JOURNAL OF MATERIALS SCIENCE 29 (1994) 5709–5714

Investigation on crystalline phases and mechanical properties of TZP ceramics prepared from sol–gel powders

N. M. GOKHALE, R. DAYAL, S. C. SHARMA, RAMJI LAL
Naval Chemical and Metallurgical Laboratory, Naval Dockyard, Bombay-400 023, India

Y_2O_3-stabilized tetragonal zirconia polycrystalline (TZP) ceramics containing 1–5 mol % Y_2O_3 were prepared by hot pressing and pressureless sintering of sol–gel-derived powders. Sintered ceramics were evaluated for their density, grain and crystallite size, width of transformation zone, crystalline phases and mechanical properties. Variation in the values of fracture toughness and flexural strength has been explained on the basis of crystallite size and proportion of transformable tetragonal phase, which are influenced by the concentration of Y_2O_3 in TZP ceramics. Correlation of the data has indicated that the transformable tetragonal phase is the key factor in controlling the fracture toughness and strength of ceramics.

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystalline (TZP) ceramics, containing metastable tetragonal phase at room temperature, undergo martensitic phase transformation from tetragonal to monoclinic ($t \rightarrow m$) phase under the influence of stress. These ceramics exhibit high toughness and high strength due to the release of strain energy stored around a propagating crack tip [1–3]. The phase transformation and associated enhancement in toughness and strength of TZP ceramics have been extensively investigated, and variations in mechanical properties have been correlated with composition, transformability of the tetragonal phase, size of transformation zone and microstructure [4–20]. It has been recognised that transformability of tetragonal phase is the paramount important parameter in determining the mechanical performance of TZP ceramics [21, 22]. It has also been reported that the stability of tetragonal phase in ZrO_2 particles is dependent on the crystallite size [23–25]. In such studies, the development of several different kinds of tetragonal phase has also been disclosed, indicating the influence of crystallite size on transformation nucleation and autocatalytic transformation [2, 6, 17, 26–32]. However, the influence of crystallite size in determining the transformability of tetragonal phase in TZP ceramics has not been adequately investigated. Efforts have been made in this respect in our earlier investigation, in which it was observed that variation in crystallite size influences the proportion of tetragonal phase in ultrafine and chemically homogeneous TZP powders prepared by sol–gel route [31]. The objective of the present paper is to investigate the influence of crystallite size on transformability of the tetragonal phase in relation to mechanical properties of TZP ceramics prepared from the sol–gel powders.

2. Experimental procedure

Powders of ZrO_2 containing 1, 2, 3, 4 and 5 mol % Y_2O_3 (referred to as 1Y, 2Y, 3Y, 4Y and 5Y TZP materials, respectively) were prepared by the sol–gel technique. The method of preparation and characteristics of the powders have been described elsewhere [31]. As-prepared powders were decomposed at 200 °C into their constituent oxides and further calcined at 500 °C for 2 h in order to facilitate the formation of well-defined crystalline phases. Powders calcined at 500 °C were milled by a specialized communition process to remove agglomeration, and then consolidated to sintered ceramics by cold isostatic pressing at 100 MPa, followed by pressureless sintering at 1700 °C for 2 h. These powders were also hot pressed at 1500 °C for 2 h at a pressure of 25 MPa in vacuum using a graphite die.

Sintered density, as determined by the Archimedes principle, was $> 98\%$ theo. for pressureless-sintered and $> 99\%$ theo. for hot-pressed ceramics. Grain size was measured by the linear intercept method [33] using SEM photomicrographs obtained from the polished and etched surfaces of the sintered bodies. Sintered specimens were cut into bars of $2.5 \times 3.5 \times 20\ \mathrm{mm}^3$ which were then polished to a 6-μm finish using diamond paste for the evaluation of mechanical properties. Fracture toughness was determined by the microindentation technique (load = 10 kg) [34], and flexural strength values were measured by a three-point-bend test with a span width of 20 mm at a cross-head speed of $0.5\ \mathrm{mm\ min}^{-1}$ [2, 21].

X-ray diffraction (XRD) techniques were used to determine the crystallite size, compositional fluctuations, width of the transformation zone and percentage of monoclinic, tetragonal and cubic phases in the sintered materials. In order to avoid peak splitting at high-order reflections, the CuK_{α_1} component of CuK_α

0022–2461 © *1994 Chapman & Hall*

radiation was used in the present investigation. Crystallite size was calculated using the $(1\,1\,1)_m$ and $(1\,1\,1)_t$ diffraction peaks from the Scherrer formula [35] as shown below

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where D is the crystallite size in nm, λ is the radiation wave length (0.1541 nm for $\mathrm{Cu}K_{\alpha_1}$), β is the corrected line width at half-peak intensity, and θ is the diffraction peak angle. The diffraction peaks in the range $2\theta = 72$–$76°$ were used to distinguish between the tetragonal and cubic forms.

