Microstructures and Mechanical Properties of Al_2O_3-30wt%ZrO_2 Doped with MgO and TiO_2

M. Akter[1], M. J. Abden[2], M. K. Newaz[3] and M. M. Haque[4]

[1]*Department of Physics, Jagannath University, Dhaka-1100, Bangladesh*
[2]*Department of Electrical and Electronic Engineering, International Islamic University Chittagong, Chittagong-4203, Bangladesh*
[3]*Institute of Computer Science, Atomic Energy Research Establishment, G.P.O Box No-3787, Dhaka-1000, Bangladesh*
[4]*Materials Science Division, Atomic Energy Centre Dhaka, P.O. Box 164, Dhaka-1000, Bangladesh*

Abstract

The vickers hardness and flexural strength of a series of ceramic composites of Al_2O_3 30wt%ZrO_2 doped with MgO and TiO_2 have been measured. The sintering temperature was kept fixed at 1550 °C for each composite. The dependence of mechanical properties on grain sizes was explained with the help of SEM micrographs. These micrographs show that the average grain size decreases with addition of different wt% of MgO. The smallest average grain size of 0.978 μm of the sample 4wt%MgO-1wt%TiO_2-Al_2O_3-30wt%ZrO_2 shows its highest relative density as well as corresponding highest flexural strength of 137 MPa.

Keywords*:* Zirconia, Alumina, MgO, TiO_2, flexural strength, vickers hardness

1. Introduction

Zirconium dioxide (ZrO_2) is a ceramic with a variety of industrial applications such in electronic packaging, biomedicine, and advanced engines. However, pure zirconia easily can be transformed into different phases, which severely limits its uses. It has been observed that through the addition of some oxides to zirconia such transformation can be controlled, which leads to significant improvements in the material. Yttrium oxide (Y_2O_3) stabilized zirconia (YSZ) is one of the most commonly used zirconia of current research area of ceramics. Discovery of crack propagation property of zirconia [1,2] attracts more attention for further study of zirconia based ceramics. Three different phases, monoclinic (m), tetragonal (t) and cubic (c), of zirconia are obtainable under certain conditions [3].The more interesting properties of zirconia are its strength, high toughness, low wear resistance, high elastic modulus, ionic conductivity, chemical inertness and high melting temperature. These make zirconia based ceramics as a potential candidate for engineering materials [4–6]. Several investigations show that a suitable percentage of MgO, CeO_2, and Y_2O_3 can be used to retain the tetragonal phase from 1170 °C to room temperature [7-9]. Such materials inhibit crack propagation, control the extent of stress induced by tetragonal → monoclinic transformation, and exhibit high fracture toughness [10–12]. Among them, presently the research efforts appeared to be more focused on the compositions for transformation toughening are those with low yttria concentrations, typically on 3 mol%Y_2O_3 additions yield an extremely fine grained microstructure known as partially stabilized zirconia polycrystals (3YSZ) which exhibited excellent mechanical properties and contained only the tetragonal phase at room temperature [13–15]. Thus, this material has been considered as a most potential candidate for load-bearing implant applications, such as dental implants [16, 17]. Though the addition of Y_2O_3 retained the tetragonal phase of the ZrO_2, the hardness of the composites was not improved enough. In order to enhance their hardness, it may be dispersed as reinforcement in various composite matrices. Alumina (Al_2O_3) is a hard ceramic possessing a wide range of applications due to its composition and many desirable properties such as high mechanical strength, thermal stability, excellent corrosion and wear resistance.

Therefore, the combination of alumina (Al_2O_3) with a high toughness ZrO_2 matrix would be a promising way to produce an excellent composite reinforcement and would improve the mechanical properties of the matrix since the composites combined the hardness and wear resistance of Al_2O_3 with the fracture toughness and bending strength of zirconia [18,19]. MgO is an interesting material in catalysis, adsorption and in the synthesis of refractory ceramics and TiO_2 is one of the most effective additives for improving mechanical properties. Hence the addition of MgO and TiO_2 to Al_2O_3-ZrO_2 composite would play an important role in the contribution to their mechanical, structural properties. Since the particle size, shape, grain densification etc. are the important factors in controlling mechanical properties of such ceramic materials, in the present study an investigation for proper combination of Al_2O_3, ZrO_2, MgO and TiO_2 was carried out for a fixed sintering temperature of 1550 °C.

