Ceramics International 22 (1996) 137–142

0272-8842/96/$15.00
0272-8842(95)00069-0

Crystallite Growth in Yttria-Doped Superfine Zirconia Powders and Their Compacts: A Comparison between Y-TZP and YSZ

J. L. Shi, M. L. Ruan & T. S. Yen

State Key Lab. of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding-Xi Road, Shanghai 200050, People's Republic of China

(Received 21 September 1994; accepted 9 March 1995)

Abstract: Crystallite growth characteristics in Y-TZP (yttria-tetragonal zirconia polycrystals) and YSZ (yttria-stabilized cubic zirconia) powders and their compacts were compared. When holding at ≤ 1000°C the crystallite size of Y-TZP is greater than YSZ both in powders and in compacted bodies, but the crystallites of YSZ grow faster than Y-TZP at elevated temperatures and the grain size of YSZ becomes larger when heated at 5°C/min to above 1200–1250°C or so, both in powders and in their compacts. It is proposed that this phenomenon results from the different crystallite surface or interface energy between different crystal phases, which affects the initial crystallite size in nucleation at crystallization temperature and crystallite/grain growth rates at higher temperatures.

1 INTRODUCTION

Zirconia ceramic is a promising material for advanced technologies.[1–6] It is mostly fabricated by sintering superfine zirconia powders which are commonly processed via chemical routes, for example, via hydroxide coprecipitation method.[7,8] Zirconium hydroxide precipitates and zirconia powders obtained by calcining the coprecipitates below 400°C are amorphous. At elevated temperatures crystalline zirconia crystallizes out and the crystallites will grow substantially as temperature increases.[8] Crystallite growth also occurs in powder compacts.[9–11] However, crystallite growth both in powders and in sintering bodies should be controlled[12] because it may harm the sinterability of the powders and the performance of the sintered bodies, so the investigation of crystallite growth behaviour both in powders and in compacts is meaningful.

Yttria-doped zirconia could be tetragonal or cubic.[1–4] At room temperature, 3 mol% Y_2O_3-doped zirconia (called Y-TZP) could mainly be tetragonal under certain conditions[10] and 7 mol% Y_2O_3-doped zirconia is cubic (called YSZ). These two kinds of material are of rather different properties and application aspects.[1–4] In addition, the microstructures of the two materials are different from each other: the grain size of YSZ is much larger than that of Y-TZP in sintered bodies under the same firing conditions. Fine microstructure of Y-TZP is a key condition for the phase-transformation toughening mechanism in Y-TZP ceramics,[13–17] and the relatively large grain size of YSZ is favourable for its higher oxygen ionic conductivity.[18,19] The reasons for the different microstructure development have not been fully understood. Winnubst and Burggraaf[20] and Chen *et al.*[12,21,22] believed that the suppressed grain growth of Y-TZP in sintered bodies is related to the yttria segregation at grain boundaries and therefore leads to solute dragging effect opposing boundary migration, while no solute dragging effect was present in YSZ.[20]

However, recently Shi *et al.*[23] found that in Y_2O_3–ZrO_2 powder, the crystallite size of Y-TZP (3 mol% Y_2O_3) was larger than that of YSZ (7 mol% Y_2O_3) when calcined at a temperature not higher than 1000°C. The phenomenon has been argued to be due to the higher surface tension of Y-TZP than YSZ, as the crystallite growth rate in powders has been thought to be proportional to the surface tension.

The present paper compares the crystallization behaviours and the crystallite (grain) growth characteristics of Y-TZP and YSZ, both in powders and in compacts, to find possible explanations for the different crystallite sizes and crystallite growth behaviours. It is also interesting to know at what temperature the crystallite size of Y-TZP surpasses that of YSZ.

