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Effect of Nb_2O_5 and Y_2O_3 Alloying on the Mechanical Properties of TZP Ceramics

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Abstract: In the ZrO_2–Y_2O_3–Nb_2O_5 ternary system, Nb_2O_5 and Y_2O_3 co-doped tetragonal ZrO_2 polycrystals (TZPs) were synthesised by sintering and hot-pressing (HPing) to evaluate the effect of alloying on the mechanical properties and phase stability of TZPs. Monolith containing the composition of 90.24 mol% ZrO_2–5.31 mol% Y_2O_3–4.75 mol% Nb_2O_5, which was prepared by both sintering and hot-pressing, exhibited a good relation between strength and toughness. Also, no t→m phase transformation after ageing at temperatures in the range of 100 to 400°C for up to 1000 h was observed. TZPs sintered at 1550°C for 10 h in air showed the flexural strength of above 500 MPa and the fracture toughness of 9 MPa $m^{1/2}$. The flexural strength increased greatly by HPing at 1400°C for 1 h under an Ar gas atmosphere from 500 MPa to above 1 GPa, while the fracture toughness decreased slightly from 9 MPa $m^{1/2}$ to 7.5 MPa $m^{1/2}$. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Several techniques have been developed to eliminate the low temperature degradation (LTD) of tetragonal zirconia polycrystals (TZPs) because TZPs experience the tetragonal (t) to monoclinic (m) phase transformation after long-term use at low temperatures (100 to 400°C). LTD is retarded by maintaining a smaller grain size and a higher stabilizer content.[1,2] Recently, the low temperature phase stability of TZPs has been achieved by alloying oxides (TiO_2, CeO_2, etc.).[3,4]

In yttria-stabilised TZPs (Y-TZPs), the substitution of Y^{+3} (0.1019 nm) for Zr^{+4} (0.084 nm) causes the distorted fluorite structure and charge imbalance due to the larger ionic size of Y^{+3} and the charge deficiency, resulting in the formation of internal strain and oxygen vacancy.[5] Therefore, both the number of oxygen vacancy and the internal strain are responsible for the m-ZrO_2 content (74%) of 3Y-TZP after ageing at 220°C for 100 h because LTD is the relaxation process of internally strained lattice by a thermally activated oxygen ion diffusion. However, the strain energy is more important than the number of oxygen vacancy because the strain energy significantly contributes to the total free energy change for the t→m phase transformation, which leads to the oxygen vacancy diffusion.[6]

Nb_2O_5 is emerging as the candidate oxide of choice for highly toughened TZPs because the alloying of pentavalent oxide to Y-TZP suppressed[7–9] the number of oxygen ion vacancies, which is formed by the substitution of Y^{+3} for Zr^{+4}, as a result of the substitution of Nb^{+5} (0.074 nm) for Zr^{+4}. However, the addition of pentavalent oxide increases the tetragonality[9] (c/a ratio) and then produces the residual stress, which is prerequisite for the t→m phase transformation. Especially, the addition of 1.5 mol% Nb_2O_5 to 3 mol% Y_2O_3–TZP (3Y(1.5N)–TZP) shows extensive m-ZrO_2 content (96%) after ageing at 220°C for 100 h due to the increased transformability[5] of Y-TZP. Therefore, the amount of residual stress controls the rate of oxygen vacancy diffusion and then the LTD rate.

In ZrO_2–Y_2O_3–Nb_2O_5 ternary system, the nontransformable[10] composition exists in the triangle enclosed with 90 mol% ZrO_2–5.4 mol% Y_2O_3–4.2 mol% Nb_2O_5, 89.0 mol% ZrO_2–6.0 mol% Y_2O_3–5.0 mol% Nb_2O_5, and 85.0 mol% ZrO_2–7.5 mol% Y_2O_3–7.5 mol% Nb_2O_5. According to Ref. 10, composites are synthesised by adding 3Y(1.5N)–TZP to the nontransformable TZPs, where 3Y(1.5N)–TZP is varied at intervals of 5 wt% in the range of 10–30 wt%. The corresponding monoliths are also prepared. The objective of the present paper is to investigate the proper composition of Nb_2O_5 and Y_2O_3 doped TZPs for the optimum mechanical properties and the low temperature phase stability.

