted against the weight per cent of alumina in the samples in Fig. 4. The FSM fraction is a maximum at 10 wt % alumina. It may be deduced that the stress-induced phase transformation is a maximum for the ZY10Al_2O_3 specimen and that the stability of the tetragonal zirconia increases with increasing alumina concentration in the material. However, it is not known exactly why the FSM value for ZY5Al_2O_3 is lower than that of ZY10Al_2O_3. It may be noted from Fig. 4 that the stability of the tetragonal grains gradually changes with sintering temperature, probably because of the change of grain size. Swain [23] has observed a similar trend for both FSM and GSM values with variation of grain size for Y-TZP materials. Another point to be noted in the figure is that the FSM value of the HIPed specimens are generally higher than those of the sintered materials.

3.4. Mechanical properties

Modulus of rupture (MOR) and stress intensity factor (K_{Ic}) values of the sintered and HIPed samples are given in Table II. The addition of alumina is very effective in improving the strength of the Y-TZP sintered bodies. It is quite interesting to note that the samples containing larger amounts of alumina exhibit a higher strength despite a decrease in volume fraction of tetragonal zirconia. The fracture strength gradually increases with increasing alumina content in the materials up to 20 wt % alumina. However, ZY30Al_2O_3 has a strength slightly lower than that of ZY20Al_2O_3 sintered at the same temperature. Tsukuma and Ueda [15] have observed a similar increase in strength values with increasing alumina concentration in the Y-TZP materials and explained the results as due to the suppression of crack initiation within the Y-TZP. However, the improvement in strength of the materials with increasing alumina content in this study may be mainly due to the increase in bulk densities (reduction of voids) of the materials. It may be noted in Table II that the fracture strength of ZY5Al_2O_3 and ZY10Al_2O_3 was degraded when they had been sintered above 1500° C.

HIPing improved the strength of all the materials substantially, irrespective of the alumina concentration in the materials. Generally they have a strength over 2.0 GPa. Maximum fracture strength of around 2.4 GPa was observed for the ZY20Al_2O_3-1600° C specimen. However, the strength of the HIPed materials could not be correlated with the alumina content of the

TABLE II Fracture strength (σ) and fracture toughness (K_{Ic}) of sintered and HIPed Y-TZP-Al_2O_3 composites

Samples	Sintered 2 h			HIPed $\frac{1}{2}$ h at 1500° C, 200 MPa	
	Temp. (° C)	σ (MPa)	K_{Ic} (MPa m$^{1/2}$)	σ (MPa)	K_{Ic} (MPa m$^{1/2}$)
ZY5Al_2O_3	1450	1030		2250	4.0
	1500	890		2030	4.15
	1550	–		1200	–
	1600	–		–	–
	1700			–	–
ZY10Al_2O_3	1450	1190	4.26	2015	4.19
	1500	1000	4.82	2065	4.50
	1550	–	–	1745	–
	1600	840	–	1620	4.86
	1700	800	–	–	
ZY20Al_2O_3	1450	1270	4.45	2145	3.98
	1500	1395	4.40	2250	4.40
	1550	–	–	2185	–
	1600	1340	–	2405	4.60
	1700	1310	5.82	–	
ZY30Al_2O_3	1450	920	4.66	2135	3.33
	1500	1310	4.21	2145	4.30
	1550	–	–	2176	–
	1600	1305	–	2235	4.50
	1700	1320	5.61	–	

Figure 5 Fracture origin in a ZY30Al_2O_3 specimen sintered at 1500° C.

samples, as even the ZY5Al_2O_3-1450° C specimen had a strength value of around 2.25 GPa. Previous studies by Tsukuma and Ueda [15] noted a gradual increase in strength with alumina content reaching a plateau between 20 and 40 wt % alumina.

The fracture strengths of the HIPed bodies, especially ZY5Al_2O_3 and ZY10Al_2O_3, were closely related to the presintering temperatures. The significant enhancement in strength achieved by HIPing was not observed when these materials were presintered above 1500° C.

