

Biotribological Properties of TZP/Al₂O₃ Ceramics for Biomechanical Applications

Deuk Yong Lee,[†] Se-Jong Lee,* Ju-Woong Jang,** Hak-Kwan Kim,** and Dae-Joon Kim***

Department of Materials Engineering, Daelim College of Technology, Anyang 431-715, Korea

**Department of Materials Engineering, Kyungsung University, Busan 608-736, Korea*

***Woori Dong Myung Dental Material Research Center, KwangMyung 423-060, Korea*

****Department of Advanced Materials, Sejong University, Seoul 143-147, Korea*

(Received May 14, 2003; Accepted June 14, 2003)

ABSTRACT

Biotribological properties, such as wear rate and friction coefficient, of 3Y-TZP and Low Temperature Degradation (LTD) free materials were investigated via a ball(SiC)-on-plate sliding wear test to evaluate the relationship between wear mechanism and phase transformation. Wear test was conducted with a sliding speed of 0.035 m/s at room temperature and at 250°C in air under a normal load of 49 N, respectively. Although friction coefficient of 3Y-TZP was the lowest due to the fine grain size, the highest wear loss and rate were observed due to the debris of monoclinic grains introduced during sliding and their values increased drastically with raising temperature. However, the biotribological properties of LTD-free materials were insensitive to temperature due to the inertness of the phase transformation, suggesting that they may be applicable to the biomechanical parts.

Key words : *Tetragonal zirconia polycrystal, Wear, Phase transformation*

1. Introduction

Tetragonal Zirconia Polycrystal (TZP), stabilized especially by alloying of 3 mol% Y₂O₃(3Y-TZP), is highly acknowledged as the candidate material of choice for biomechanical applications such as dental prostheses on osseointegrated implant fixture and artificial joints because of its high fracture toughness and strength.¹⁻⁴⁾ In the area of biomechanical replacements, such as dental implant abutment, hip and knee prostheses, heart valves and bone implants, wear resistance, cyclic fatigue,⁷⁾ biocompatibility, chemical stability and aesthetics are critical issues. It has been documented that TZPs possess a good biocompatibility,²⁾ the natural tooth-colored aesthetics,⁶⁾ excellent fatigue properties⁷⁾ and the chemical resistance.⁸⁻¹⁰⁾ Lawn⁵⁾ reported that the states of loading may be complex due to the mechanics of the human body, but the most common and most severe forms involved concentrated forces(P) from contacts of characteristic radius(r), e.g. bruxism(teeth, P≈200–700 N, r≈1–10 mm) and body-weight support(hips, P≈6000 N, r≈30 mm). Prosthetic structures should be engineered to withstand such contacts for clinical treatments.

Commercial zirconia dental implant abutments and hip joint femoral heads have been implanted worldwide by using 3Y-TZPs since 1985.^{4,11,12)} However, 3Y-TZPs experi-

ence a detrimental strength degradation because of the spontaneous tetragonal to monoclinic phase transformation when the materials is exposed to a low temperature range of 100 to 400°C, so called Low Temperature Degradation (LTD).^{8-10,13)} LTD leads to an abrupt decrease in strength due to the formation of macrocracks as a result of interaction of microcracks accompanied by the phase transformation.^{13,14)} Several researchers^{4,11,12)} argued that LTD may not be a critical factor because the temperature of the human body is just 37°C, which is far lower than LTD's temperature region, and the reduction in strength of 3Y-TZPs tested in short-term in vivo environments such as phosphate buffer solution or saline solution is not severe. However, LTD occurred even in the human body environment when 3Y-TZPs were implanted for a long period of time since LTD is governed by the kinetics of the phase transformation and accelerated in the presence of water and water vapor.^{2,6,9,13)} Therefore, their short-term experiments did not verify the feasibility of 3Y-TZPs because the slightest damage may signal the end of safe function. The problem is exacerbated in prolonged or cyclic loading, where small scale damage can evolve steadily but inexorably over time into catastrophic failure.⁵⁾ Also, fracture strength is not a key factor in designing prosthetic structures for an extended period of time because of the complicated mechanics and environments of the human body. Clinically, wear, fatigue properties and R-curve behavior¹⁵⁾ have been known to be main factors.

Recently, a LTD-free TZP/alumina composites without compromising their mechanical properties have been pro-

[†]Corresponding author : Deuk Yong Lee

E-mail : dylee@daelim.ac.kr

Tel : +82-31-467-4835 Fax : +82-31-467-4830

posed by several researchers.^{9,16)} Our previous study¹⁷⁾ showed that the strength and fracture toughness of isostatically hot-pressed TZP/Al₂O₃ composites were 944 MPa and 9.9 MPam^{1/2}, respectively, and the phase stability of the composites were sustained even under water vapor condition. In the present study, wear properties of 3Y-TZP and LTD-free TZP/Al₂O₃ composites were investigated to evaluate the feasibility of the implant biomaterials for Total Hip Replacements (THR) applications because the debris introduced by the friction may induce osteoclast.