Compositional fluctuation in the sintered ceramics was examined using a Williamson–Hall plot based on the following equation [24, 36, 37].

$$\beta\cos\theta/\lambda = 1/D + \eta\sin\theta/\lambda \qquad (2)$$

where η is the lattice strain β, θ, D and λ are the same as mentioned in Equation 1.

The volume fraction of the monoclinic (V_m), transformable tetragonal (V_t), non-transformable tetragonal ($V_{t'}$) and cubic (V_c) phases present in the sintered ceramics were determined from Equations 3–7 using the intensities of the diffraction patterns from the $t(1\,1\,1)$, $c(1\,1\,1)$, $m(1\,1\,\bar{1})$, $m(1\,1\,1)$, $t(4\,0\,0)$, $t(0\,0\,4)$, $t'(4\,0\,0)$, $t'(0\,0\,4)$ and $c(4\,0\,0)$ reflections [21, 38, 39]. For compositions containing $(m + t)$ phases:

$$V_m = [I_m(1\,1\,\bar{1}) + I_m(1\,1\,1)]/[I_m(1\,1\,\bar{1}) + I_m(1\,1\,1) + I_t(1\,1\,1)] \qquad (3)$$

$$V_t = (1 - V_m) \qquad (4)$$

For compositions containing $(t + t' + c)$ phases:

$$V_c = [I_c(4\,0\,0)]/[I_t(4\,0\,0) + I_t(0\,0\,4) + I_c(4\,0\,0) + I_{t'}(4\,0\,0) + I_{t'}(0\,0\,4)] \qquad (5)$$

$$V_t = [I_t(4\,0\,0) + I_t(0\,0\,4)]/[I_c(4\,0\,0) + I_t(4\,0\,0) + I_t(0\,0\,4) + I_{t'}(4\,0\,0) + I_{t'}(0\,0\,4)] \qquad (6)$$

$$V_{t'} = (1 - V_c - V_t) \qquad (7)$$

I_m, I_t, $I_{t'}$ and I_c are the intensities of monoclinic, transformable tetragonal, non-transformable tetragonal and cubic reflections, respectively.

The width of the transformation zone (d) of the fracture surface of the sintered ceramics was determined by examining the bending-test piece using XRD [40, 41]. The following equation was used

$$d = -\frac{\sin\theta}{2\mu}\ln\left(\frac{f - x}{f}\right) \qquad (8)$$

where f is the fraction of transformable tetragonal phase in the sintered material, x the fraction of monoclinic phase on the fracture surface, θ the diffraction angle ($\theta = 15°$), and μ the linear absorption coefficient of the bulk material. In this case, the value of μ was taken as 652.2 cm^{-1}, as reported in the literature [21].

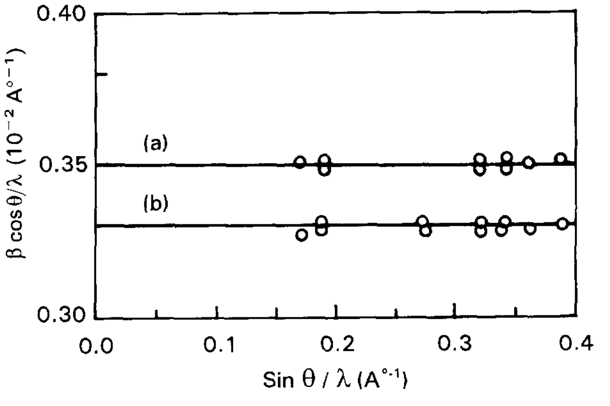

Figure 1 Williamson–Hall plot for (a) hot-pressed and (b) pressureless sintered 3Y-TZP ceramics.

3. Results and discussion

3.1. Compositional homogeneity and phase analysis

Variation of $\beta\cos\theta/\lambda$ as a function of $\sin\theta/\lambda$ (Williamson–Hall plot) based on the XRD data of sintered 3Y-TZP ceramics is shown in Fig. 1. The slope of the linear curves of the figure is zero (being parallel to the x axis), which indicates that there is no lattice strain (η) in the material according to Equation 2. The compositional fluctuation in TZP solid solution would otherwise have resulted in continuous lattice parameter change, causing lattice strains in the ceramics. The value of lattice strain being zero (Fig. 1) confirms that there is no compositional fluctuation and the material is chemically homogeneous.