The sintered and HIPed Y-TZP–Al_2O_3 bodies were examined in the SEM in an attempt to understand the strength enhancement obtained by HIPing. Generally in sintered samples, large or accumulated pores were observed at the fracture origin (Fig. 5) whereas the fracture origin of the HIPed samples was often difficult to find except for low-strength specimens. The fracture origin of the HIPed materials seemed to be at impurities or inclusions of silica, magnesia or occasional large alumina grains. One such instance of a lower strength (822 MPa) material, Fig. 6, consisted of a pore of $\sim 20\,\mu m$ diameter adjacent to the surface with a much larger alumina inclusion below that. A simple fracture mechanics analysis suggested that if the smaller pore was the fracture origin, then the

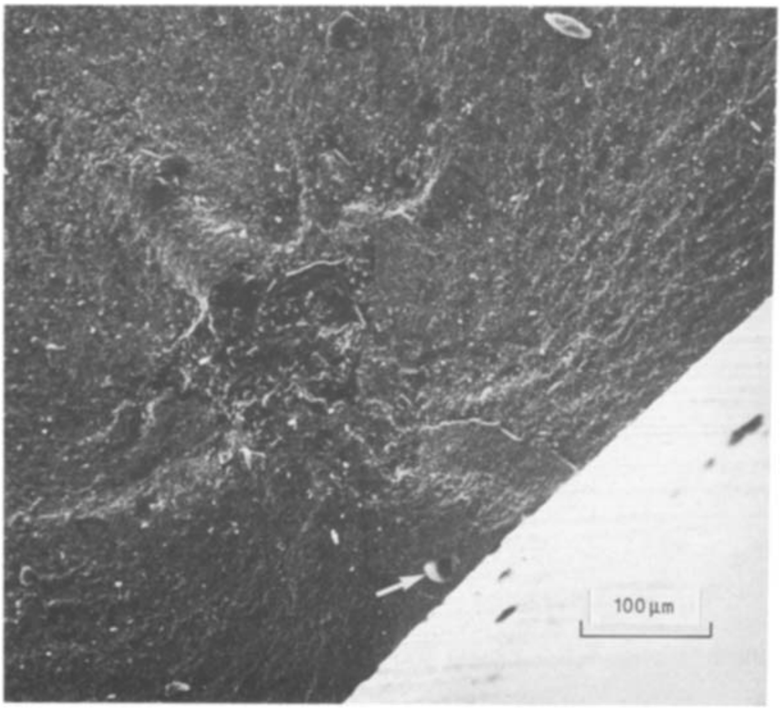

Figure 6 Fracture origin in a HIPed ZY5Al_2O_3-1450° C specimen.

TABLE III Fracture strength (MPa) of HIPed Y-TZP–Al_2O_3 composites before and after autclaving in water at 175° C for 24 h

Samples	Sintering temperature (° C) 2 h			
	1500		1550	
	As-prepared	Autoclaved	As-prepared	Autoclaved
$ZY5Al_2O_3$	2030	1275	1200	1045
$ZY10Al_2O_3$	2065	1360	1745	1240
$ZY20Al_2O_3$	2250	1480	2185	1445
$ZY30Al_2O_3$	2145	1470	2175	1410

toughness was comparable to that determined using the indentation technique.

The fracture toughness (K_{lc}) of the materials generally increased with increasing sintering temperature. This is probably due to the larger grain size of the materials: an effect commonly observed in PSZ. As expected from the fractured surface monoclinic content, (Fig. 4), the K_{lc} value of the $ZY10Al_2O_3$ specimen is higher than that of the other samples. The results show that the fracture toughness is due to the stress-induced phase transformation of tetragonal to monoclinic zirconia. As the alumina content in the materials increases, the stability of the tetragonal zirconia increases, the grain size decreases and the stress intensity factor decreases. This is in agreement with the prediction obtained from Lange's theory [24] of stress-induced phase transformation toughening.

3.5. Durability of Y-TZP–Al_2O_3 composites in water

It is well documented [25–29] that the mechanical properties of Y-TZP are degraded severely if the material annealed in air at low temperatures (150 to 400° C) or immersed in hot aqueous solutions. The water has a severe effect and in many cases the materials were reported to have disintegrated when they were autoclaved in water at about 200° C. Because the materials used in this study were prepared by coprecipitation the stability of the materials in water was tested.

