The Korean Journal of Ceramics, 1 [4] 214-218 (1995)

High-Strength Mg-PSZ of Fine Grains Containing TiC Particles

Joon Hyuk Jang and Jaehyung Lee

Dept. of Mater. Sci. and Eng., Yeungnam Univ., 214-1 Dae-dong, Kyungsan, Kyungbuk 712-749, Korea

(Received November 8, 1995)

Partially stabilized zirconia with magnesia (Mg-PSZ) is known as one of the toughest monolithic ceramics. However, the very large grain sizes obtained after sintering at a high solution-heat treatment temperature in the cubic region of the phase diagram limit the strength of this material rather modest. In this study fine-grained Mg-PSZ materials were fabricated by adding TiC particles as a dispersed phase. Samples were hot-pressed at 1750°C and then annealed at 1420°C for various times. Grain growth was retarded severely by the TiC particles resulting in grain sizes smaller by more than one order of magnitude than those of PSZ without TiC. The fine-grained microstructure lead to doubly-increased fracture strength while maintaining the same level of high fracture toughness as that of conventional Mg-PSZ without TiC particles.

Key words : Mg-PSZ, TiC, Transformation toughening, Fracture strength, Toughness

I. Introduction

Magnesia-partially stabilized zirconia (Mg-PSZ) is known as one of the toughest monolithic ceramics owing to the well known transformation toughening phenomena.[1-3] To fabricate Mg-PSZ materials, the powder compact is sintered at over 1700°C, and then heat-treated at near 1400°C to obtain tetragonal precipitates in the cubic matrix. During the solution-heat treatment at the high temperature in the cubic region of the ZrO_2-MgO phase diagram, the grains grow easily to the size of 50 μm or larger. In brittle ceramics, the fracture strength is usually a function of the grain size by which the critical flaw size is decided.[4] As a result, Mg-PSZ containing large grains exhibits only moderate fracture strength even though it has very high toughness.[5]

Grain growth can be hindered by second-phase inclusions, which are dragged by moving grain boundaries.[6] A well known example is an Al_2O_3-ZrO_2 composite, where ZrO_2 particles control grain growth of Al_2O_3.[7,8] Also, very fine particles of SiC, which are substantially smaller than 1 μm, inhibit grain growth of matrices, such as Si_3N_4, Al_2O_3, etc.[9,10] Recently, fine-grained (Mg,Y)-PSZ was fabricated by F. Meschke, et. al. by adding $MgAl_2O_4$.[11] The average grain size was 12 μm but the bend strength showed only modest improvement from that of normal Mg-PSZ. In order to be effective for grain growth inhibition, the inclusions should not react with the matrix. For Mg-PSZ the inclusions should not deprive the matrix of MgO during sintering. In addition, a smaller thermal expansion mismatch between the inclusions and matrix may be preferable not to give large residual stresses around the inclusions, which may change the stress-induced transformation behavior of Mg-PSZ adversely. In this study, fine TiC particles are used as grain growth inhibitor. TiC has a relatively small thermal expansion mismatch with Mg-PSZ. Thus, without lowering fracture toughness, addition of TiC particles may produce fine-grained Mg-PSZ with high fracture strength.

II. Experimental

High purity ZrO_2 (Grade TZ-0, Tosoh Corp., Japan) and 99.9% MgO (Yakuri Pure Chemicals Co., Ltd., Japan) powders were used in this study. The TiC powder (Grade 120, H.C. Starck, Germany) had an average particle size of less than one μm. The powder mixture was prepared to have 9.5 mol% MgO in ZrO_2 and 5 vol% TiC of the composites. It was ultrasonically mixed in ethanol and then ball-milled using a polyurethane jar for 20 hours with zirconia balls. The slurry was dried using a rotary evaporator. The dried soft pieces were crushed lightly with hands and passed an 120 mesh sieve. It was hot-pressed in vacuum at 1750°C for one hour under the pressure of 36 MPa to obtain a pellet having a diameter of 30 mm. The cooling rate was 15°C/min. The hot-pressed pellets were machined to $2\times3\times24$ mm bars. The final surface grinding was done with a 800-grit diamond wheel. Aging of the bars were performed in an argon atmosphere at 1420°C for various times. The test bars were broken by an universal testing machine using a span of 20 mm at a loading speed of 0.5 mm/min to determine 3-point bend strength. Bars were polished with 6, 1 and 0.25 μm diamond paste sequentially to measure fracture toughness by the indentation method.[12] The polished section was etched in HF for 1 to 3 minutes to examine the microstructure, especially for grain sizes, tetragonal particles and TiC particles. Average grain sizes were determined by the linear intercept method using 1.5 as conversion factor.[13] SEM was used to examine the fracture surface as well as polished and etched surface. EDS and XRD were also used to identify TiC and ZrO_2 polymorphs.