Fig. 2 shows the XRD profiles of the $\{1\,1\,1\}$, $\{2\,0\,0\}$ and $\{4\,0\,0\}$ reflections in the sintered ceramics taken at room temperature. XRD patterns of 1Y, 2Y and 3Y ceramics are composed of reflections corresponding to monoclinic and tetragonal phases. The intensity of monoclinic peaks decreases and that of tetragonal peaks increases with increasing Y_2O_3 content, whereas XRD patterns of 4Y and 5Y ceramics consist of cubic and tetragonal peaks. The axial (c/a) ratio of the unit cell calculated on the basis of tetragonal reflections was found to be 1.016. These peaks therefore correspond to those of the equilibrium or transformable tetragonal (t) phase. In addition, there are two extra peaks suffixed with t′ in the 2θ range between 73° and 75°. These peaks correspond to another tetragonal phase known as the non-transformable tetragonal phase [28, 37, 42–44]. The t′ phase is clearly distinguishable from the equilibrium tetragonal (t) phase in the diffraction pattern (Fig. 2). Assuming that the a-axis of the t′-phase has almost the same length as the cubic phase, its axial ratio is determined to be 1.006. Peak intensities of the cubic and t′ phases increase, whereas those of the t phase decrease with the increase in Y_2O_3 content of the ceramics. The reduction in c/a ratio, taking place due to addition of Y_2O_3, also favours the formation of cubic phase as observed in case of 4Y and 5Y ceramics. Similar XRD patterns were also obtained for the corresponding hot-pressed ceramics.

Proportions of m, t, t′ and c phases present in the sintered ceramics are shown in Fig. 3. With increasing Y_2O_3 content in the ceramics, the percentage of m-phase decreases approximately linearly, whereas t-phase increases initially and attains maximum value at 3 mol % Y_2O_3. Increase in the content of Y_2O_3 bey-

