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Mechanical Properties of Y-PSZ After Aging at Low Temperature

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SUMMARY

Y-PSZ (partially stabilized zirconia) materials containing 2·0, 2·5, 3·0, 4·0 and 5·0 mol% of yttrium oxide, which had been prepared by cold isostatic pressing and sintering, hot pressing, or hot isostatic pressing, were aged in air between 200 and 500 °C for 500–9000 h. The materials were examined to determine their mechanical properties and microstructure. It was confirmed that Y-PSZ containing 2·5–5·0 mol% yttrium oxide showed little degradation in strength after 2000 h of aging at 200 °C with no changes in monoclinic/tetragonal ratio and density, when the grain size of the sintered material was less than 0·5 μm and the density was greater than 6·07 Mg m^{-3}.

1. INTRODUCTION

In the ZrO_2–Y_2O_3 system Y-TZP* with nearly 100% tetragonal crystal structure has been actively studied as a sintered material with very high strength and toughness.[1–3] The high toughness of Y-TZP is considered to be due to the martensitic transformation from tetragonal (t) to monoclinic (m) crystal structure near propagating cracks and to the volume expansion associated with this transformation.[4] It was reported for the first time by the author and co-workers[5] that, while having excellent mechanical properties at room temperature, the Y-TZP shows conspicuous degradation in

* Editor's footnote: The author describes the materials with 2–3 mol % yttrium oxide as TZP (tetragonal zirconia polycrystal) but he generally (i.e. 2–5 mol %) designates them as Y-PSZ.

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strength when aged at temperatures as low as 200–300 °C. The strength degradation, which is said to start at the surface, is thought to be due to the transformation from t to m during aging.[6–8] It was reported that the main cause of the transformation is the destabilization of zirconia resulting from the reaction of zirconium dioxide or yttrium oxide with water from the air.[9]

The author has studied the composition, particle size, and density of bodies densified by sintering, hot pressing and hot isostatic pressing (hipping) and examined the effects of aging conditions on the mechanical properties and microstructure in relation to the manufacturing conditions.

2. EXPERIMENTAL PROCEDURES

Zirconium dioxide was admixed with 2·0, 2·5, 3·0, 4·0, and 5·0 mol % yttrium oxide. A mixed solution having a predetermined composition was prepared from hydrous chlorides ($ZrOCl_2$, YCl_3) of 99·9 % ZrO_2, and 99·5 % Y_2O_3 purity, respectively, as starting materials. A zirconium dioxide powder was produced by thermally decomposing the solution, followed by calcining and grinding. The calcination was conducted by keeping the decomposed material at 1000 °C for several hours, and the grinding was done in water, using zirconia balls in a mill lined with polyurethane.

The powder thus obtained was dried and then isostatically pressed into blocks 40 × 30 × 100 mm at a pressure of 100 MPa or 200 MPa. The samples were heated from room temperature to 900 °C at a rate of 100 °C h^{-1} and from 900 °C to the sintering temperature (1350, 1400, 1450, or 1500 °C) at a rate of 30 °C h^{-1}, and were kept at that temperature for 2 to 3 h.

Hot pressing was carried out using a high frequency induction heating apparatus (output 20 kW). The dried powder was put into a carbon die and heated to 1500 °C at a rate of 700 °C h^{-1} under a nitrogen gas atmosphere, and kept at this temperature for 1 h; during heating-up the pressure was maintained at 5 MPa, and then raised to 25 MPa; the hot-pressed sample was 80 mm × 10 mm.

Hipping was carried out on samples pressed at 200 MPa and presintered for 2 h at 1400 or 1450 °C so as to obtain material with a density not less than 97 % of the theoretical density; the unencapsulated sample was raised from room temperature to the maximum temperature at a rate of 700 °C h^{-1} in an argon atmosphere; the gas pressure was adjusted to rise slowly so as to reach 200 MPa at maximum temperature; the samples were treated at 1400 or 1450 °C for 1·5 h.

The densified Y-PSZ samples were aged for 100 to 8000 h in air at 200, 250, 300, 400, and 500 °C in an electric furnace.

Specimens $3 \times 3 \times 24\,mm^3$ were prepared by cutting these samples with a diamond saw after aging. A 3-point-bend test (span 20 mm) was conducted with a loading rate of $0{\cdot}5\,mm\,min^{-1}$. The density was calculated from the volume and weight of the bending test specimens.