2 EXPERIMENTAL PROCEDURES

3Y-TZP, 3Y(1.5N)–TZP, non-transformable TZPs (5.75 mol% Y_2O_3–5.00 mol% Nb_2O_5-89.25 mol% ZrO_2 and 5.50 mol% Y_2O_3–4.75 mol% Nb_2O_5–89.75 mol% ZrO_2), composite, and the corresponding monolith were prepared, respectively, by using zirconia powders containing 0 to 3 mol% yttria (Tosoh Inc., Tokyo, Japan), yttria (Aldrich Inc., USA), and Nb_2O_5 powders (Aldrich Inc., USA). The powders were mixed by ball mill with zirconia balls for 24 h. After drying, the mixed powders were calcined for 4 h at 1100°C with a heating rate of $10°C\,min^{-1}$ to 1100°C, furnace cooled, and then attrition milled for 1 h.

The dry sieved powders (100 mesh) were uniaxially pressed into rectangular plates (34×34×5 mm) at 98 MPa, and then isostatically pressed at 138 MPa for the conventional sintering. The specimens were sintered at temperatures of 1500 to 1650°C with heating rates of $6°C\,min^{-1}$ to 900°C and $3°C\,min^{-1}$ up to 1650°C, and then furnace cooled to room temperature.

Also, the uniaxially pressed plates were inserted in a graphite die and heated to the hot-pressing (HPing) temperatures (1300 to 1500°C) at a rate of $12°C\,min^{-1}$ under an Ar gas atmosphere (Astro Industries, Inc., USA). The samples were then kept at each sintering temperature for 1 h. A pressure of 5 MPa was first applied and then maintained from the room temperature to the HPing temperature. At the sintering temperature, the pressure increased to 30 MPa. Then, the pressure reduced to 15 MPa just after HPing and then removed completely at 1200°C. The final dimension of HPed material was 34×34×4 mm. The sintered materials were then ground and cut with diamond saw to a size of 34×4×3 mm. Finally, the specimens were polished down to a 1 μm diamond finish.

The bulk density of the specimens was determined by the Archimedes' method. Young's modulus was measured acoustically using the pulsed-echo overlap method.[11] Fracture toughness of bar was measured using the dummy indentation method[12] by placing three equally spaced Vickers diamond indents of 294 N on the tensile-sided surface after polishing to a 1μ diamond finish. The flexural strength was measured in 3 or 4-point bending with outer and inner spans of 20 and 8 mm at a crosshead speed of $0.5\,mm\,min^{-1}$ (Model 4204, Instron, UK), respectively.

Low temperature ageing was carried out at 220°C to 400°C for up to 1000 h because the strength degradation was observed greatly at these temperatures.[2,5] Ground and polished bar specimens were used for X-ray diffraction pattern (XRD). The proportion of the t, m, and c-phase was estimated from the peak height of (111)m, $(11\bar{1})$m, (111)t,c, (004)t, (400)t, and (400)c of XRD using the Cu Kα radiation at 40 kV and 30 mA within the scan angles (2θ) of 27.5° to 76° using the method of Garvie and Nicholson.[13]

The surfaces of polished and fractured bars were examined with a scanning electron microscope (SEM). Then, the linear intercept method of SEM was used to determine the average grain size with the use of a correction factor of 1.56 after Mendelson.[14]

3 RESULTS AND DISCUSSION

The variation of flexural strength and fracture toughness for monolith (90.24 mol% ZrO_2–5.31 mol% Y_2O_3–4.75 mol% Nb_2O_5), composite A (15 wt% of 3Y(1.5N)–TZP plus 85 wt% of 89.25 mol% ZrO_2–5.75 mol% Y_2O_3–5.00 mol% Nb_2O_5), and composite B (15 wt% of 3Y(1.5N)–TZP plus 85 wt% of 89.75 mol% ZrO_2–5.50 mol% Y_2O_3–4.75 mol% Nb_2O_5) as a function of sintering time is shown in Fig. 1. These results indicate that only a composite composition comprising a mixture of an 85 wt% nontransformable TZP and a 15 wt% transformable TZP, and the corresponding monolith are observed as the best material for strength, toughness, and phase stability after being sintered at 1550°C for up to 10 h . Although a 15 % of strength reduction occurs after heat treatment at 220 to 1000°C for up to 1000 h, no t→m phase transformation is found, which means no LTD and high temperature degradation (HTD). However, only the monolith having a composition corresponding to composite B shows a similar mechanical property and chemical stability (Fig. 2). The absence of LTD and HTD in composite implies