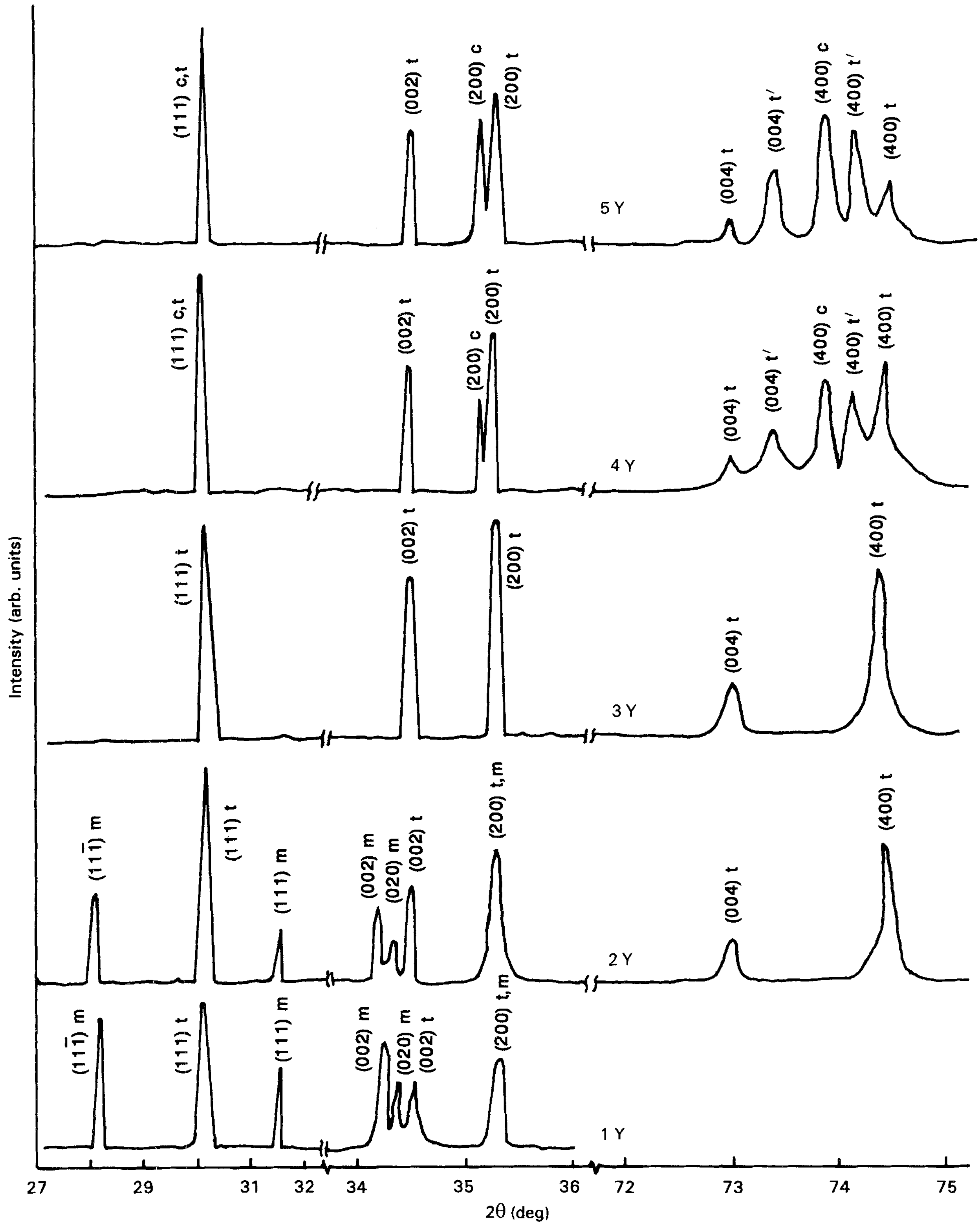

Figure 2 XRD patterns of pressureless sintered Y-TZP ceramics.

ond 3 mol % results in the formation of t′ and cubic phases, and the proportions of t′ and c phases increase with increasing amount of Y_2O_3. The content of t phase in hot-pressed ceramics is greater compared to that of pressureless sintered material. However, the trend of variation of crystalline phases in hot-pressed and pressureless sintered ceramics is similar.

The crystallite size dependence of the transformable tetragonal (t) phase is similar in both hot-pressed and pressureless sintered ceramics, as shown in Fig. 4. Proportions of t-phase varies with the crystallite size and attains maximum value at a particular crystallite size which has been found to be lower (~25 nm) in hot-pressed ceramics than to that (~28 nm) of pressureless sintered materials. These values of crystallite size are in good agreement with the critical size calculated by Garvie [23] for stabilizing the tetragonal phase in TZP powders. Smaller crystallites ($\ll$25 nm) do not transform and remain as non-transformable tetragonal phase, whereas larger crystallites ($\gg$25 nm)

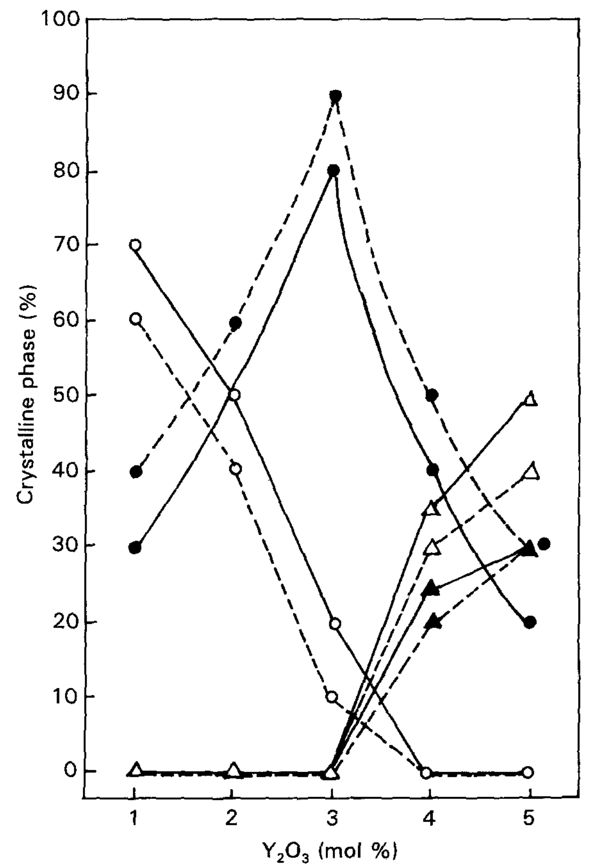

Figure 3 Variation of crystalline phases with Y_2O_3 content in TZP ceramics. (——) Pressureless sintered; (– – –) hot-pressed; ○, V_m; ●, V_t; △, $V_{t'}$; ▲, V_c.