The microstructure of the sample was observed by transmission electron microscopy on thin films (less than 500 Å) produced by ion-thinning, and changes in the crystal structure after aging were determined using the X-ray diffraction method:[10]

$$\text{monoclinic/tetragonal ratio} = \frac{m(111) + m(11\bar{1})}{t(111) + m(111) + m(11\bar{1})} \times 100\ (\%)$$

The ZrO_2–Y_2O_3 material powder was chemically analyzed by induction coupled plasma (ICP) emission analysis. The results for the powder containing 2·5 mol % yttrium oxide are shown in Table 1. Although 0·03 % of Na_2O was contained in the powder, this was reduced to 0·01 % or less by

TABLE 1
Chemical Analysis of the 2·5 mol % Y-TZP Powder

	Wt %
SiO_2	0·016
Al_2O_3	0·020
Fe_2O_3	0·005
Na_2O	0·030
MgO	0·001
CaO	0·032
TiO_2	0·021
Y_2O_3	4·52
HfO_2	2·65

evaporation during sintering. Therefore, the purity of the powder including zirconium dioxide and hafnium dioxide is 99·9 %.

The grain size was measured by direct TEM observation and the so-called traverse method.

The theoretical density of Y-PSZ was taken from the value determined by the X-ray diffraction method.[11] The Y-PSZs containing 2·0 mol % and 5·0 mol % yttrium oxide had theoretical densities of $6{\cdot}10\,Mg\,m^{-3}$ and $6{\cdot}03\,Mg\,m^{-3}$, respectively.

3. RESULTS

Figures 1–6 show changes in the bend strength (σ) and monoclinic ratio of the Y-PSZs after aging at 200, 300, 400, and 500 °C.

The density of the sintered material was 97·5–98·7 % of the theoretical density, that of the hot-pressed material 99·6 %, and that of the hipped material 99·8 %.

The average grain size of Y-PSZ is 0·45–0·5 μm for the material sintered at 1500 °C, 0·5 μm for the material hot pressed at 1500 °C, and 0·4 μm for the material hipped at 1450 °C.

Figure 1 shows that the Y-TZPs containing 2–3·0 mol % yttrium oxide degrade greatly in strength when aged at 200 °C. Since the monoclinic ratio increases during aging at 200 °C (Fig. 2) this degradation is considered to be due to the transformation from the t to m structure. The ratio of the monoclinic structure increases with the decrease in mol % of yttrium oxide. However, the Y-PSZ containing 5·0 mol % yttrium oxide shows no deterioration in strength and no change in monoclinic ratio.

Figure 3 shows that the hot-pressed Y-TZP containing 2·0 mol % yttrium

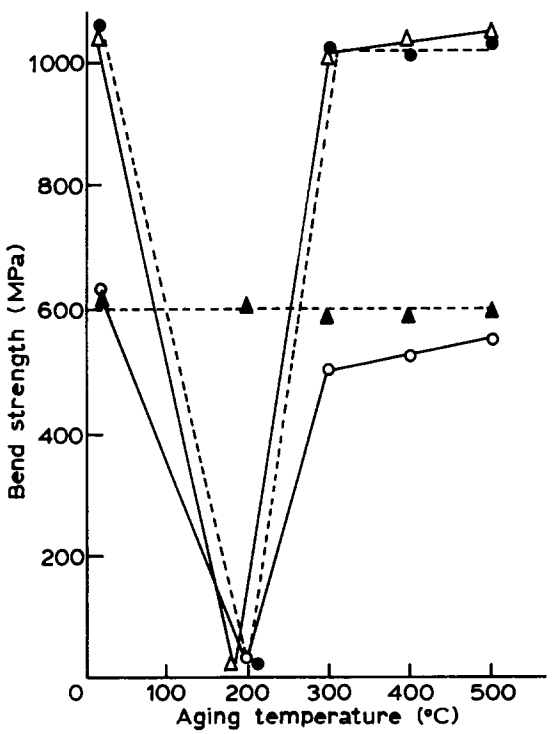

Fig. 1. Change in the bend strength of sintered (1500 °C) Y-PSZ after aging at low temperature for 2000 h. ○, 2·0; ●, 2·5; △, 3·0; ▲, 5·0 mol % yttrium oxide.