2. Materials and Methods

2.1 Sample Preparation

For the preparation of the materials under study α-Al_2O_3 of purity 99.85% and average particle size of ~150 nm, 3 mol% Y_2O_3 stabilized ZrO_2 (3YSZ) of purity of 99.9% and average particle size of ~ 30–60 nm, MgO of purity 99.9% and average particle size of ~ 35 nm and TiO_2 of purity 99.9% and average particle size ~ 40 from Inframat corporation, US were used. The composite powders of xwt%MgO + ywt%TiO_2 + 3YSZ–30wt%Al_2O_3 (where x=1, 2, 3, 4 and y =4, 3, 2, 1) were prepared by wet ball-milling

Corresponding author: mahbub405@yahoo.com

for 24 h in ethanol. Zirconia balls of 10 mm in diameter were used for milling purpose in order to get homogeneous mixture. The ethanol used was removed by drying the mixture at 90^{o}C for 21 hours. During crashing the mixture with mortar and pestle a few drops of PVA solution was added as a binder. The mixture was then dried at 110 °C for 6 hours in order to eliminate the water content from the binder solution. Pellets of dimensions of 5 mm × 4 mm × 35 mm were made using a uniaxial pressure of 210 MPa. The pellets were then sintered at 1550°C for 3 h in air. The heating rate was varied as 8°C/min up to 600°C, 5°C/min up to 1400°C, 3°C/min at the final sintering temperature of 1550°C for 3 h in air. The cooling rate was 5°C/min down to until the inertia of the furnace prevailed.

2.2 Characterization Techniques

The Archimedes' method, using distilled water as the immersion medium, was implied to the sintered samples. The theoretical densities of Al_2O_3, 3YSZ, MgO and TiO_2 were taken as 3.99 gm/cm^3, 6.09 gm/cm^3, 3.60 gm/cm^3 and 3.89 gm/cm^3, respectively. These density values were used to calculate the theoretical densities of all the individual samples using rule of mixtures. A D8 ADVANCE X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu-Kα radiation (λ=0.15406 nm) was used to investigate the crystalline phases of the specimen in a continuous mode where 2θ ranges from 20 to 90°. The angular step was 0.02° with a fixed counting time of 0.6 s/step. The voltage and current were set at 40 kV and 40 mA, respectively.

The average grain size of the xwt%MgO + ywt%TiO_2 + 3YSZ–30wt%Al_2O_3 were measured with the help of scanning electron micrographs (SEM) of randomly selected areas of the fracture surfaces using the linear intercept method. Flexural strength was determined using three point bending test on five bars for every specimen by universal tensile tester (Hounsfield H10K-S, UK) with the inner span set to 25 mm and a velocity of the crosshead displacement of 0.5 mm/min. The hardness of the sintered samples was evaluated at room temperature by amicro-Vickers hardness tester (Shimadzu, HMV-2, Japan) with an indent load on polished surfaces of 19.614 N for 6 s. The measurement was repeated 12 times for a sample and the average value was determined in which the maximum and minimum values were excluded.

3. Results and Discussion

3.1 X-ray Diffractometry

Fig.1 shows XRD spectrum of the as received 3 mol%Y_2O_3 stabilized ZrO_2 (3Y-SZ) and Al_2O_3 powder, respectively. It is shown that the main phases are tetragonal (t) along with a small amount of monoclinic (m) phase of ZrO_2 was observed, which was characterized by diffraction peak approximately at 2Θ=28° and a cubic (c) phase at around 2Θ=74.54° in Fig. 1(a) [20].

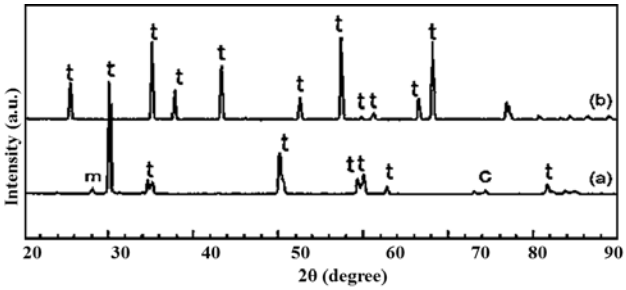

Fig. 1(a) Shows XRD spectra of the as received 3 mol%Y_2O_3 stabilized ZrO_2 (3Y-SZ) and (b) shows that of Al_2O_3 powder

3.2 Phase Analysis

The Fig. 2 shows the X-ray diffraction pattern of Al_2O_3-30wt% ZrO_2 + xMgO + yTiO_2 (x=1,2,3,4 and y= 4,3,2,1) composites samples sintered at 1550^{O}C for 3 h. From these figures it is shown that a slight change in phase occurred. Such variation is due to the presence of dopant MgO and TiO_2 content. It is well known that a suitable percentage of MgO are most commonly used to retain the tetragonal phase from 1170^{o}C to room temperature, inhibit crack propagation, controlling the extent of stress induced by t→m transformation [21]. TiO_2 additive that has a considerable solubility in the matrix affects the densification by the formation of a transitory liquid phase, depending on the amount of addition [22].