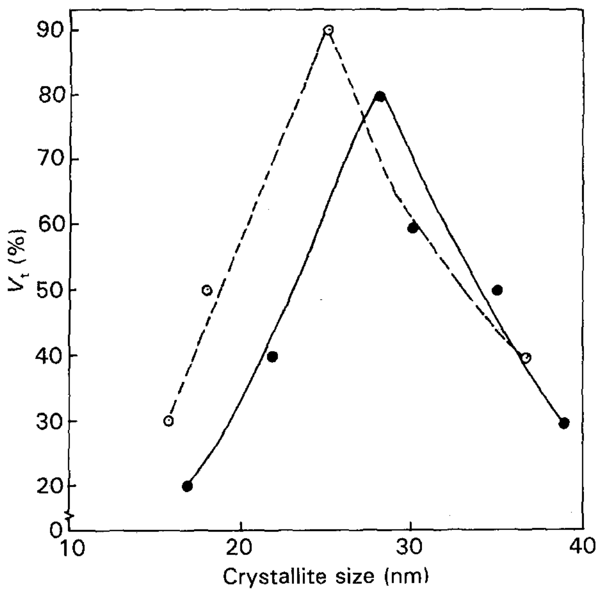

Figure 4 Variation of transformable tetragonal phase (V_t) with crystallite size in TZP ceramics. ⊙, Hot-pressed; ●, pressureless sintered.

transform spontaneously to the monoclinic phase while cooling from the sintering temperature, thereby reducing the proportion of t-phase in the ceramics. Thus when the size of tetragonal crystallites reaches a value close to the critical crystallite size (~30 nm) determined by Garvie [23], formation of the monoclinic phase takes place. In this case, growth of crystallites beyond the critical limit appears to trigger the transformation, probably due to the unavailability of adequate active nucleation sites, or to a decrease in surface area favouring t → m phase transformation [29, 30, 45].

Variation of grain size and crystallite size as a function of Y_2O_3 content in the sintered ceramics is shown in Fig. 5. Crystallite size decreases sharply with the increase in Y_2O_3 content and the critical crystallite size (25–28 nm) is obtained with the addition of 3 mol % Y_2O_3, whereas there is no significant change in the grain size. Crystallites and grains in hot-pressed ceramics are slightly smaller, which is believed to be due to differences in the constraint present in hot-pressed and pressureless sintered ceramics [13]. Thus with the addition of 3 mol % Y_2O_3, the tetragonal particles reach a value close to the critical crystallite size in the material at which the transformable tetragonal (t) phase is maximum (Fig. 3).

3.2. Mechanical properties

Variation of fracture toughness (K_{IC}) and flexural strength (σ_f) as a function of the transformable tetragonal (V_t) phase of sintered ceramics is shown in Fig. 6. Values of K_{IC} and σ_f increase with an increase in V_t in both hot-pressed and pressureless sintered ceramics. The relationship between fracture toughness and transformation zone size ($V_t d^{1/2}$) of sintered ceramics is shown in Fig. 7. Fracture toughness increases linearly with the increase in transformation zone size. The linear relationship shown in Fig. 7 is consistent with the theoretical predictions of McMeeking & Evans and of Lambropoulos [46, 47], and indicates that the theoretical approach is actually applicable to the fracture behaviour of TZP ceramics. In view of these results, it is emphasized that transformability of tetragonal crystallites must be taken into account to understand the mechanism of stress-induced transformation in TZP ceramics. Thus the volume fraction

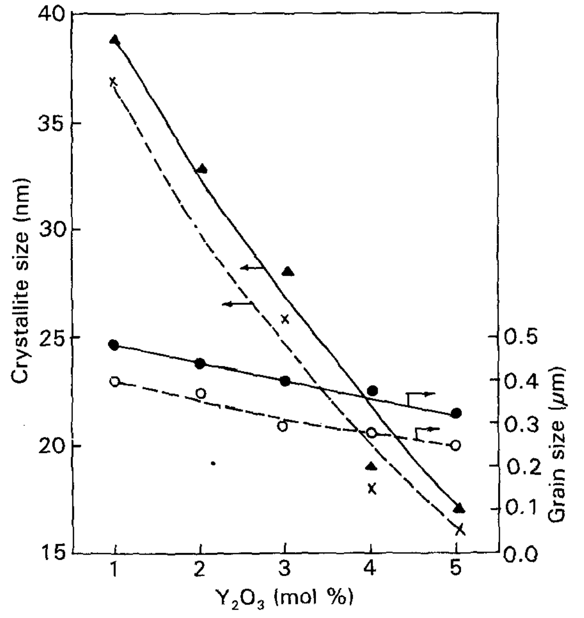

Figure 5 Variation of crystallite and grain size with Y_2O_3 content in TZP ceramics. (– – –) Hot-pressed; (——) pressureless sintered.