III. Results and Discussion

1. *Fine-Grained microstructures*

Fig. 1 shows the SEM micrographs of the polished and etched surfaces of hot-pressed samples with and without TiC particles. As expected, TiC inhibited grain growth and the average grain size was 4.1 μm, which is much smaller than the average grain size, 71 μm, of the Mg-PSZ hot-pressed without second-phase inclusions. The grain size of the hot-pressed sample without TiC is larger than that of conventional pressurelessly-sintered Mg-PSZ probably because of the absence of pores during grain growth. In general, large TiC particles are at the grain boundaries and small particles are inside the grains. In Fig. 2, XRD patterns of samples with and without TiC are presented. TiC peaks with those of cubic and tetragonal zirconia are observed in the sample added with TiC. Fig. 3 shows the SEM micrographs of the polished and etched surfaces of the TiC-added Mg-PSZ after aging for 10, 30, 60 and 180 minutes each. During etching, the cubic matrix was leached out, and the tetragonal particles were no longer constrained by the matrix and were transformed to the monoclinic symmetry. Small monoclinic particles, which were originally tetragonal precipitates, are shown in the 10-minute aged sample. After further aging, the particles, which were also tetragonal before etching, grew and appeared more lens-shaped. The large particles arrowed in the pictures were confirmed as TiC particles by EDS. The thermal expansion mismatch between TiC (8 to $9\times10^{-6}/°C$)[14] and Mg-PSZ (10 to $12\times10^{-6}/°C$)[5] did not seem to affect the precipitation behavior of the tetragonal phase even around the TiC particles. The average lengths of the precipitated lenses are shown as a function of aging time in Fig. 4.

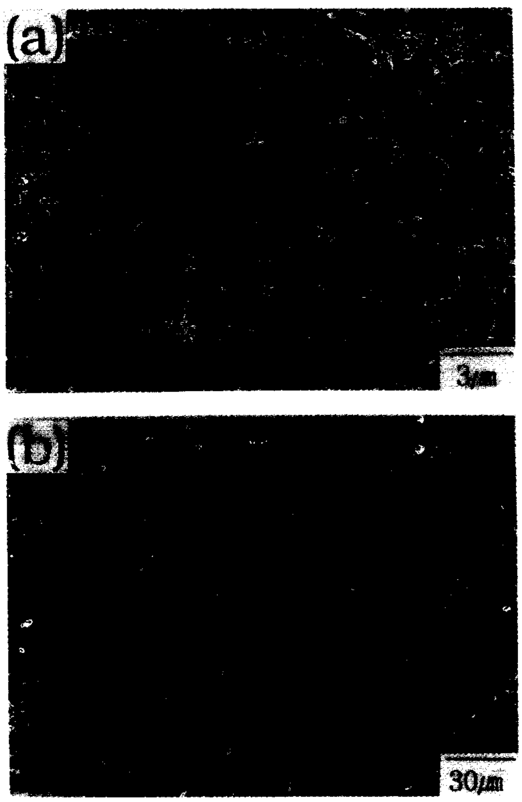

Fig. 1. SEM micrographs of polished and etched sections of hot-pressed Mg-PSZ (a) with and (b) without TiC addition. The samples were etched with HF.

2. *Mechanical properties as a function of aging time*

In addition to the average precipitate sizes, shown also in the Fig. 4 is fracture toughness as a function of aging time. Fracture toughness increased to 8.4 $MPa\cdot m^{1/2}$ as the aging time increased to one hour, which seemed to be the optimum aging time for these samples. The tetragonal precipitate size of around 250 nm obtained after one-hour aging was just enough for martensitic transformation to occur during crack propagation. With further aging fracture toughness decreases somewhat because the tetragonal precipitates grew too large and some of them were transformed to monoclinic symmetry during cooling, which decreased the effective tetragonal volume in the sample for transformation toughening.[2,3] The maximum fracture toughness obtained with these TiC-added Mg-PSZ samples is at the same level as that of normal Mg-PSZ without TiC.[5] After 5-hour of over-aging the sample shattered spontaneously into many pieces when cooled to a room temperature. Although fracture toughness increases as the tetragonal lenses grow up to one-hour aging, it is interesting to note that the 10-minute aged sample shows abnormally high toughness. It was found that fracture of this sample occurred intergranularly while samples aged longer times showed an transgran-