2 EXPERIMENTAL PROCEDURE

Y-TZP and YSZ powders were prepared by the coprecipitation method which has been described elsewhere.[24,25] A brief introduction is as follows: (1) preparation of mixed solution of yttria chloride and zirconium oxychloride with appropriate ratio of Y^{3+}/Zr^{4+}; (2) addition of mixed solutions to ammonia solution which resulted in coprecipitation while pH was maintained not lower than 9·5; (3) washing the coprecipitates repeatedly with distilled water to remove Cl^- (to <10 ppm in filtrate); (4) washing the cake with ethanol for at least six times to replace water (to water content in filtrate less than 4 vol%, and finally (4) calcining at various temperatures (from 420 to 1350°C) for various time periods.

Powders calcined at 600°C and 750°C were compacted at 250 MPa uniaxally and then sintered at a constant heating rate (5°C/min) to various temperatures and/or isothermal holding. The powder micrographs were observed with TEM (transmission electron microscopy, JEM-200CX, JEOL) after ultrasonically treating for 10 min to break down soft agglomerates, and the crystallite sizes of powders or compacts were determined by XRD-LB(X-ray diffraction-line broadening) technique.[8] The crystallite sizes were calculated from the following equation:

$$D = 0{\cdot}89\lambda/\cos\theta{\cdot}B \qquad (1)$$

where λ is the wavelength of X-ray used (CuK_α), θ is the Bragg angle of selected diffraction peak ((111) peak of Y-TZP and YSZ was used in this study) and B is the calibrated peak breadth by subtracting the instrumental broadening from the total peak breadth.

3 RESULTS

3.1 Crystallite growth in powder

Figures 1–4 are the photomicrographs (TEM) of Y-TZP and YSZ powders calcined for 30 min at

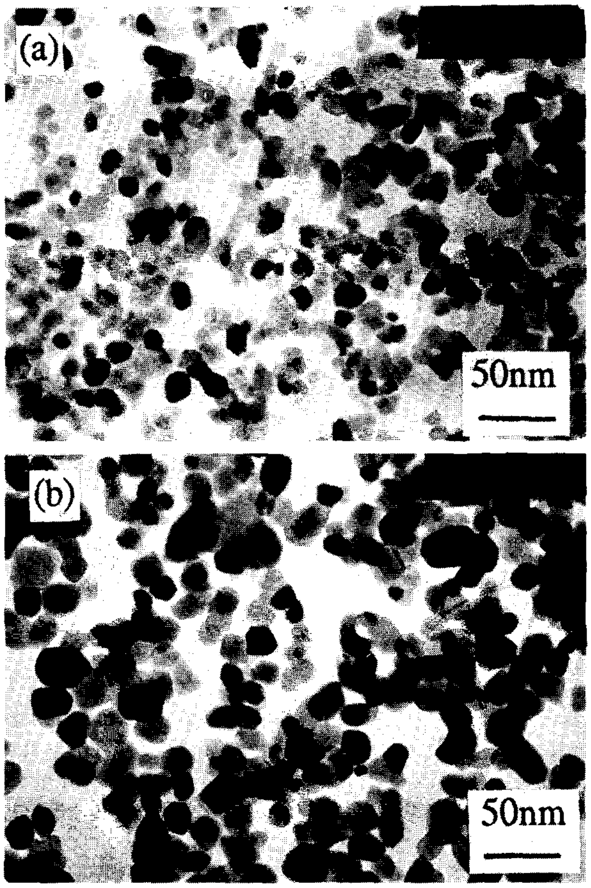

Fig. 1. TEM micrographs of (a) YSZ and (b) Y-TZP powder calcined at 800°C–25 min.