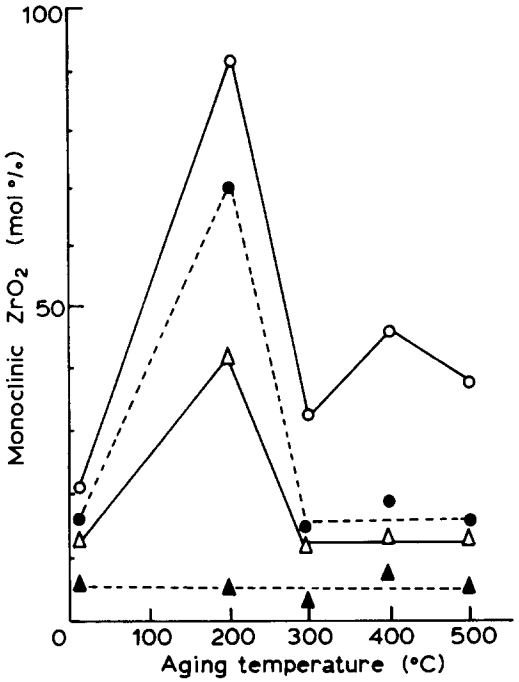

Fig. 2. Change in the monoclinic ratio of the sintered (1500 °C) Y-PSZ after aging at low temperature for 2000 h. ○, 2·0; ●, 2·5; △, 3·0; ▲, 5·0 mol % yttrium oxide.

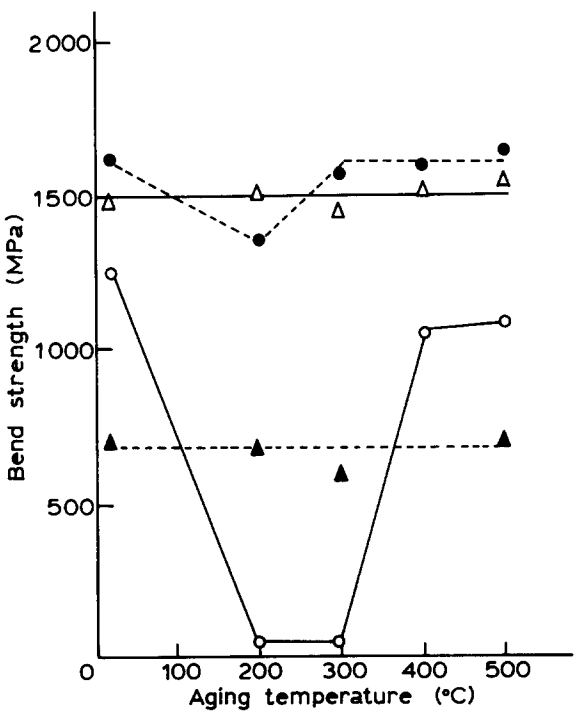

Fig. 3. Change in the bend strength of hot-pressed (1500 °C) Y-PSZ after aging at low temperature for 2000 h. ○, 2·0; ●, 2·5; △, 3·0; ▲, 5·0 mol % yttrium oxide.

oxide degrades greatly in strength when aged at 200 °C and 300 °C, that Y-TZP containing 2·5 mol % yttrium oxide decreases a little in strength, but those containing other molar ratios of yttrium oxide show no changes. Figure 4 shows that only the Y-PSZ containing 2·0 mol % yttrium oxide shows any change in monoclinic ratio. These results prove that a great improvement is achieved when the Y-PSZ is prepared by hot pressing as compared with the sintered material.

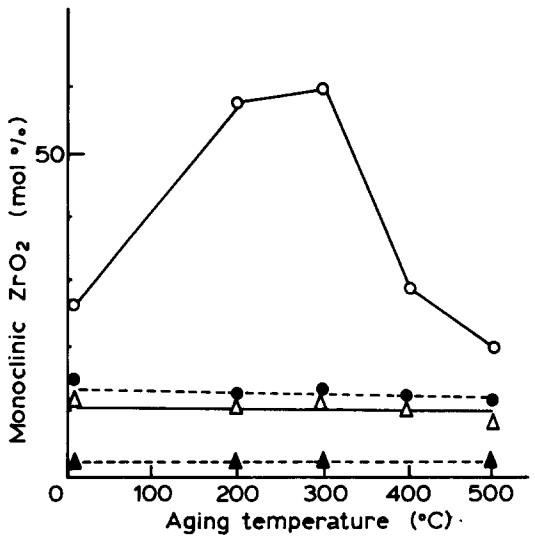

Fig. 4. Change in the monoclinic ratio of the Y-PSZ hot pressed at 1500 °C after aging at low temperature for 2000 h. ○, 2·0; ●, 2·5; △, 3·0; ▲, 5·0 mol % yttrium oxide.