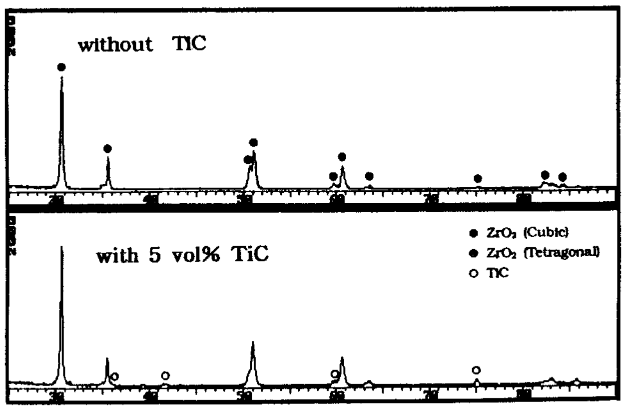

Fig. 2. XRD patterns of Mg-PSZ with (bottom) and without (top) TiC addition.

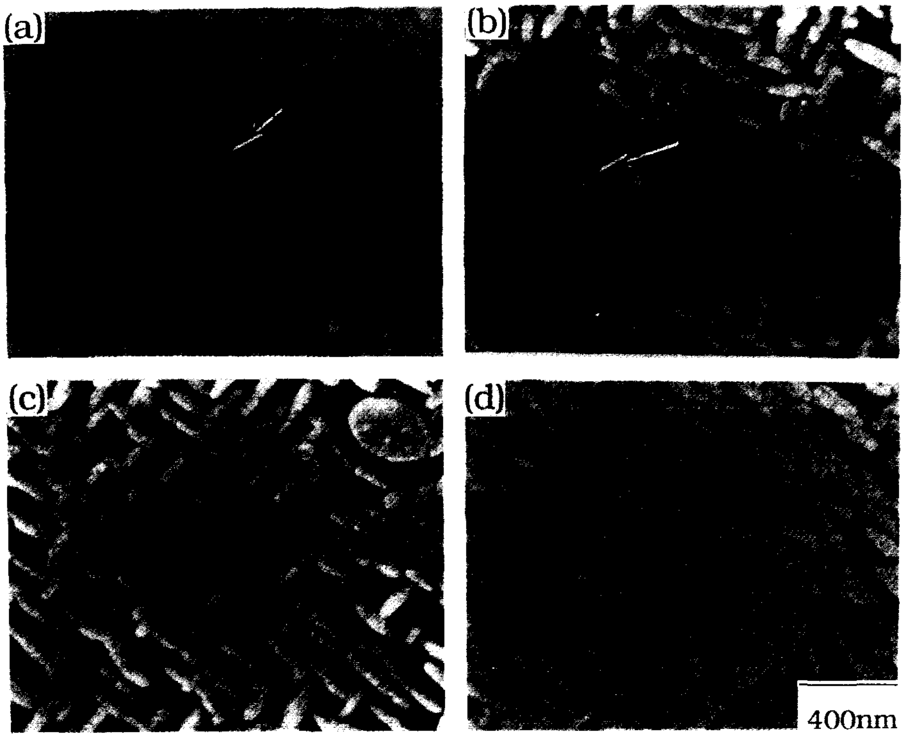

Fig. 3. SEM micrographs of polished and etched sections of TiC-added Mg-PSZ aged at 1420°C for (a) 10, (b) 30, (c) 60 and (d) 180 minutes each. The growth of precipitates during aging are shown. Arrows in (a) and (b) indicate TiC particles.

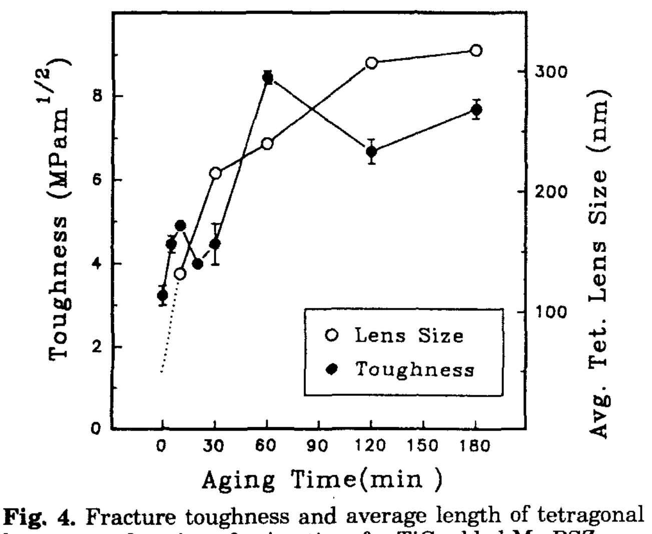

Fig. 4. Fracture toughness and average length of tetragonal lenses as a function of aging time for TiC-added Mg-PSZ.