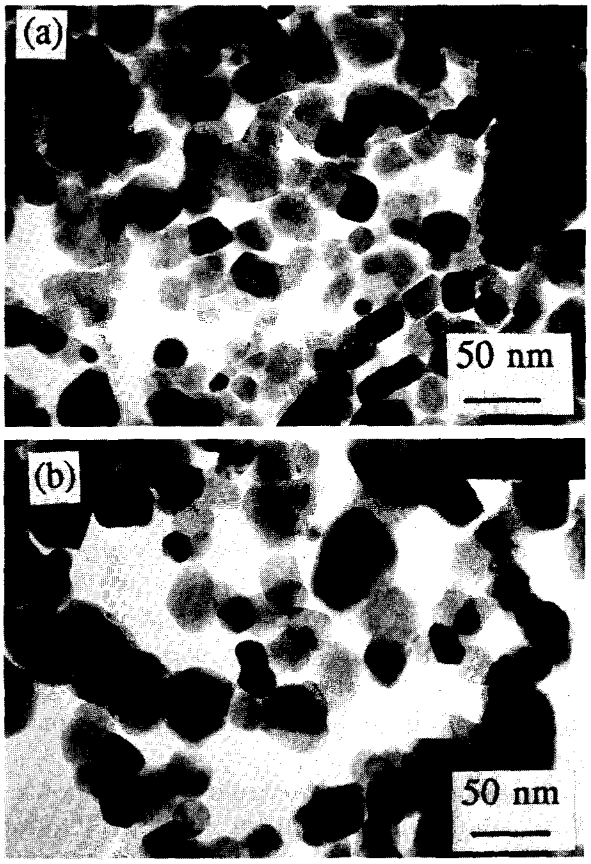

Fig. 2. TEM micrographs of (a) YSZ and (b) Y-TZP powder calcined at 1000°C–25 min.

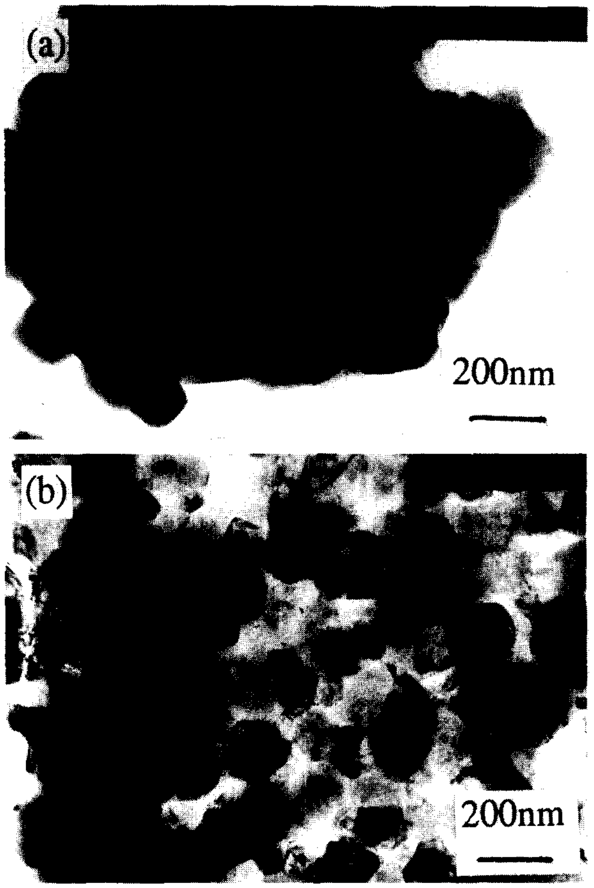

Fig. 3. TEM micrographs of (a) YSZ and (b) Y-TZP powder calcined at 1250°C–25 min.