In Fig. 2, from the XRD patterns it can also be seen that the main phase is tetragonal (t), which is characterized by the

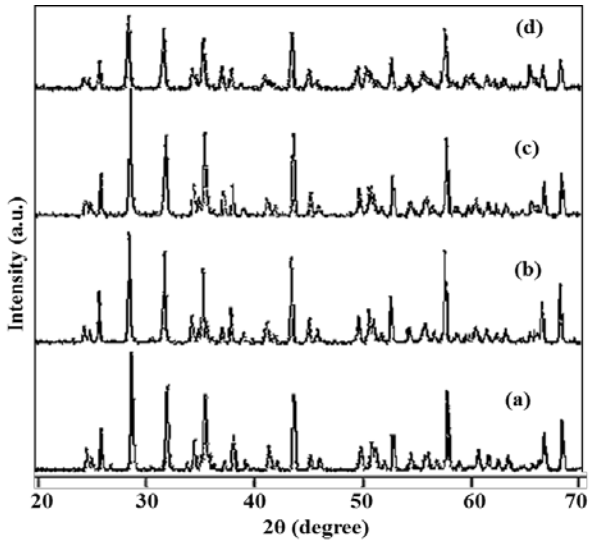

Fig. 2 X-ray diffraction profiles of Al_2O_3-30wt% ZrO_2 ceramic composite doped with (a) 1wt%MgO-4wt% TiO_2, (b) 2wt%MgO-3wt% TiO_2, (c) 3wt%MgO-2wt% TiO_2 and (d) 4wt%MgO-1wt% TiO_2 sintered at 1550 °C for 3 h in air

diffraction peak approximately at 2Θ=28°. In Fig. 1 a few amount of monoclinic (m) phase was observed only for 3YSZ, which is characterized by the diffraction peak at 2Θ=28°. But for Al_2O_3 content shown in Fig. 2 there is no

trace of monoclinic (m) phase of ZrO_2, which confirms that the m-ZrO_2 phase content in the initial powder has completely been transformed into tetragonal phase, indicating the complete stabilization of the tetragonal phase for Al_2O_3 containing sintered samples [23].

3.3 SEM Data Analysis

Figs 3 (a-d) shows the scanning electron micrographs obtained from four different samples. It can easily be seen that the average largest grain is present in Fig. 3(a) while the average smallest grain is present in Fig. 3(d). Also, all four micrographs show a gradual decrease in grain-size from Figs. 3(a-d). In Fig. 3(d) the grains are almost homogeneous and uniform in size and shape. The smallest average grain size of 0.978 µm is measured from this sample.

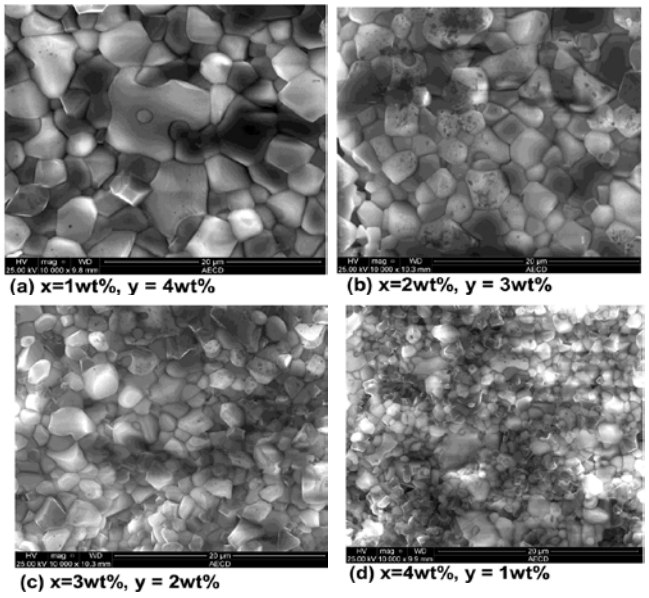

Fig. 3(a-d) SEM of Al_2O_3-30wt% ZrO_2 + xMgO + yTiO_2 at 1550 °C, where x = 1,2,3,4 and y =4, 3, 2, 1