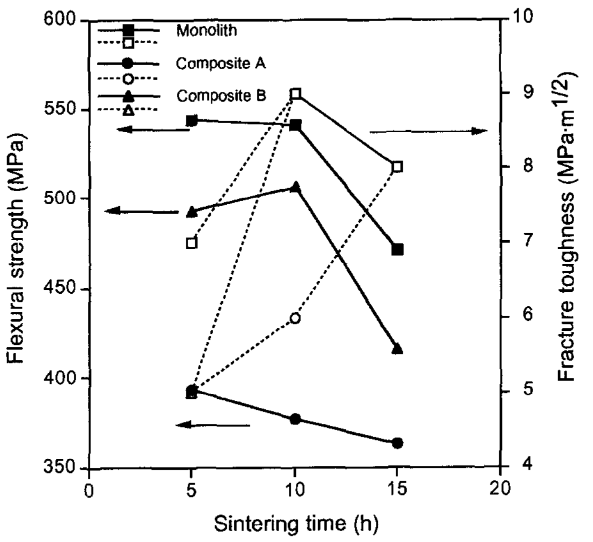

Fig. 1. Variation of flexural strength and fracture toughness of Nb_2O_5 and Y_2O_3 co-doped TZPs as a function of sintering time. Samples are sintered at 1550°C (5 to 15 h).

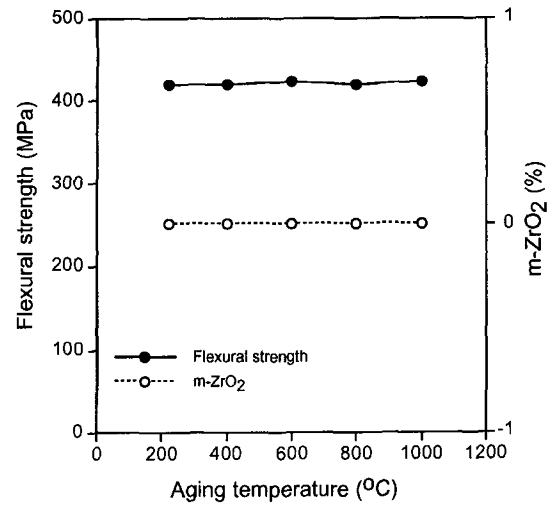

Fig. 2. Flexural strength and m-ZrO_2 content of monolith after ageing at each temperature for 100 h.

that the nontransformable TZP as a stable matrix plays a significant role in resisting the volume expansion of the t-lattice accompanying a t→m phase transformation. It is confirmed experimentally that the t-grains grow uniformly with increasing sintering time, as shown in Fig. 3. However, monolith having a composition corresponding to composite A promotes the t→m transformation after sintering at 1550°C, resulting in LTD.

Even though both composite and monolith exhibit excellent phase stability and toughness, the strength is still lower than that of a commercial sample of 3Y-TZP. Therefore, all samples are HPed at temperatures in the range of 1300 and 1500°C for 1 h in an Argon atmosphere, respectively. HPing process raises final densities from >97% to >99.6% of theoretical.