ular mode of fracture. The fracture surfaces of samples aged 10 and 30 minutes are presented in Fig. 5. The 10-minute aged sample shows the intergranular fracture compared to transgranular fracture of the 30-minute aged sample. The 10-min sample has a very rough surface due to the TiC particles on the grain boundaries except occasional transgranular fracture shown at the lower part of Fig. 5 (a). Fig. 6 shows the crack paths made by indentation. The crack for the 10-minute aged sample propagated mostly along the grain boundary which has a monoclinic layer shown in the picture and found always in aged Mg-PSZ.[15] The increase of the aging time made the crack propagation straight passing through the grains. It was speculated that the intergranular fracture was due to the microcracks around the monoclinic layers and also might be assisted by the residual stresses around TiC particles caused by the thermal expansion mismatch with the matrix. The intergranular fracture resulted in crack deflection to increase toughness. After further aging, microcracks were annealed and residual stresses around TiC particles could be relaxed to some extent for transgranular fracture to occur. A similar but rather small peak in the initial toughness curve as a function of aging time has been reported in hot-pressed Mg-PSZ.[15] It was also attributed to the microcracks formed by the monoclinic grain boundary. However, strength of their samples aged for a short time dropped significantly due to the microcracks becoming large critical flaw sizes. In Fig. 7, 3-point bend strength is shown as a function of aging time for the samples with and without TiC particles. The bend strength of the samples without TiC particles is relatively low due to the large grain sizes as shown earlier in Fig. 1. On the other hand, the bend strength of the TiC-added sample is high in general and over 1 GPa for the optimally-aged sample for maximum toughness. Also, after 10-minute aging, it increases abruptly to 1.1 GPa and is even slightly higher than that of the optimally-aged sample. In this fine-grained mi-

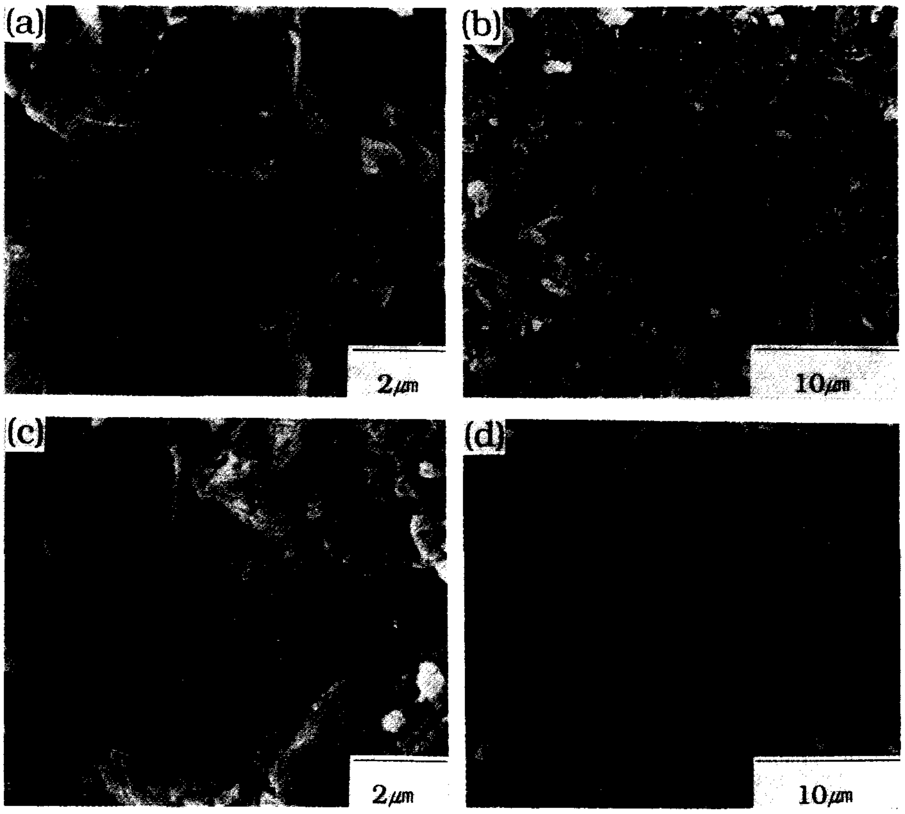

Fig. 5. SEM micrographs of fracture surfaces for TiC-added Mg-PSZ after aging for (a, b) 10 and (c, d) 30 minutes.