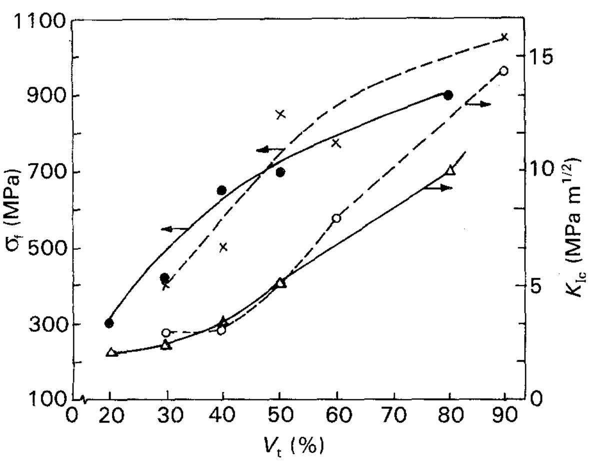

Figure 6 Variation of flexural strength (σ_f) and fracture toughness (K_{IC}) with transformable tetragonal phase (V_t) in TZP ceramics. (– – –) Hot-pressed; (——) pressureless sintered.

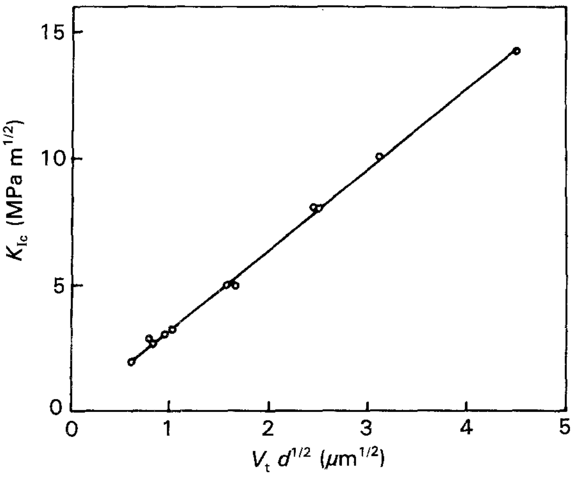

Figure 7 Variation of fracture toughness (K_{IC}) with transformation zone size ($V_t d^{1/2}$) in TZP ceramics.

of the transformable tetragonal phase (V_t) calculated from the XRD data (Fig. 3) is another important factor in evaluating the transformation toughening behaviour of TZP ceramics, and can be observed experimentally by determining the volume fraction of transformable tetragonal phase in the sintered ceramics.

Fig. 8 shows crystallite size dependence of the fracture toughness and flexural strength of the sintered ceramics. Trends of variation in K_{IC} and σ_f match with the variation of transformable tetragonal phase shown in Fig. 4. The presence of larger as well as smaller crystallites than the critical size in the material has a negative effect on toughness and strength, as a consequence of the reduced amount of transformable tetragonal phase (Fig. 4) in TZP ceramics. The optimum crystallite size exhibiting peak values of K_{IC} and σ_f has been found to be ~25 nm and ~28 nm for hot-pressed and pressureless sintered ceramics, respectively. Thus there is a critical crystallite size at which transformable tetragonal phase and consequently toughness and strength are maximum.

Dependence of fracture toughness (K_{IC}) and flexural strength (σ_f) on the concentration of Y_2O_3 in the sintered ceramics is shown in Fig. 9. Fracture toughness and strength increase initially with the increase in Y_2O_3 concentration and show a peak at 3 mol % Y_2O_3. Increase in Y_2O_3 content beyond 3 mol % decreases the values of K_{IC} and σ_f. Hot-pressed ceramics exhibit higher values of K_{IC} and σ_f in comparison to those obtained by pressureless sintering. The variation of K_{IC} and σ_f shown in Fig. 9 can be correlated with the relationship shown in Figs 3–5 and Fig. 8. The increase in the values of K_{IC} and σ_f with Y_2O_3 content can be attributed to the increase in the amount of V_t, as has been observed in Fig. 6. Addition of Y_2O_3 in TZP ceramics decreases the crystallite size linearly, and critical crystallite size (25–28 nm) is obtained at 3 mol % (Fig. 5) at which the transformable t-phase (V_t) is maximum (Fig. 4), giving rise to maxima in the values of K_{IC} and σ_f (Fig. 8). Increase in Y_2O_3 content beyond 3 mol % decreases the proportion of t-phase in the ceramics (Fig. 3) due to the decrease in crystallite size (below the critical size), and therefore lowers the values of K_{IC} and σ_f of ceramics.