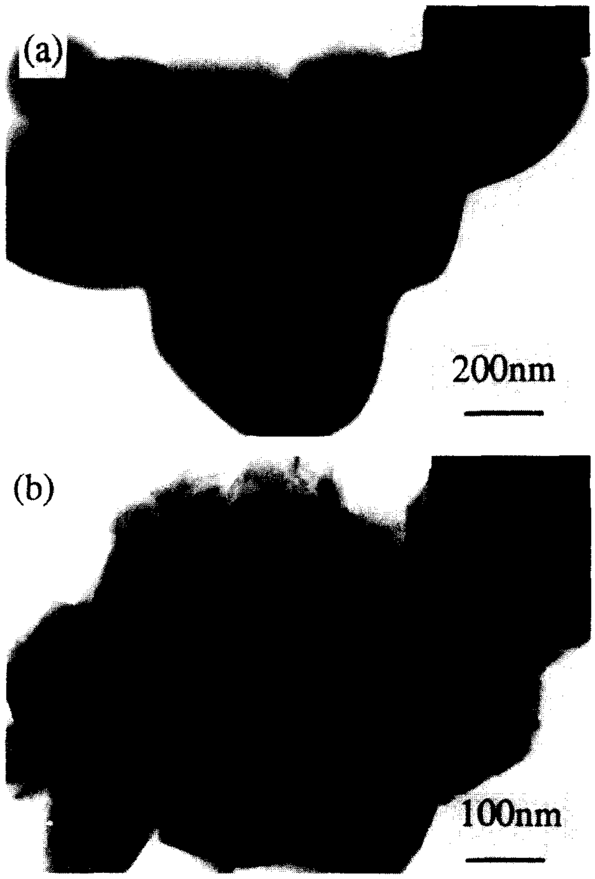

Fig. 4. TEM micrographs of (a) YSZ and (b) Y-TZP powder calcined at 1350°C–25 min.

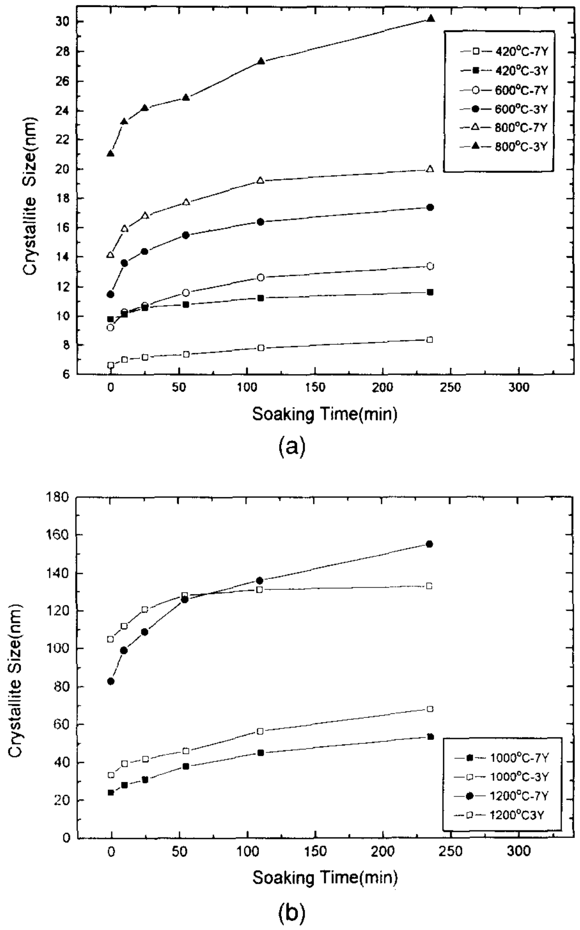

Fig. 5. Calculated crystallite size of Y-TZP and YSZ powders as a function of calcination temperature and holding time.

800°C, 1000°C, 1250°C and 1350°C, respectively. The particles in these figures can be taken to be the crystallites as has been stated in the author's previous works[8] and the powders prepared contain no hard agglomerates.[26] It can be seen that at temperatures not higher than 1000°C, the crystallite size of Y-TZP is larger than that of YSZ on average, whilst at 1250°C, the crystallite size of Y-TZP became smaller than that of YSZ. Figure 5 shows the dependence of crystallite sizes of Y-TZP and YSZ powders on holding time at different temperatures. It can be seen that crystallite size increased with increase of calcining temperature and holding time. At relatively low temperatures ($\leq$ 1000°C), the crystallite size of Y-TZP was larger than that of YSZ, while as temperature increased the crystallite growth rate of Y-TZP became lower than that of YSZ, and during holding at 1200°C or heating at a constant rate to 1250°C and above, the crystallite size of YSZ became larger than that of Y-TZP. The intersecting point for the crystallite sizes of Y-TZP and YSZ is at about 125 nm.