The hipped material shows a similar trend to those prepared by hot pressing (Figs 5 and 6). The Y-TZP containing 2·0 mol % yttrium oxide degrades in strength when aged at 200 °C.

While Fig. 1 shows the dramatic degradation on aging at 200 °C there was no apparent change on aging at 300 °C for compositions containing 2·5, 3 and 5 mol % yttrium oxide. Even after 8000 h there was no degradation, nor any change of the monoclinic ratio; nor were any changes observed after 5000 h at 400 °C and 500 °C.

Figure 7 indicates changes in the strength of the Y-PSZs containing 2·5, 3·0 and 4·0 mol % yttrium oxide, prepared by sintering, hot pressing and hipping, after aging at 200 and 250 °C for 2000 h in relation to density and grain size.

Materials with high densities were obtained by hot pressing and hipping; materials with different grain sizes were prepared at different temperatures.

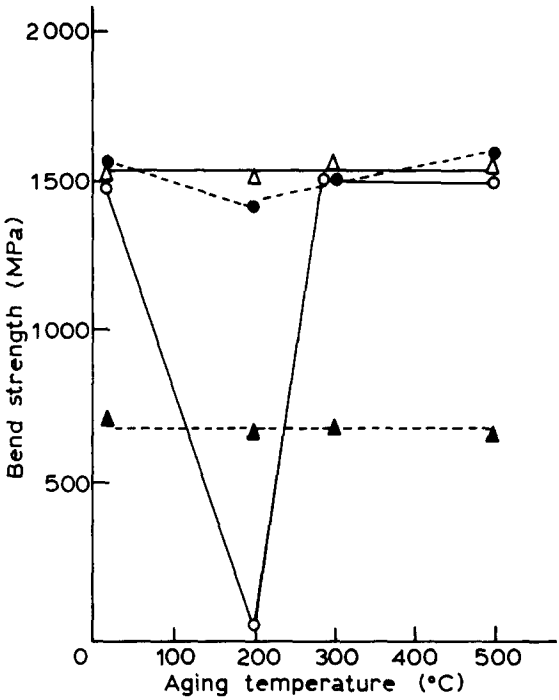

Fig. 5. Change in the bend strength of Y-PSZ hipped at 1400 °C after aging at low temperature for 2000 h. ○, 2·0; ●, 2·5; △, 3·0; ▲, 5·0 mol % yttrium oxide.

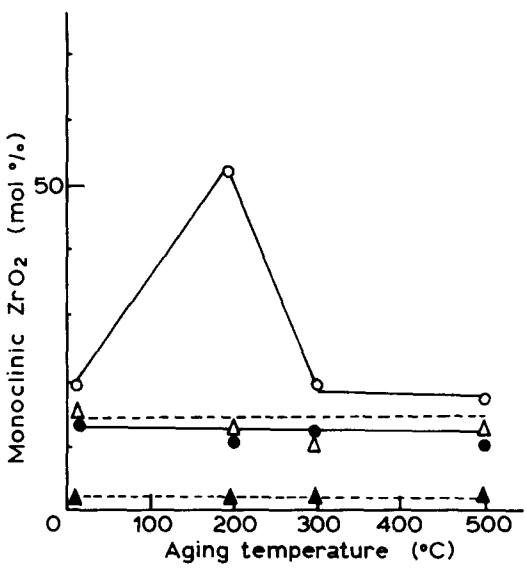

Fig. 6. Change in the monoclinic ratio of the Y-PSZ hipped at 1400 °C after aging at low temperature for 2000 h. ○, 2·0; ●, 2·5; △, 3·0; ▲, 5·0 mol % yttrium oxide.