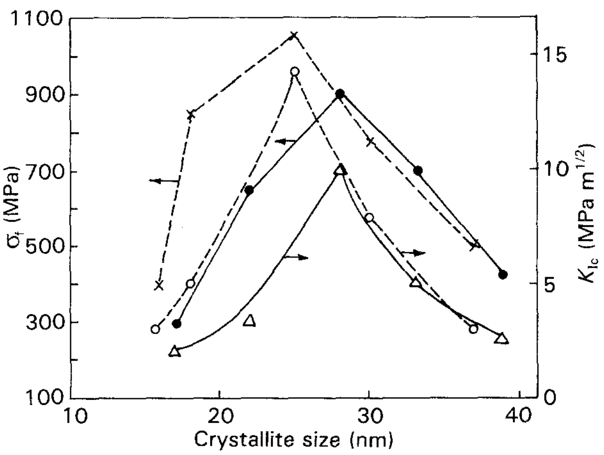

Figure 8 Variation of flexural strength (σ_f) and fracture toughness (K_{IC}) with crystallite size of TZP ceramics. (– – –) Hot-pressed; (——) pressureless sintered.

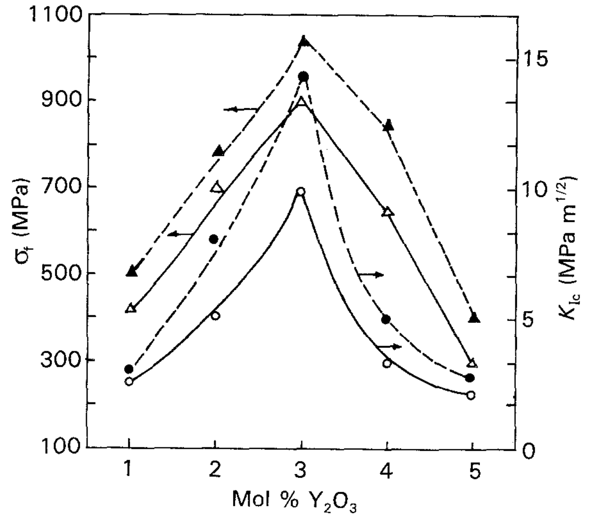

Figure 9 Variation of flexural strength (σ_f) and fracture toughness (K_{IC}) as a function of composition of TZP ceramics. (– – –) Hot-pressed; (——) pressureless sintered.

4. Conclusions

Chemically homogeneous TZP ceramics composed of monoclinic transformable and non-transformable tetragonal as well as cubic phases were obtained by hot pressing and pressureless sintering of sol–gel derived powders. Addition of Y_2O_3 in TZP ceramics reduces crystallite size and considerably influences the proportion of crystalline phases.

The volume fraction of the transformable tetragonal phase is dependent on the crystallite size and attains maximum value in ceramics having a crystallite size in the range 25–28 nm. Fracture toughness and strength increase with the content of transformable tetragonal phase, and achieve a maximum value in ceramics containing 3 mol % Y_2O_3. The expected linear relationship between the fracture toughness and transformation zone size was observed.

Acknowledgements

The authors are grateful to Dr R. Krishnan and Dr P. C. Deb for their interest in this work.