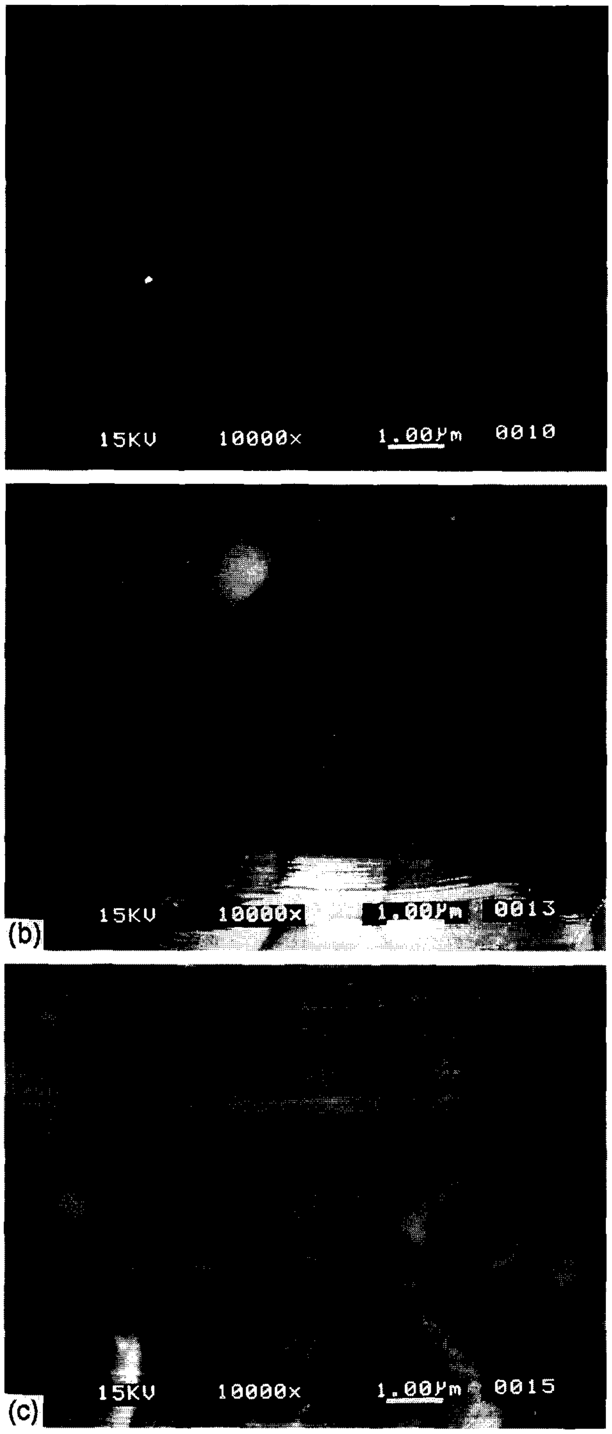

Fig. 3. Scanning electron micrographs of the thermally etched surface of composite B sintered at 1550°C for (a) 5 h, (b) 10 h, and (c) 15 h.

The flexural strength and fracture toughness as a function of HPing temperature is shown in Fig. 4. Maximum strength of above 1 GPa and toughness of 7.5 MPa $m^{1/2}$ are observed for monolith HPed at 1400°C for 1 h. A negligible m-ZrO_2 content (less than 1%) of monolith, composite, and nontransformable TZP is also observed at this temperature (Fig. 5). Strength (800 to 950 MPa) and toughness (2.5 to 4.9 MPa $m^{1/2}$) of 3Y-TZP increases with increasing temperature. The maximum mechanical properties of 3Y-TZP are obtained at

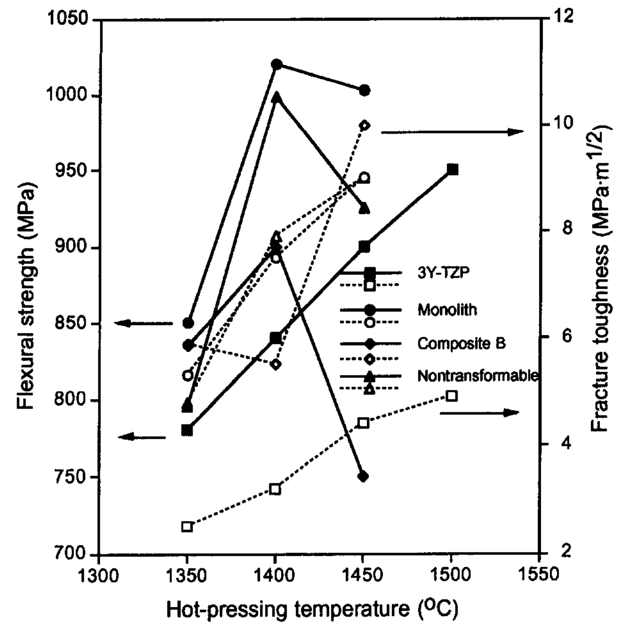

Fig. 4. Variation of flexural strength and fracture toughness as a function of hot-pressing temperature. All samples are hot-pressed for 1 h.

1500°C and they are 950 MPa and 4.9 MPa m$^{1/2}$. No m-ZrO$_2$ content of 3Y-TZP is observed at temperatures in the range of 1300 and 1500°C due to the smaller grain size (< 0.5 μm).