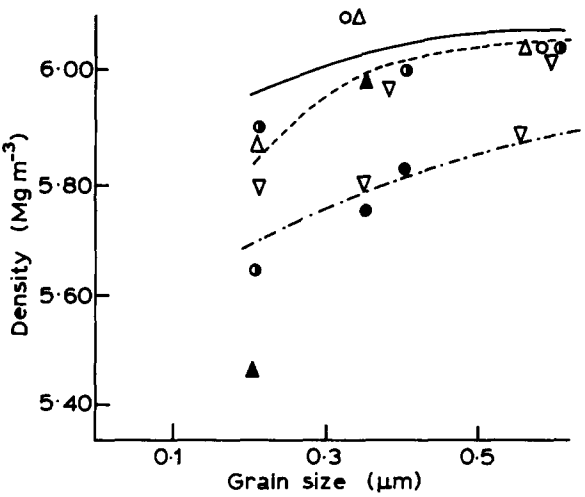

Fig. 7. The interrelation of density and grain size with degradation of the bend strength of Y-PSZ prepared by sintering, hot pressing and hipping, after aging at 200 or 250 °C. ○, ——, 2·5; △, – – –, 3·0; ▽, – · – ·, 4·0 mol % yttrium oxide.

Experiments were carried out on the Y-PSZs with grain sizes of 0·2–0·5 μm and densities of 90–99·7 % of the theoretical density.

The solid circles and triangles show sintered materials, the strength of which decreased greatly after aging; the extent of the black area in each circle corresponds to the degree of degradation in strength.

Figure 7 shows that the higher the content of yttrium oxide (3·0 to 4·0 mol %), the higher the density (not less than 99·6 % of the theoretical density), and the smaller the grain size, the less the degradation in strength after aging. The figure also shows curves of critical densities and grain sizes for degradation after aging with respect to the Y-PSZs containing 2·5, 3·0 and 4·0 mol % yttrium oxide. The area above the curve is a region where degradation after aging is not found.

These results prove that the degradation is associated with the interrelation between the density (or voids), the grain size and the composition. The Y-PSZ containing 4·0 mol % yttrium oxide does not deteriorate after aging.

Figure 8 shows the microstructure of the 2·0 mol % Y-TZP prepared by hot pressing at 1500 °C. The same sample exhibits various microstructures: a uniform granular structure (Fig. 8(a)); a mixed structure (Fig. 8(b)), consisting of fine grains (monoclinic structure) transformed from the tetragonal structure, and t grains; and a structure having clear intra-twins (monoclinic structure) or moiré patterns in the crystal grain (Fig. 8(c)). A material having these microstructures was reported to have a very high fracture toughness.[12]