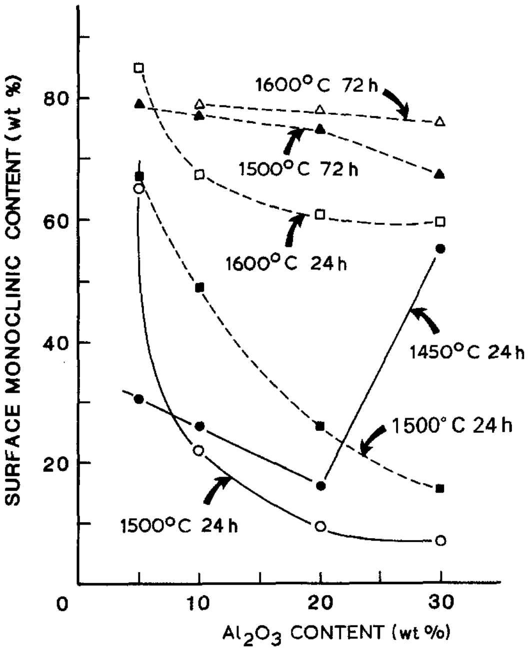

Figure 7 Change in surface monoclinic percentage with alumina content in specimens that have been autoclaved in water at 175° C. (– – –) HIPed, (——) sintered.

The fracture strength of HIPed Y-TZP–Al_2O_3 bodies after autoclaving in water at 175° C for 24 h is given in Table III. Considerable degradation of fracture strength occurred compared to unautoclaved materials. Materials of lower alumina content were degraded more than those of higher alumina content.

The fraction of monoclinic zirconia in the surface of autoclaved samples as a function of their alumina content is shown in Fig. 7. There is a clear trend of decreasing surface monoclinic content with increasing alumina concentration in both HIPed and unHIPed materials. However, the GSM fractions of HIPed materials were higher than those of unHIPed materials. The GSM fraction of all the samples gradually increased with increasing immersion time and reached a saturation value. None of the materials crumbled into powder even after autoclaving them at 175° C for 5 days. It can also be noted (Fig. 7) that the materials sintered at higher temperatures have higher monoclinic content.

To examine the extent of degradation and phase transformation after autoclaving for 5 days at 175° C, polished cross-sections of the bars (sintered and HIPed at 1500° C) were examined optically and the results are given in Fig. 8. The thickness of the transformed surface layer is less than 70 μm in all cases and the figure shows that the transformation starts at the surface. The figure also shows that the samples of higher alumina content have the least extent of transformation.

The decrease in bending strength of the materials after autoclaving in water may be due to the tetragonal to monoclinic transformation of zirconia: the volume expansion associated with the transformation imposes a shear strain on the subsurface tetragonal grains, thereby producing microcracks. Such microcracking would facilitate further entry of water. Many investigators [25–30] have reported that the stability of Y-TZP materials in water depends on grain size, bulk density and concentration and distribution of yttria. The results from this study indicate that, irrespective of the alumina content of the samples, density (or voids) and grain size play important roles in determining the surface monoclinic content and fracture strength of the materials. These observations are similar to those of Masaki [28]. The alumina in the materials studied seems to influence the grain size, density and porosity of the materials, and to increase the elastic modulus of the composite. Both kinetic and thermodynamic arguments may be used to explain the influence of alumina in improving the stability of the tetragonal zirconia to water [31, 32].

The kinetic argument is based on the concept of heterogeneous nucleation in a region where t- to