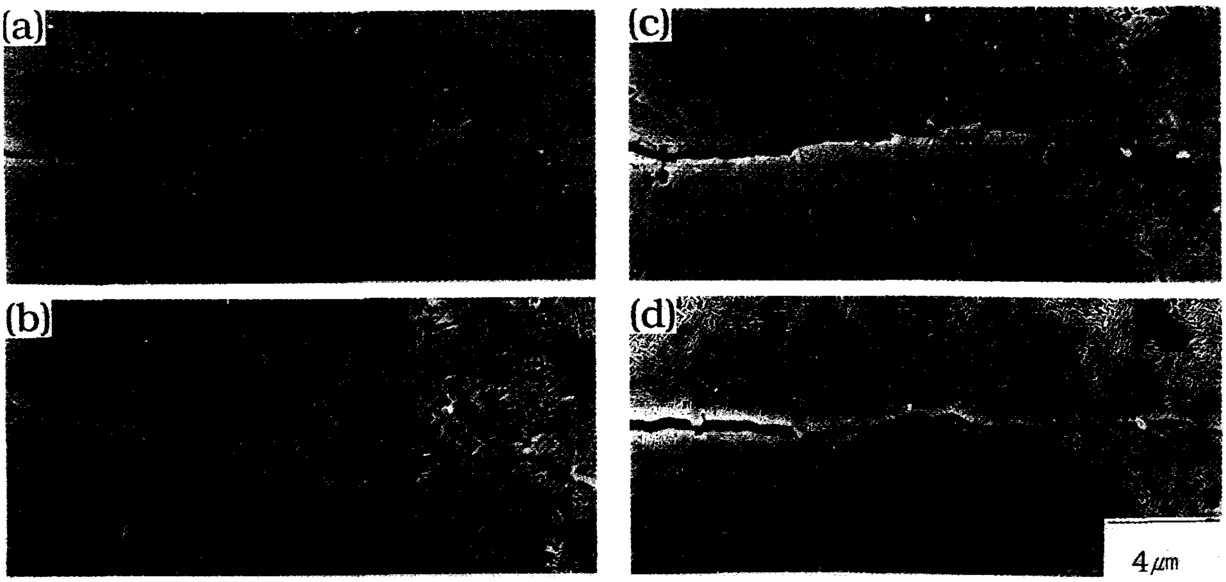

Fig. 6. SEM micrographs of indentation cracks for TiC-added Mg-PSZ after aging for (a) 10, (b) 30, (c) 60 and (d) 180 minutes. Note the intergranular mode of fracture for the 10-minute aged sample.

crostructure, microcracking around the monoclinic grain boundary did not increase the critical flaw size considerably. TiC particles might help prevent microcracks from combining each other. It is still not clear why strength of the 10-minute aged sample was at least as high as that of the optimally-aged sample. In any case, this level of bend strength is very high considering the maximum strength of around 550 MPa obtained for the conventional Mg-PSZ without second-phase inclusions. Fine grain sizes could decrease the inherent flaw sizes in the samples, which increased fracture strength significantly without sacrifice of fracture toughness.

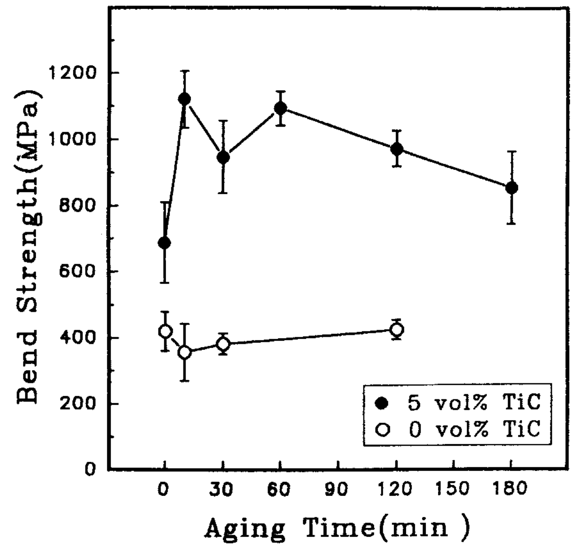

Fig. 7. Bend strength as a function of aging time for Mg-PSZ with and without TiC.