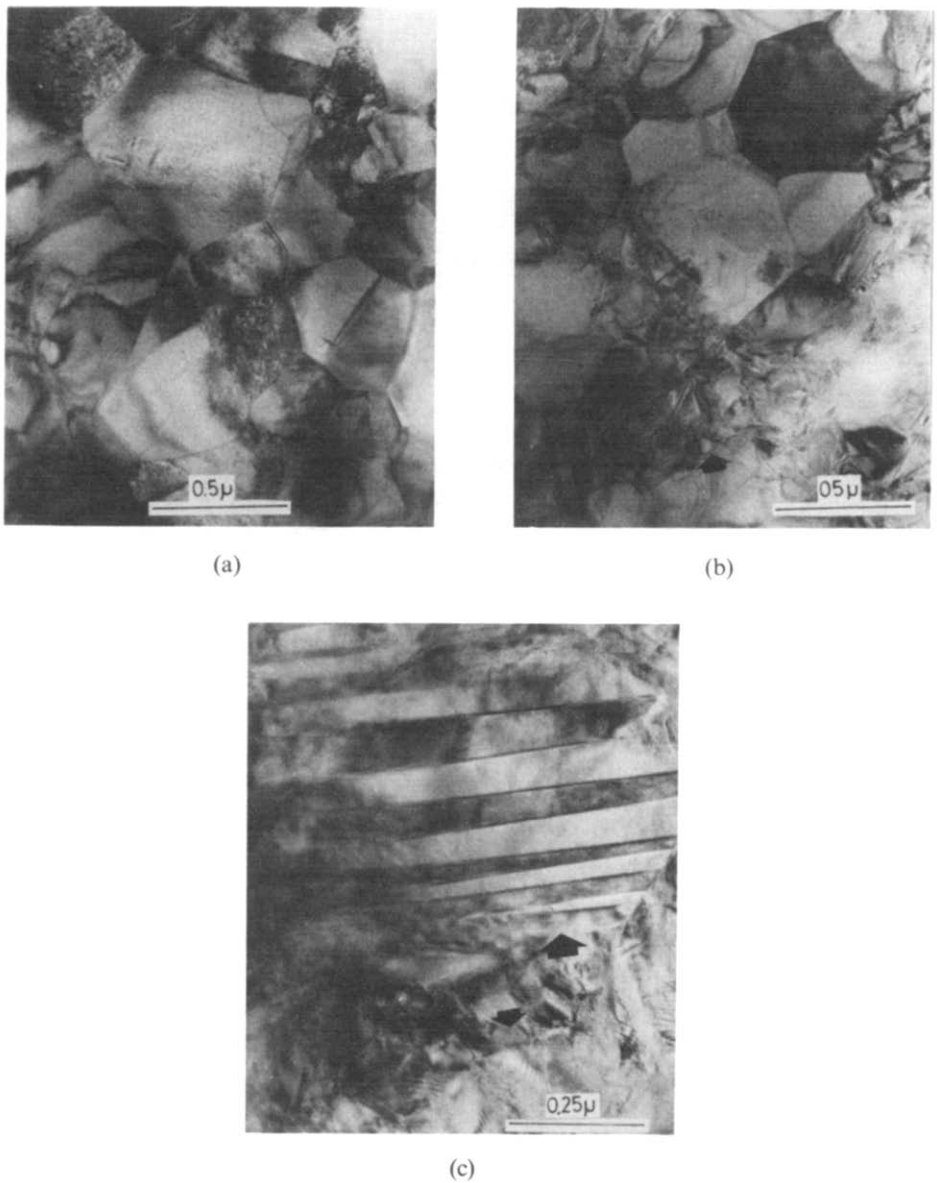

Fig. 8. The microstructures of 2·0 mol% Y-PSZ, hot-pressed at 1500°C. (a) Granular structure; (b) mixed structure of granular and transformed grains, in which a complicated microstructure other than crystal grains can be observed (arrow mark); (c) twins and moiré structure can be observed in the grain (arrow mark).

Figure 9 shows the microstructures of 3·0, 4·0 and 5·0 mol % Y-PSZs. The 3·0 mol % Y-TZP has a uniform granular structure with the t structure, and the 4·0 mol % Y-PSZ, a mixed structure consisting of fine and large grains. The former is of t structure and the latter of c structure. The 5·0 mol % Y-PSZ has a small number of fine grains with t structure and large grains ($\sim 0{\cdot}5\ \mu m$) with c structure.