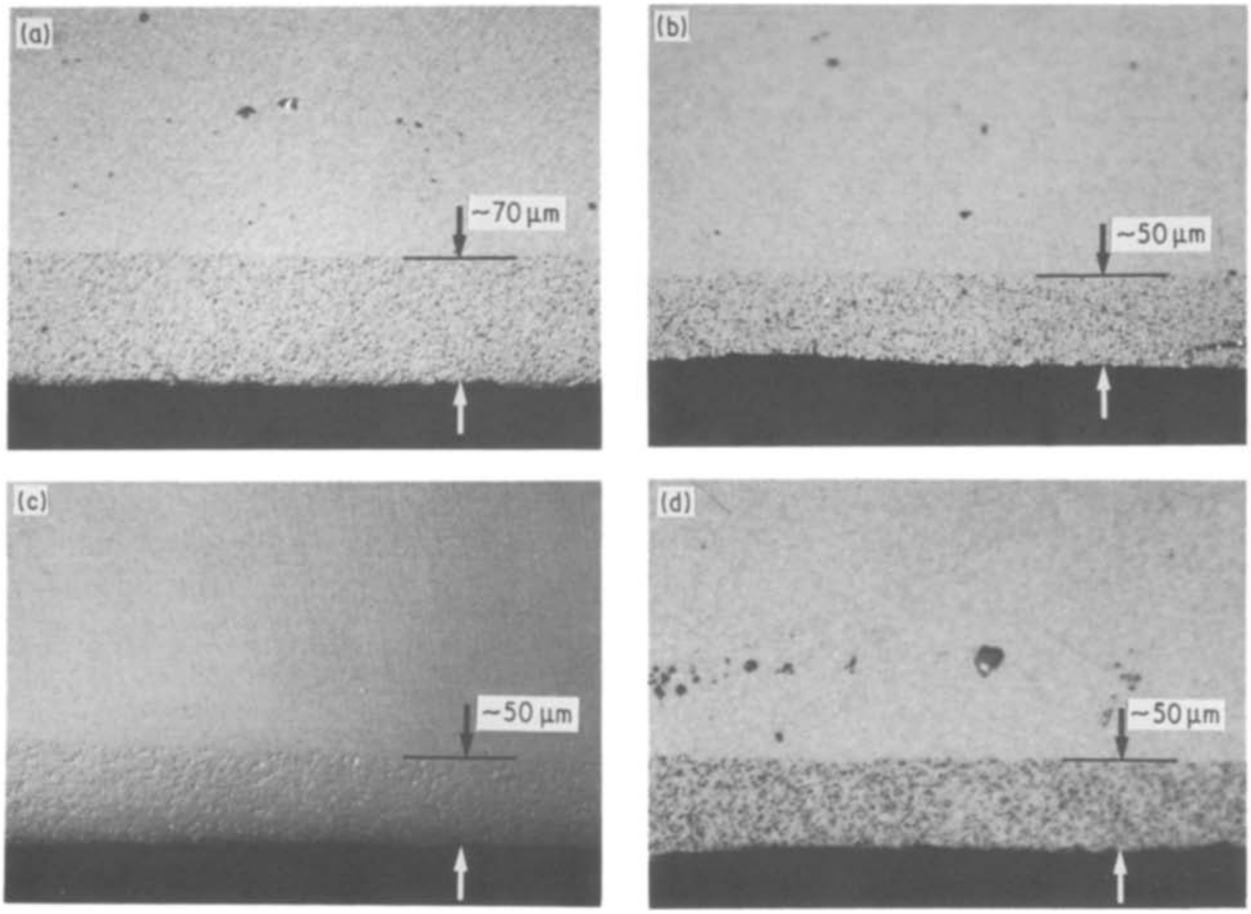

Figure 8 Optical micrographs of polished ZY*XX*Al_2O_3 specimens after autoclaving at 175° C for 5 days, (a) ZY5Al_2O_3, (b) ZY10Al_2O_3, (c) ZY20Al_2O_3 and (d) ZY30Al_2O_3.

m-ZrO_2 transformation starts by the reaction of H^+ or OH^- of water with Y_2O_3 or ZrO_2. With this region as the starting point the transformation develops along grain boundaries causing considerable degradation in strength. The smaller the grain size and the higher the density of the materials, the more difficult the nucleation and less likely the occurrence of the phase transformation. Masaki [28] has observed this type of behaviour for Y-TZP materials.

The thermodynamic argument is based on the free energy change associated with the transformation ($\Delta G_{t\rightarrow m}$) and its relationship with the change in chemical (ΔG_c), surface- (ΔG_s) and strain- (ΔG_{sc}) free energies of the material. This may be represented as $\Delta G_{t\rightarrow m} = \Delta G_c + \Delta G_{se} + \Delta G_s$, where $\Delta G_c < 0$.

When the grain size is below a critical value there would not be any transformation as the change in surface- and strain-free energies are greater than the change in chemical-free energy. The strain-free energy depends on the elastic modulus of the material. The higher the elastic modulus, the more positive ΔG_{sc} becomes so that the probability of transformation becomes smaller.

The distribution of yttria was analysed by energy dispersive X-ray analysis (EDXA) and a very uniform distribution of yttria in the Y-TZP–Al_2O_3 composites was observed. In Y-TZP ceramics a uniform distribution of yttria is essential if the lifetime of the composites is to be maximized [29] and probably this is one of the reasons why the material in this study is more stable to hot water.

4. Conclusions

1. Alumina improves the maximum attainable densities of the materials and suppresses porosity development at higher sintering temperatures.
2. Irrespective of the concentration of the alumina in the composites, fracture strengths over 2.0 GPa have been achieved and a maximum strength of around 2.4 GPa has been obtained for ZY20Al_2O_3 specimens after HIPing.
3. None of the materials tested in an autoclave at 175° C crumbled into powder, and a maximum thickness of the transformed surface layer was less than 70 µm after 5 days exposure.

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