References

1. T. MASAKI, *J. Amer. Ceram. Soc.* **69** (1986) 519.
2. K. TSUKUMA, Y. KUBOTA and T. TSUKIDATE, in "Advances in Ceramics", Vol. 12, Science and Technology of Zirconia II, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1984) p. 382.
3. A. G. EVANS and A. H. HEUER, *J. Amer. Ceram. Soc.* **63** (1980) 241.
4. R. H. J. HANNINK and M. V. SWAIN, *ibid.* **18** (1982) 53.
5. A. H. HEUER, in "Advances in Ceramics", Vol. 3, Science and Technology of Zirconia, edited by A. H. Heuer and L. W. Hobbs (American Ceramic Society, Columbus, Ohio, 1981) p. 98.
6. N. CLAUSSEN, in "Advances in Ceramics", Vol. 12, Science and Technology of Zirconia II, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1984) p. 325.
7. T. MASAKI and Y. MURATA, *J. Mater. Sci.* **22** (1987) 407.
8. C. A. ANDERSON and T. K. GUPTA, in "Advances in Ceramics", Vol. 3, Science and Technology of Zirconia, edited by A. H. Heuer and L. W. Hobbs (American Ceramic Society, Columbus, Ohio, 1981) p. 184.
9. I. NETTLESHIP and R. STEVENS, *Int. J. High Tech. Ceram.* **3** (1987) 1.
10. Y. L. CHEN and R. J. BROOK, *Brit. Ceram. Trans. J.* **88** (1989) 7.
11. H. G. SCOTT, *J. Mater. Sci.* **10** (1975) 1527.
12. T. MASAKI, *J. Amer. Ceram. Soc.* **69** (1986) 638.
13. T. K. GUPTA, J. H. BECHTOLD, R. C. KUZNICKI, L. H. CADOFF and B. R. ROSSING, *J. Mater. Sci.* **12** (1977) 2421.
14. M. V. SWAIN and L. R. F. ROSE, *J. Amer. Ceram. Soc.* **69** (1986) 511.
15. T. KATO and M. SHIMADA, *ibid.* **68** (1985) 356.
16. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 240.
17. J. WANG, M. RAINFORTH and R. STEVENS, *Brit. Ceram. Trans. J.* **88** (1989) 1.
18. A. H. HEUER, M. RUHLE and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **73** (1990) 1984.
19. D. J. KIM, *ibid.* **73** (1990) 115.
20. T. MASAKI and K. SINJO, *Ceram. Int.* **13** (1987) 13.
21. T. MASAKI and K. SHINJO, in "Advances in Ceramics", Vol. 24, Science and Technology of Zirconia III, edited by S. Somiya, N. Yamamoto and H. Yenegida (American Ceramic Society, Columbus, Ohio, 1988) p. 709.
22. A. G. EVANS and R. M. CANNON, *Acta Met.* **34** (1986) 761.
23. R. C. GARVIE, *J. Phys. Chem.* **69** (1965) 1238.
24. M. I. OSENDI, J. S. MOYA, C. J. SERNA and J. SORIA, *J. Amer. Ceram. Soc.* **68** (1985) 135.
25. Y. MURASE and E. KATO, *ibid.* **66** (1983) 196.
26. C. A. ANDERSON, J. GREGGI Jr., and T. K. GUPTA, in "Advances in Ceramics", Vol. 12, Science and Technology of Zirconia II, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1984) p. 78.
27. T. SAKUMA, Y. YOSHIZAWA and H. SUTO, *J. Mater. Sci.* **20** (1985) 2399.
28. M. SUGIYAMA and H. KUBO, *Yogyo-Kyokai-Shi* **94** (1986) 30.
29. M. RUHLE and A. H. HEUER, in "Advances in Ceramics", Vol. 12, Science and Technology of Zirconia II, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1984) p. 14.
30. A. H. HEUER and M. RUHLE, *Acta Met.* **33** (1985) 2101.
31. R. DAYAL, N. M. GOKHALE, S. C. SHARMA, RAMJI LAL and R. KRISHNAN, *Brit. Ceram. Trans. J.* **91** (1992) 45.
32. J. F. JOE and A. V. VIRKAR, *J. Amer. Ceram. Soc.* **73** (1990) 365.
33. M. I. MENDELSON, *ibid.* **52** (1989) 443.
34. D. MUNZ, R. BUBSEY and J. L. SHANNON Jr., *ibid.* **63** (1980) 300.
35. H. P. KLUG and L. E. ALEXANDER, "X-ray Diffraction Procedures" (Wiley, New York, 1954) ch. 9.
36. W. H. HALL, *Proc. Phys. Soc. Lond.* **62** (1949) 741.
37. H. ISHIZAWA, O. SAKURAI, N. MIZUTANI and M. KATO, *Amer. Ceram. Soc. Bull.* **65** (1986) 1399.
38. H. K. SCHMID, *J. Amer. Ceram. Soc.* **70** (1987) 367.
39. C. J. HOWARD and R. J. HILL, *J. Mater. Sci.* **26** (1991) 127.
40. T. KOSMAC, R. WAGNER, and N. CLAUSSEN, *J. Amer. Ceram. Soc.* **64** (1981) C-72.
41. R. C. GARVIE, R. H. J. HANNINK and M. V. SWAIN, *J. Mater. Sci. Lett.* **1** (1982) 437.
42. R. A. MILLER, J. L. SMIALEK and R. G. GARLICK, in "Advances in Ceramics", Vol. 3, Science and Technology of Zirconia, edited by A. H. Heuer and I. W. Hobbs (American Ceramic Society, Columbus, Ohio, 1981) p. 241.
43. R. A. MILLER, R. G. GARLICK and J. L. SMIALEK, *Amer. Ceram. Soc. Bull.* **62** (1983) 1355.
44. V. LANTERI, A. H. HEUER and T. E. MITCHELL, in "Advances in Ceramics", Vol. 12, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1984) p. 118.
45. T. MITSUHASHI, M. ICHIARA and V. TATSUKE, *J. Amer. Ceram. Soc.* **57** (1974) 97.
46. R. McMEEKING and A. G. EVANS, *ibid.* **65** (1982) 242.
47. J. C. LAMBROPOULOS, *ibid.* **69** (1986) 218.

Received 30 March
and accepted 10 December 1993