3.2 Grain growth in compacts

Figure 6 shows the X-ray determined crystallite

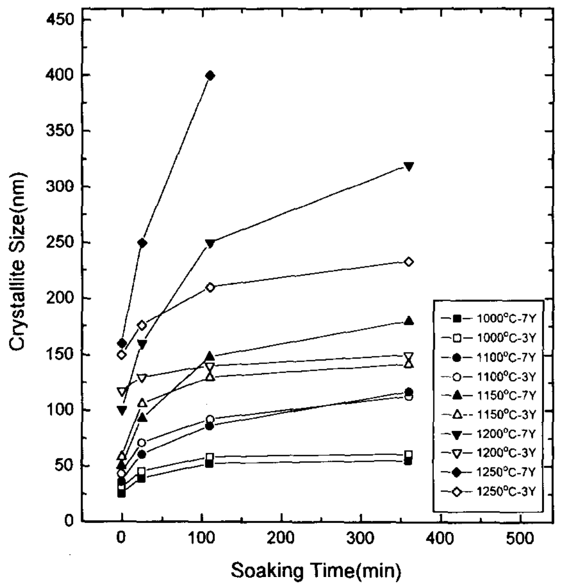

Fig. 6. Calculated crystallite sizes of Y-TZP and YSZ powder compacts as a function of firing temperature and holding time.

sizes in Y-TZP and YSZ powder compacts. It can be seen that the grain growth characteristics of Y-TZP and YSZ in compacts were similar to those in powder, i.e. at low temperatures (≤ 1000°C) the crystallite size of Y-TZP was larger than that of YSZ but at elevated temperatures the YSZ grains grew at a much higher rate. During holding at 1100–1200°C, or heated at a rate of 5°C/min to 1200–1250°C or above, the crystallite size of YSZ surpassed that of Y-TZP. Figure 7 shows the temperature dependence of grain size (the term 'grain' is used here instead of 'crystallite' because the materials are under sintering or sintered) in Y-TZP and YSZ compacts during constant-rate heating (without holding). It is shown that beyond about 1100–1150°C the grain growth rate of Y-TZP became lower than that of YSZ and as the temperature increased the grain growth rate of YSZ still remained relatively high, and the crystallite size of Y-TZP became smaller than that of YSZ at ~1230°C during constant-rate heating. The densities of the YSZ and Y-TZP compacts, at which Y-TZP and YSZ have the same crystallite size of ~110–130 nm, were around 85% TD.

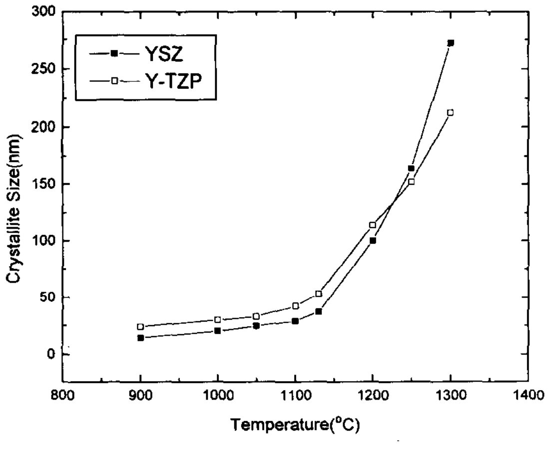

Fig. 7. Crystallite size of Y-TZP and YSZ powder compacts vs temperature during constant heating rate (5°C/min.)