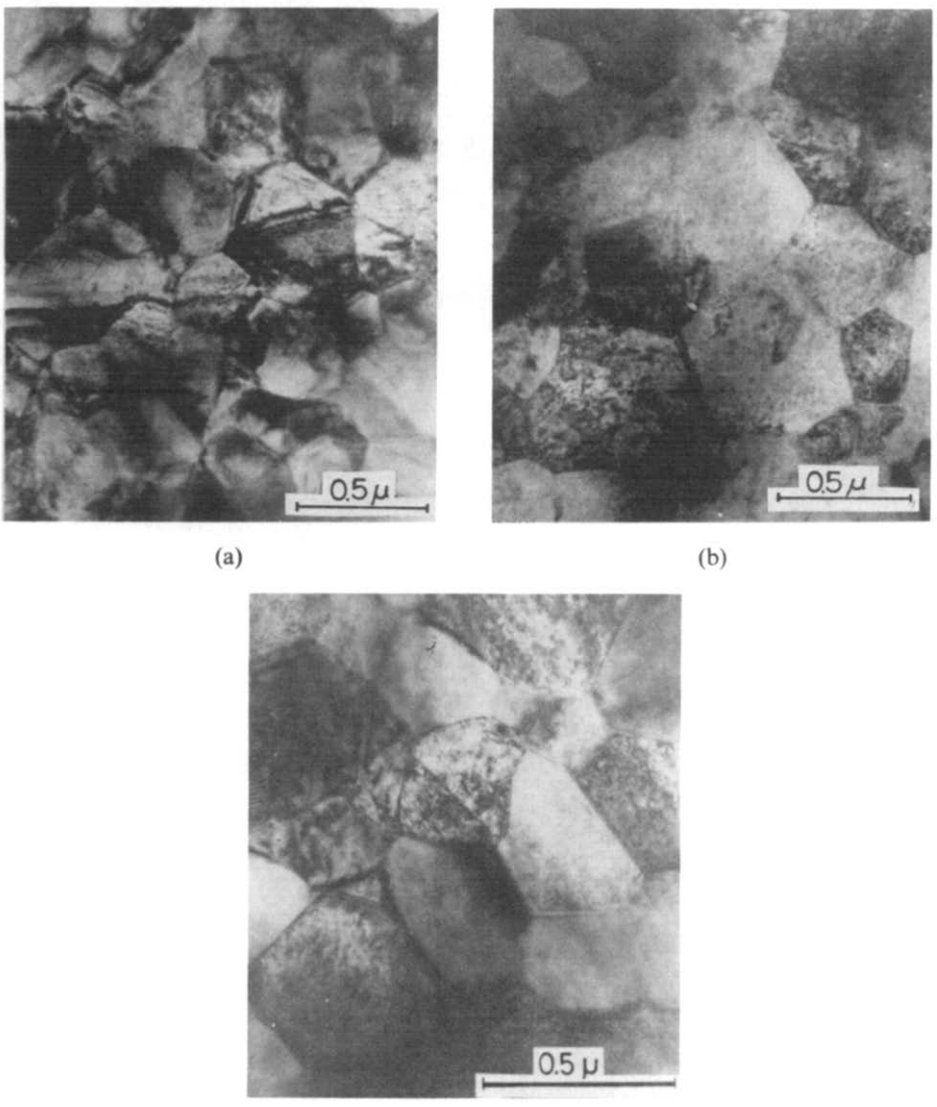

Fig. 9. The microstructure of the Y-PSZ hot-pressed at 1500 °C. (a) 3·0 mol % Y-TZP; (b) 4·0 mol % Y-PSZ; (c) 5·0 mol % Y-PSZ.

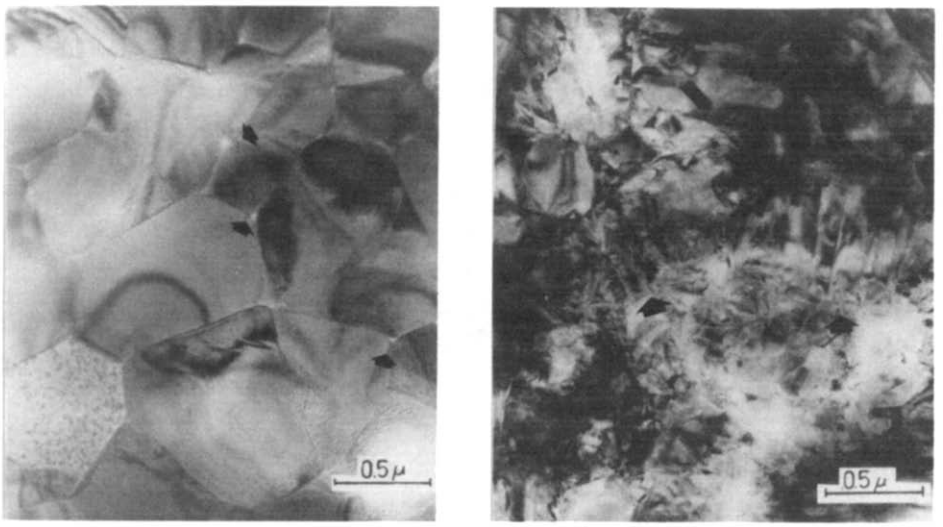

Fig. 10. The microstructures of 2·5 mol % Y-TZP sintered at 1500 °C before and after aging at 200 °C. (a) Microstructure before aging; (b) microstructure after aging at 200 °C for 1000 h, in which many twins and cracks can be observed (arrow mark).

The microstructure of 2·5 mol % Y-TZP, prepared by hot pressing, shows no change in the structure after aging at 200 °C.