IV. Conclusions

Addition of TiC particles in Mg-PSZ retarded grain growth remarkably and produced fine-grained PSZ with an average grain size less than 5 μm. TiC particles did not seem to affect the tetragonal precipitation behavior during aging. Fracture toughness was maximum at 8.4 MPa·$m^{1/2}$ after one-hour aging at 1420°C, which was at the same level of that of normal Mg-PSZ without TiC particles. The sample aged for 10 minutes showed intergranular fracture, which caused crack deflection to increase fracture toughness abnormally. Owing to the fine-grained microstructure, fracture strength of the TiC-added Mg-PSZ reached over 1 GPa.

Acknowledgment

We thank Mr. Jungho Ryu for various experimental help and Mr. Seok Ho Na for the hot pressing work. Appreciation is also due to Dr. Seong Jai Cho at KRISS for the permission to use a hot press.

References

1. A. G. Evans and A. H. Heuer, "REVIEW-Transformation Toughening in Ceramics: Martensitic Transformations in Crack-Tip Stress Fields," *J. Am. Ceram. Soc.*, **63**[5-6], 241-248 (1980).
2. J. Budiansky, W. Hutchinson and J. C. Lambropoulos, "Continuum Theory of Dilatant Transformation Toughening in Ceramics," *Int. J. Solid Structures*, **19**, 337-355 (1983).
3. M. Mcmeeking and A. G. Evans, "Mechanics of Transformation-Toughening in Brittle Materials," *J. Am. Ceram. Soc.*, **65**[5], 242-246 (1981).
4. B. Lawn, "Fracture of Brittle Solids-Second Edition," pp. 332-334, Cambridge Univ. Press, Cambridge, 1993.
5. R. H. Green, J. Hannink and M. V. Swain, "Transformation Toughening of Ceramics," pp.107-126, CRC Press, Florida, 1989.
6. P. G. Shewmon, "The Movement of Small Inclusions in Solids by a Temperature Gradient," Trans. AIME, **230**, 1134-1137 (1964).
7. F. Lange and M. M. Hirlinger, "Hindrance of Grain Growth in Al_2O_3 by ZrO_2 Inclusions," *J. Am. Ceram. Soc.*, **67**[3], 164-168 (1983).
8. K. Okada and T. Sakuma, "The Role of Zener's Pinning Effect on the Grain Growth in 'Al_2O_3-ZrO_2,'" *J. Ceram. Soc. Jpn. Int. Edition*, **100**[4], 382-386 (1992).
9. G. Sasaki, H. Nakase, K. Suganuma, T. Fujita and K. Niihara, "Mechanical Properties and Microstructure of Si_3N_4 Matrix Composite with Nano-Meter Scale SiC Particles," *J. Ceram. Soc. Jpn. Int. Edition*, **100**[4], 536-540 (1992).
10. L. C. Stearns, J. Zhao and M. P. Harmer, "Processing and Microstructure Development in Al_2O_3-SiC 'Nanocomposites'," *J. Eur. Ceram. Soc.*, **10**, 473-477 (1992).
11. F. Meschke, N. Claussen, G. De Portu and J. R (del, "Phase Stability of Fine-Grained (Mg,Y)-PSZ," *J. Am. Ceram. Soc.*, **78**[7], 1997-99 (1995).
12. J. Zhao, L. C. Stearns, M. P. Harmer, H. M. Chan and G. A. Miller, "Mechanical Behavior of Alumina-Silicon Carbide Nanocomposites," *J. Am. Ceram. Soc.*, **76**[2], 503-510 (1993).
13. R. L. Fullman, "Measurement of Particle Sizes in Opaque Bodies," *J. Metals Trans. AIME*, **197**, 447-452 (1953).
14. "Engineering Property Data on Selected Ceramics," pp. 5.2.4-5-6, Vol. II. Carbides, Ed. by J. F. Lynch, Battelle's Columbus Lab., Ohio, 1979.
15. R. Stevens and A. Yuksel, "Grain Boundary Precipitation Phenomena and Related Mechanical Properties in Dense (Hot Pressed) Mg-PSZ," *Br. Ceram. Trans. J.*, **83**, 146-150 (1984).