4 DISCUSSION

4.1 *Crystallization behaviour and crystallite growth at low temperature*

A careful study of the crystallite size at temperatures not higher than 1000°C shows that though the crystallite size of Y-TZP is larger than that of YSZ, the crystallite growth rates do not differ from each other very much. When calcined at a given temperature (even as low as 420°C), the size difference between the two kinds of powder or compact already exists at the beginning of holding and this difference does not alter much as the holding periods increase (Figs 6 and 7). As a matter of fact, this size difference may already be present immediately after crystallization (or nucleation).

Small Y-TZP or YSZ nuclei crystallize out from the amorphous precursors by overcoming the barrier of the surface energy for the formation of the crystalline nuclei, so there will be a critical size (diameter) termed d_c for nucleation in the amorphous powder. Assuming that the nuclei were spherical and separated from their amorphous precursor, we have:

$$\gamma_s \cdot \pi d_c^2 = \Delta G \frac{{}^4\!/_3 \pi d_c^3 \rho}{M} \qquad (2)$$

where ΔG is the Gibbs' energy increment for the phase transformation from the amorphous phase of the precursors to the crystalline phase, γ_s is the surface energy, ρ is the density of the crystallized phases and M is the molecular weight concerned. For the nucleation to take place, the initial crystallite (nuclei) size d would be:

$$d \geq d_c = \frac{3\gamma_s M}{4\rho \Delta G} \qquad (3)$$

The above formula suggests that the factors affecting the critical initial crystallite size are Gibbs' energy increment, molecular weight, density and surface energy. The former three items may play a role in affecting the critical size as the molecular weights and the densities of Y-TZP and YSZ, though close to each other, are different. However, the difference of the surface energy between these two materials might, to a certain extent, also be responsible for the initial crystallite size difference immediately after crystallization.

The surface energy of cubic YSZ has been found to be smaller than that of tetragonal Y-TZP,[23] thus leading to the smaller crystallite size of YSZ than that of Y-TZP. This initially present difference between the two phases persists up to 1000°C, and the crystallite growth rates of the two materials do not differ from each other very much. This means the size difference below 1000°C might be mainly related to the initial crystallization process and is insensitive to the later crystallite growth processes. This argument may also be applicable to the results found in Ref. 23.

4.2 Grain growth behaviour at higher temperatures

Grains were observed to grow even in very porous compacts[9–11] accompanying the densification process. In densified ceramic bodies grains grow by boundary migration,[27,28] however, in porous compacts the grain growth mechanism may be different. Grains grow by grain boundary motion in dense or nearly dense materials.[27] The grain growth law is given by the following equation:[24–27]

$$G^n - G_0^n = Kt \tag{4}$$

where t is the time period at a given temperature, G_0 and G are the grain sizes at $t = 0$ and $t = t$, n is a constant determined by grain growth mechanism and K is also a constant at a fixed temperature. The value of K is proportional to the diffusion coefficient and interface tension

$$K \propto \gamma_b \cdot D_b \tag{5}$$

for grain-boundary-migration-controlled grain growth, where γ_b and D_b are interface (grain boundary) tension and boundary diffusion coefficient, respectively.

The crystallite growth at relatively low temperature (≤ 1000°C), according to Harmer and Brook,[29] may proceed via surface diffusion. However, the fact that during holding at 1100 or 1200°C, (or heating to 1250°C) the crystallite size of Y-TZP, both in powder and in compacts, became smaller than that of YSZ (as shown in Figs 5 and 6) is believed to be caused by the changed crystallite growth mechanisms, i.e. at the elevated temperatures the crystallites no longer grow via surface diffusion. From Figs 3 and 4, it is clear that extensive interfaces (grain boundaries) are formed at 1250°C and above, so under these conditions grains grow via grain boundary migration. As a matter of fact, at 1250°C for 30 min the compacts have been sintered to above 95% of the theoretical densities for non-agglomerated Y-TZP and YSZ compacts,[29] and grain boundary migration becomes a dominant mechanism for grain growth either in powders or in sintered bodies. Lee and Chen[21] measured the relative values of the interface energy for Y-TZP and YSZ in sintered bodies. They obtained the following relation:

$$\gamma_{cc} : \gamma_{tc} : \gamma_{tt} = 1 : 0{\cdot}76 : 0{\cdot}63 \tag{6}$$

where γ_{cc}, γ_{tc} and γ_{tt} are the interface (grain boundary) energies for cubic–cubic, cubic–tetragonal and tetragonal–tetragonal grain boundaries. The interface energy of Y-TZP (γ_{tt}) is lower than that of YSZ (γ_{cc}), so according to eqn (5) grains in Y-TZP ceramics grow more slowly than those of YSZ when grain boundaries form between primary particles, as in this case grains grow by boundary migration.