3.4 Densification

Volume shrinkage has been calculated using dimensions of the sintered specimens. The elimination of pore and grain growth of the respective crystalline phases are responsible for the firing shrinkage at 1550 °C. Fig. 4(a) shows that volume shrinkage decreases with doping percentage of MgO. The composition with 1wt%MgO-4wt%TiO_2 shows highest value, which is 49.35%, among all the compositions. This is due to the formation of solid solution with Al_2O_3-ZrO_2 composite by the dopant TiO_2 in the reaction during the sintering process [24].

3.5 Analysis of Apparent Porosity

Fig. 4(b) shows the porosity of Al_2O_3-30wt%ZrO_2 composites sintered at 1550°C. It is observed that additive of MgO and TiO_2 have significant effect on the reduction of porosity. The apparent porosity of the samples decrease with the increase of MgO concentration while the TiO_2 concentration was decreased. The reduction of porosity also depends on the phase, secondary crystallization, lattice expansion, micro-crack formation of additive MgO and TiO_2. The sample with 1wt%MgO-4wt%TiO_2 shows a higher porosity value, which may be due to poor filling of the inter-granular voids and the presence of abnormal grains. This porosity usually originates from entrapped pore during green compaction and the elimination of hydrated water from additive during sintering. These pores could be removed at higher sintering temperature.

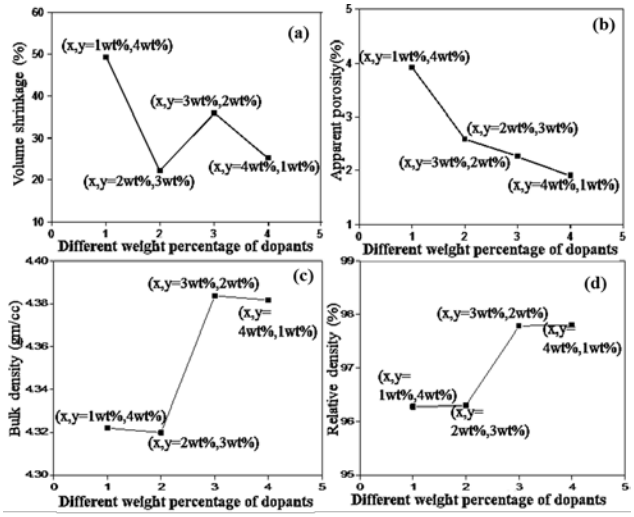

Fig. 4(a) Volume shrinkage, (b) apparent porosity, (c) bulk density and (d) relative density of Al_2O_3-30wt% ZrO_2 ceramic composite doped with 1wt%MgO-4wt% TiO_2, 2wt%MgO-3wt% TiO_2, 3wt%MgO-2wt% TiO_2 and 4wt%MgO-1wt% TiO_2 respectively, sintered at 1550 °C

3.6 Bulk Density

From Fig. 4(c) it can be seen that the bulk density of Al_2O_3-30wt%ZrO_2 composites significantly increases with the increase of dopant MgO while the concentration of TiO_2 is decreased. A slight decrease occurs for the sample with doping percentage of 2wt%MgO-3wt%TiO_2 might be due to a small amount of volume shrinkage in this sample.

3.7 Relative Density

The estimated relative densities of the sintered samples are shown in Fig. 4(d). It shows that the relative densities of the specimens increase with the variation of dopant. The maximum relative density, which is about ~98%, was achieved for the composition Al_2O_3-4wt%MgO-1wt%TiO2-30wt%ZrO_2. Since the apparent porosity of the samples decreases with the increase of doping percentage of MgO, hence the bulk density and relative density increase.

3.8 Mechanical Properties

Fig. 5(a) shows that in the case of 4wt%MgO-1wt%TiO_2-30wt% the increase in flexural strength is comparatively higher than that of others. From the corresponding SEM micrograph shown in Fig. 3(d) for 4wt%MgO-1wt%TiO_2-30wt%ZrO_2, it can be seen that the sub-micrometer size zirconia and alumina are homogenously distributed. An improvement of grain boundary structure and a reduction of the grain size results an improvement in mechanical properties of this sample [25]. It can also be stated that the

formed solid solution interface strengthened the bonding of alumina-zirconia grains and improves the densification as well as mechanical properties.