Unlike the conventional sintering, composite B hot-pressed (HPed) at 1300 and 1500°C and monolih HPed at 1500°C are cracked. The prepared powders of composite should be less reactive compared to the as-received 3Y-TZP, which results in the loss of the constraint on t-ZrO$_2$ lattice of nontransformable TZP as a matrix. Although Young's modulus of monolith shows the intermediate value between 3Y-TZP and nontransformable TZP (89.75 mol% ZrO$_2$–5.50 mol% Y$_2$O$_3$–4.75 mol% Nb$_2$O$_5$), composite shows the irregular curve compared to monolith (Fig. 6). Therefore, HPing process is better for monolith than for composite and monolith presents the best relation between strength and toughness. Also, no LTD (100 to 400°C) is observed for monolith, composite, and nontransformable TZP HPed at 1400°C. It is believed that Nb$_2$O$_5$ co-doping annihilates the oxygen vacancies, which are produced by the substitution of Y^{+3} for Zr^{+4}. That is, the charge neutrality is well balanced and oxygen vacancies are eliminated or ordered by the proper substitution of Nb^{+5} and Y^{+3} for Zr^{+4}, resulting in retention of the LTD rate.

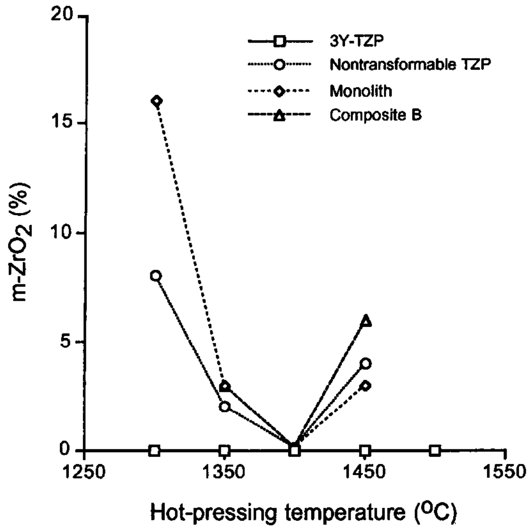

Fig. 5. Fraction of m-ZrO$_2$ as a function of hot-pressing temperature.

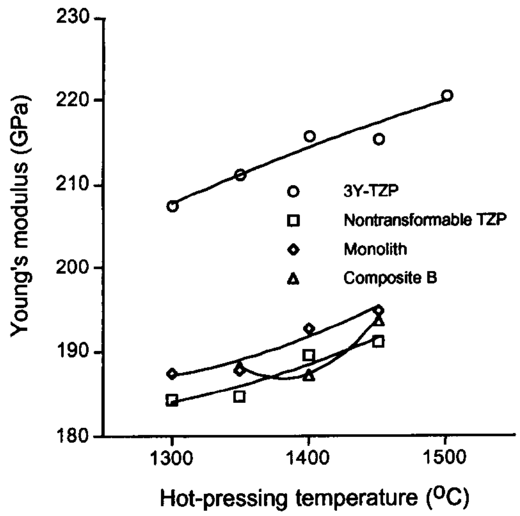

Fig. 6. Young's modulus of hot-pressed TZPs as a function of hot-pressing temperature.

4 CONCLUSIONS

Two material preparation methods are employed to investigate the mechanical properties of Nb$_2$O$_5$ and Y$_2$O$_3$ co-doped TZP ceramics. First, the conventional sintering method is better for composite than for monolith because composite containing a composition, comprising adding transformable TZP to nontransformable TZP in an amount of not more than 20% by weight based on the total weight of the resulting mixture, shows no t→m phase transformation even after heat treatment at temperatures in the range of 220 and 1000°C for 1000 h. It is believed that nontransformable TZP acts as a matrix to constrain the t-lattice, resulting in the absence of LTD and HTD. Second, HPing is better for monolith than for composite because the monolith exhibits more reliable mechanical properties without compromising the phase stability at temperatures in the range of 100 to 400°C. However, composite does not show any longer the previous-mentioned properties. It is believed that the nontransformable TZP does not function properly due to the reactivity of the prepared powders, the smaller grain size, and the carbon contamination.[15,16]

From the above-mentioned results, it is found that Nb_2O_5 doping to yttria stabilised TZPs enhances the toughness as well as the chemical stability without compromising the strength. Monolith (corresponding to composite B), 90.24 mol% ZrO_2–5.31 mol% Y_2O_3–4.75 mol% Nb_2O_5, is found as the best composition, which is applicable to both the conventional sintering and the HPing. However, the amount of Nb_2O_5 should always be less than the amount of Y_2O_3 in both the transformable TZP and the nontransformable TZP, and the resulting composite.[10]

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