Another reason for the suppressed grain growth of Y-TZP materials was considered to be yttria segregation at boundaries.[19,20] Solutes enriched at boundaries act as an impedance for boundary migration (e.g. solute dragging effect), and alter the value of n in eqn (4) from 2 to 3[27] and therefore inhibit the grain growth of Y-TZP ceramics.

5 CONCLUSION

Crystallite sizes of Y-TZP are larger at low temperatures (holding at ≤ 1000°C) than those of YSZ, and such a size difference is found to result mainly from the initial crystallization process, and is not affected by the later crystallite growth up to 1000°C. When heated to high temperatures (≥ 1100–1150°C, 5°C/min) the crystallites (or grains) of Y-TZP grow more slowly than those of YSZ in either coprecipitated powders or their compacts (sintered bodies), and when heated to above 1200–1250°C (or during holding at 1100 or 1200°C) the crystallite size of YSZ surpasses that of Y-TZP.

The relative magnitudes of the surface and interface energies of Y-TZP and YSZ, together with some other factors, in different temperature ranges are presumed to be responsible for the differences in the initial crystallite size in nucleation at the crystallization temperature and the grain growth rates above 1100–1150°C, at which grains are found to grow by boundary migration, either in powder or compact form.

REFERENCES

1. GARVIE, R. C., HANNINK, R. H. & PASCOE, R. T., Ceramic steel. *Nature (London)*, **258** (1975) 703.
2. HAGENMULLER, P. & GOOL, W. V. (eds), *Solid Electolytes*. Academic Press, New York, 1978.
3. HEUER, A. H. & HOBBS, L. W. (eds), *Advances in Ceramics, Vol. 3, Science and Technology of Zirconia I*. Am. Ceram. Soc., Columbus, OH, 1981.
4. CLAUSSEN, N., RUHLE, M. & HEUER, A. H. (eds), *Advances in Ceramics, Vol. 12, Science and Technology of Zirconia II*, ibid., 1984.