Figure 10 shows the microstructure of sintered 2·5 mol % Y-TZP, before and after aging at 200 °C. It is observed that the strength is greatly degraded after aging, and that twins and cracks develop in the microstructure. These changes are considered to be due to the transformation from t to m structure.

4. DISCUSSION

Results of the bend strength (Fig. 1), the monoclinic ratio (Fig. 2), and the observation of the microstructure (Fig. 10), confirm that the degradation of the strength of the Y-TZPs containing 2·0 to 3·0 mol % yttrium oxide after aging at around 200 °C is caused by the transformation from the tetragonal (t) to the monoclinic (m) crystal structure. Changes in microstructure are observed by the increase in twins and cracks. However, the degradation of Y-TZP varies greatly according to the composition, density and grain size of the material. The materials prepared by hot pressing or hipping show no deterioration in strength after low temperature aging, as compared with the sintered material. Almost no deterioration is observed in the 2·5–3·0 mol %

Y-TZPs prepared by hot pressing, as compared with those having almost the same grain size ($\sim 0{\cdot}5\,\mu m$) prepared by sintering.

However, even in a high density material the transformation cannot be prevented when the yttrium oxide composition is as low as 2·0 mol %. From these results, it is confirmed that the degradation after low temperature aging is affected by the composition and property of the material, such as yttrium oxide content, grain size and density. While the degradation in strength is confirmed from the experimental results as being caused by the martensitic transformation from t to m structure, the mechanism of the transformation has been widely studied and discussed;[6] the stability of tetragonal grains is being examined from the points of thermodynamics and kinetics.

The thermodynamic argument is that when the grain size is small, the grain is stabilized because the surface and strain energy become larger than the change in chemical free energy from t to m structure.[13,14]

The kinetic argument is based on the concept that the transformation takes place through heterogeneous nucleation, wherein the nucleus, in the case of the PSZ, is formed mainly by the dislocation of the interface and as the dislocation grows, the transformation develops.[15]

According to the above arguments, as the grain size becomes smaller, the defect on the grain boundaries becomes less, making the nucleation difficult. The fact that the transformation is inhibited by the higher density can be understood qualitatively from the fact that defects and cracks are decreased by the increase in density, whereby nucleation will become difficult. Recently, the author obtained experimental results indicating that there was almost no dependence of the high fracture toughness of high purity Y-TZP upon the grain size.[16] This fact contradicts the concept of the dependence of the transformation upon the grain size, supporting the argument that nucleation is essential for the transformation.

Chen *et al.* proposed a statistic discussion on the relation between nucleation and grain size, explaining that when the grain size is small the nucleation probability decreases.[15]

There are many studies on the aging of Y-TZP and its behavior in aqueous solutions.[17,18] There are reports that the degradation of Y-TZP is accelerated in such aqueous solutions as distilled water, sulfuric acid and caustic soda, as compared with aging in air. The degradation mechanism is considered as follows: a region where zirconia is destabilized is formed by the reaction of OH^- and H^+ in H_2O with Y_2O_3 or ZrO_2; with the region as starting point, the transformation from t to m crystal develops along grain boundaries; as a result, zirconia particles lose coherency with the matrix, causing the great decrease in strength.

The reason why Mg-PSZ is less degraded by low temperature aging than

Y-TZP is possibly that it is difficult for nucleation for the transformation to proceed because, in the case of Mg-PSZ, tetragonal grains are finely precipitated in the cubic matrix, and that since only a small number of tetragonal grains are present on grain boundaries, it is difficult for the transformation to take place along grain boundaries, thus stabilizing the tetragonal grains.

Many methods are proposed in order to avoid the deterioration of Y-TZP after aging.[19,20] Among them are an increase in Y_2O_3 content, small grain size and an increase in the density of the sintered material. Besides these methods, high purification of raw materials is effective for inhibiting the transformation. In particular, when oxides such as TiO_2, Fe_2O_3 and Al_2O_3 are present as impurities or additives, which do not form solid solutions with ZrO_2, strain and thermal stress develop, possibly because these oxides have thermal expansion coefficients and elastic constants different from the matrix. As a result, they will form a starting point at which the transformation occurs along grain boundaries.

On the other hand these oxides act as sintering aids, and hence different results will occur depending on their amount. This problem is an important subject to be studied in the future.

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