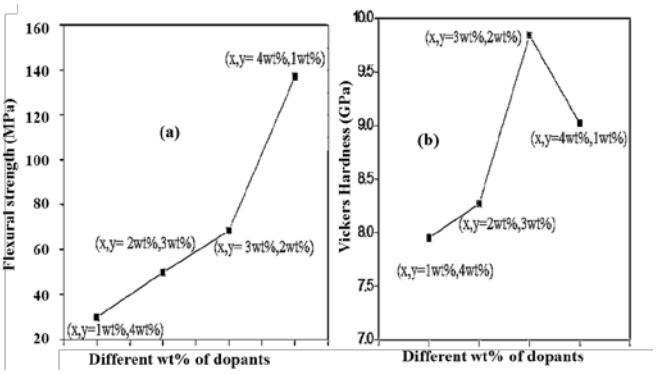

Fig. 5(a) Flexural strength and (b) Vickers hardness of Al_2O_3-30wt% ZrO_2 ceramic composite doped with 1wt%MgO-4wt% TiO_2, 2wt%MgO-3wt% TiO_2, 3wt%MgO-2wt% TiO_2 and 4wt%MgO-1wt% TiO_2 respectively, sintered at 1550°C

3.9 Vickers Hardness

Fig. 5(b) shows the Vickers hardness of the samples. The lowest value obtained for the sample is 1wt%MgO-4wt%TiO_2-Al_2O_3-30wt%ZrO_2. This is because of its lower density, which is also one of the parameters that influence the hardness. Other important parameter that matters to its hardness is its porosity. The sample 3wt%MgO-2wt%TiO_2-Al_2O_3-30wt%ZrO_2 shows its maximum hardness of 9.84 GPa due to its homogeneous microstructure with lower porosity.

4. Conclusion

The mechanical properties, flexural strength and Vickers hardness for a series of alumina and zirconia based ceramic materials doped with different weight percentage of MgO and TiO_2 has been investigated. All the samples were sintered at 1550 °C in air. Densification of these materials has also been studied. Phase analysis on these materials shows that the main phases of all the samples are tetragonal (t). A slightly change in phase occurs due to the variation of doping concentration of MgO and TiO_2. The dependence of mechanical properties on grain sizes was observed from the SEM micrographs. The smallest average grain size of 0.978 µm of the sample 4wt%MgO-1wt%TiO_2- Al_2O_3-30wt% ZrO_2 shows its highest relative density and corresponding highest flexural strength of 137 MPa and ~9.1 GPa of Vickers hardness.

Acknowledgement

The authors acknowledge Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka and Materials Science Division, Atomic Energy Centre, Dhaka for providing the experimental laboratory facilities.

References

1. R. C. Garvie, R. H. Hannink and R. T. Pascoe, Ceramic steel? Nature, **258**, 703 (1975).
2. R. H. Hannink, P. M. Kelly and B. C. Muddle, Transformation Toughening in Zirconia Containing Ceramics, J. Am. Ceram. Soc., **83**, 461 (2000).
3. S. Tekeli, M. Erdogan and B. Aktas, Influence of -Al_2O_3 Addition on Sintering and Grain Growth Behavior of 8 mol% Y_2O_3-Stabilisedcubic Zirconia (*c*-ZrO2), Ceram. Int., **30**, 2203 (2004).
4. D. Ai and S. Kang, Synthesis of 3Y–ZrO2 Nano-Powders Via A W/O Emulsion, Ceram. Int., **30**, 619 (2004).
5. S. R. Choi and N. P. Bansal, Mechanical Behavior of Zirconia/Alumina Composites, Ceram. Int., **31**, 39 (2005).
6. Y. Zhang, J. Chen, L. Hu and W. Liu, Pressureless-Sintering Behavior of Nanocrystalline ZrO2-Y2O3-Al_2O_3 System, Mater. Lett., **60**, 2302 (2006).
7. R. C. Garvie, C. Urbani, D. R. Kennedy and J. C. McNeuer, Biocompatibility of Magnesia Partially Stabilized Zirconia (Mg-PSZ) Ceramics, J. Mater. Sci., **19**, 3224 (1984).
8. S. Ban, H. Sato, Y. Suehiro, H. Nakahishi and M. Nawa, Biaxial Flexure Strength and Low Temperature Degradation of Ce-TZP/Al_2O_3 Nanocomposite and Y-TZP as Dental Restoratives, J. Biomed. Mater. Res., B **87**, 492 (2008).
9. J. Chevalier, S. Deville, E. Munch, R. Jullian and F. Lair, Critical Effect of Cubic Phase on Aging in 3 mol% Yttria-Stabilized Zirconia Ceramics for Hip Replacement Prosthesis, Biomater., **25**, 5539 (2004).
10. J. Chevalier, L. Gremillard, A. V. Virkar and D. R. Clarke, The Tetragonal–Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends, J. Am. Ceram. Soc., **92**, 1901 (2009).
11. J. K. M. F. Daguano, C. Santos, R. C. Souza, R. M. Balestra, K. Strecker and C. N. Elias, Properties of ZrO2-Al_2O_3 Composite As A Function of Isothermal Holding Time, Int. J. Ref act Met. Hard Mater., **25,** 374 (2007).
12. I. Denry and J. R. Kelly, State of Art of Zirconia for Dental Applications, Dent. Mater., **24**, 299 (2008).
13. T. K. Gupta, F. F. Lange and J. H. Bechtold, Effect of Stress Induced Phase Transformation on the Properties of Polycrystalline Zirconia Containing Metastable Tetragonal Phase, J. Mater. Sci., **13**, 1464 (1978).
14. J. L Lorca, J. Y. Pastor, P. Poza, J. I. Pena, I. Francisco, A. Larrea and V. M. Orera, Influence of the Y2O3 Content and Temperature on The Mechanical Properties of Melt-grown Al_2O_3-ZrO_2 Eutectics, J. Am. Ceram. Soc., **87**, 633 (2004).
15. S. C. Farmer and A. Sayir, Tensile Strength and Microstructure of Al_2O_3-ZrO_2 Hypo-Eutectics Fibers, Eng. Fract. Mech., **69**, 1015 (2002).