5. SOMIYA, S., YAMAMOTO, N. & YANAHIDA, H. (eds), *Advances in Ceramics, Vol. 24, Science and Technology of Zirconia III*, ibid., 1988.
6. VAN DE GRAAF, M. A. C. G. & BURGGRAAF, A. J., Wet-chemical preparation of zirconia powders: Their microstructure and behavior. In *Advances in Ceramics, Vol. 12, Science and Technology of Zirconia*, ed. N. Claussen, M. Ruhle & A. H. Heuer. Am. Ceram. Soc., Columbus, OH, 1984, p. 744.
7. HABERKO, K., Characteristics and sintering behavior of zirconia ultrafine powders. *Ceram. Int.*, **5** (1979) 148.
8. SHI, J. L., LU, C. W., KUO, C. L., *et al.*, Determination of crystallite size as function of calcination temperature. *Ceram. Int.*, **18** (1992) 155.
9. LAY, K. W., Grain growth during sintering. In *Material Science Research, Vol. 6. Sintering and Related Phenomena*, ed. G. C. Kuczynski. Plenum Press, New York, 1973.
10. GRESKOVICH, C. & LAY, K. W., Grain growth in very porous Al_2O_3 compacts. *J. Am. Ceram. Soc.*, **55** (1972) 142.
11. BRUCH, C. A., Sintering kinetics for the high density alumina process. *Am. Ceram. Soc. Bull.*, **41**(2) (1962) 199.
12. CHEN, I-WEI & XUE, L. A., Development of superplastic structural ceramics. *J. Am. Ceram. Soc.*, **73** (1990), 2585.
13. HABERKO, K. & PAMPUCH, R., Influence of yttria content on phase composition and mechanical properties of Y-PSZ. *Ceram. Int.*, **9** (1983) 8.
14. LANGE, F. F., Transformation toughening: I. Size effects associated with the thermodynamics of constrained transformations. *J. Mater. Sci.*, **17** (1982) 115.
15. GUPTA, T. K., BECHTOLD, J. H. & KUZNICKI, R. C., Stabilization of tetragonal phase in polycrystalline zirconia. *J. Mater. Sci.*, **12** (1977) 2421.
16. GUPTA, T. K., LANGE, F. F. & BECHTOLD, J. H., Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing tetragonal phase. *J. Mater. Sci.*, **13** (1978) 1464.
17. GAO, L., YEN, T. S. & GUO, J. K., Influence of ZrO_2 particle size on toughening in hot-pressed Y-TZP. In *Advances in Ceramics, Vol. 24, Science and Technology of Zirconia III*, ed. S. Somiya, N. Yamamoto & H. Yanahida. Am. Ceram. Soc., Columbus, OH, 1988, p. 405.
18. SHI, J. L., Effect of grain boundary properties on conductivity for polycrystalline fast ionic conductors. *J. Chinese Ceram. Soc.*, **19**(3) (1991) 210.
19. MIYAYAMA, M. & YANAGIDA, R. J., Dependence of grain boundary resistivity on grain boundary density in yttria stabilized zirconia. *J. Am. Ceram. Soc.*, **67** (1984) c-194.
20. WINNUBST, A. J. A. & BURGGRAAF, A. J., The aging behavior of ultrafine-grained Y-TZP in hot water. In *Advances in Ceramics, Vol. 24, Science and Technology of Zirconia III*, ed. S. Somiya, N. Yamamoto & H. Yanahida. Am. Ceram. Soc., Columbus, OH, 1988, p. 39.
21. LEE, I. G. & CHEN, I. W., Sintering and grain growth in tetragonal and cubic zirconia. In *Sintering '87*, ed. S. Somiya, *et al.* Elsevier Applied Sciences, London, 1988, p. 340.
22. HWANG, S. L. & CHEN, I. W., Grain size control of tetragonal zirconia polycrystals using space charge concept. *J. Am. Ceram. Soc.*, **73**(11) (1990) 3269.
23. SHI, J. L., LIN, Z. X. & YEN, T. S., Effect of dopants on the crystallite growth of superfine zirconia powders. *J. Europ. Ceram. Soc.*, **8** (1991) 117.
24. SHI, J. L. & LIN, Z. X., Characterization of nano-sized zirconia powder. *Powder Technology*, **74**(1) (1993) 7.
25. SHI, J. L., GAO, J. H. & LIN, Z. X., Preparation of YSZ powder by coprecipitation spray-drying method and its effect on sintered density. *J. Chinese Ceram. Soc.*, **17**(5) (1989) 417.
26. SHI, J. L., GAO, J. H., LIN, Z. X. & YAN, D. S., Effect of agglomerates in superfine zirconia powder compacts on the microstructure development. *J. Mater. Sci.*, **28** (1993) 342.
27. BURKE, J. E., Grain growth. In *Ceramic Microstructure '66*, ed. R. M. Fulrath & J. A. Pask. Wiley, New York, 1968, p. 680.
28. BROOK, R. J., Controlled grain growth. In *Treatise on Mater. Sci. and Tech., Vol. 9, Ceramic Fabrication Process*, ed. F. F. Y. Wang. Academic Press, New York 1976, p.331.
29. HARMER, M. P. & BROOK, R. J., Fast firing–microstructure benefits. *J. Brit. Ceram. Soc.*, **80**(5) (1980) 147.