16. B. I. Ardlin, Transformation-Toughened Zirconia for Dental Inlays, Crowns and Bridges: Chemical Stability and Effect of Low Temperature Aging on Flexural Strength and Surface Structure, Dent. Mater., **18**, 590 (2002).
17. M. C. Correa de Sá e Benevides de Moraes, E. C. Nelson, F. J.Duailibi and L. Gulmaraesde Oliveira, Mechanical Properties of Alumina-Zirconia Composites For Ceramic Abutments, Mater. Res.,**7**, 643 (2004).
18. A. Nevarez-Rascon, A. Aguilar-Elguezabal, E. Orrantia and M. H.Bocanegra-Bernal, on the Wide Range of Mechanical Properties of ZTA and ATZ Based Dental Ceramic Composites By Varying the $Al_2O_3$and ZrO_2 content, Int. J. Refract. Met. Hard Mater., **27**, 962 (2009).
19. D. J. Kim, M. H. Lee, D. Y. Lee and J. S. Han, Mechanical Properties, Phase Stability, and Biocompatibility of (Y, Nd)-TZP/Al_2O_3 Composite Abutments for Dental Implant, J. Biomed. Mater. Res., **53**, 438 (2000).
20. H. Toroya, M. Yoshimura and S. Somiya, Quantitative Analysis of Monoclinic Stabilized Cubic ZrO_2 systems by X-ray diffraction, J. Am. Ceram. Soc., **67** 183-184 (1984).
21. J. Chevalier, S. Deville, E. Munch, R. Jullian and F. Lair, Critical Effect of Cubic Phase on Aging in 3 mol% Yttria-Stabilized Zirconia Ceramics for Hip Replacement Prosthesis, Biomater., **25**, 5539-5545 (2004).
22. B. Kerkwijk, E. Mulder and H. Verweij, Zirconia-Alumina Ceramic Composites With Extremely High Wear Resistance, Advanced Engineering Materials, **1**, 69-71 (1999).
23. M. Kagawa, M. Kikuchi, Y. Syono and T. Nagae, Stability of Ultrafine Tetragonal ZrO_2 Coprecipitated with Al_2O_3 by the Spray-ICP Technique, J. Am. Ceram. Soc., **66**, 751 (1983).
24. J. M. Rincon, J. S. Moya and M. E. Melo, Microstructural Study of Toughened ZrO_2/mullite Ceramic Composites Obtained By Reaction Sintering With TiO_2 Additions, Trans. Br. Ceram. Soc., **85**, 201-206 (1986).
25. F. F. Lange, Transformation Toughening Part 4: Fabrication, Fracture Toughness and Strength of Al2O3-ZrO2 Composites, J. Mater. Sci., **17**, 247-254 (1982).