2. Experimental Procedure

The chemical composition of samples and the specimen designations are listed in Table 1. Oxides such as ZrO₂, Al₂O₃, Nb₂O₅, Y₂O₃, CeO₂, and Fe₂O₃ were weighed according to the composition, mixed using ball mill, calcined for 4 h at 1100°C, crushed by attrition mill for 2 h at 500 rpm and sieved, and then green compacts were sintered for 2 h at 1550°C in air. The samples having a dimension of 40×20×10 mm³ were polished using a SiC grit of 2000, surface treated using ultrasonic cleaner for 30 min and subsequently annealed for 2 h at 1200°C to remove the possible residual stress. The sintered density was measured by the Archimedes method, using distilled water as the immersion medium. Microhardness was measured using Vickers microhardness tester (MVK-H2, Akashi, Japan) with a load

Table 1. Chemical Composition and Phases of the Specimens

Designation	Specimen	Composition (in mol%)	Phase
S1	3Y-TZP	3Y ₂ O ₃ · 97ZrO ₂	t-ZrO ₂
S2	(Y,Nb,Ce)-TZP	99 S1 · Nb ₂ O ₅ : CeO ₂ = 96 : 4	t-ZrO ₂
S3	(Y,Nb,Ce)-TZP/Al ₂ O ₃	S2 : Al ₂ O ₃ = 8 : 2(vol%)	t-ZrO ₂ Al ₂ O ₃
S4	(Y,Nb,Ce,Fe)-TZP/Al ₂ O ₃	99.8S3 · 0.2Fe ₂ O ₃ : Al ₂ O ₃ = 8 : 2(vol%)	t-ZrO ₂ Al ₂ O ₃

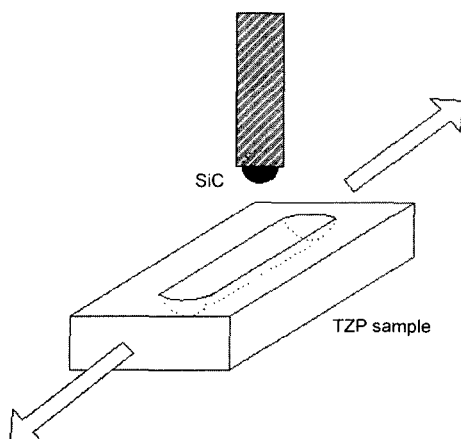


Fig. 1. Schematic representation of the ball-on-plate wear apparatus.

of 9.8 N. The linear intercept method was employed to determine the average grain size with the use of a correction factor of 1.56 after Mendelson.¹⁸⁾

Wear experiments were performed with a ball-on-plate apparatus, which is shown in Fig. 1. A SiC ball with a diameter of 10 mm slides reciprocally against a stationary 3Y-TZP and TZP/Al₂O₃ plates. Tests were conducted at room temperature and at 250°C in air under a normal load of 49 N, respectively. The sliding speed was 0.035 m/s and the distance travelled was 600 m. At the end of each test, the weight loss of the plates and balls was measured and then the relative volumetric wear rates were calculated by observing the profile of the track using a profilometer (Dek-Tak 3030, USA). Worn tracks were analyzed by SEM (S-2400, Hitachi, Japan).

3. Results and Discussion

The relative density of the specimens was almost the same, corresponding to 98% of the theoretical density. The hardness increased in the order of S1 to S4 as shown in Fig. 2. It is conceivable that hardness and wear resistance of zirconia/alumina composites were superior to those of TZPs because alumina has a higher value of hardness (18 GPa) than TZPs (10–12 GPa).¹⁹⁾ The lowest hardness of S1 (3Y-TZP) was observed due to higher content of Y₂O₃. The amount of Y₂O₃ should be suppressed to increase hardness, however, lower content of Y₂O₃ may cause higher LTD phenomena. On the other hand, the LTD-free specimens (S2, S3, S4) showed a higher hardness value than S1 because of co-doping effects of Y₂O₃ and CeO₂ and the presence of rigid alumina particles.

Grain size of the specimens (S1 to S4) were determined to be 0.5, 1.3, 0.7 and 0.7 μm, respectively. Higher strength (800 MPa) of S1 as compared with that (550 MPa) of S2 was achieved by reducing the grain size due to the Hall-Petch relation, indicating that larger grain size caused by co-alloying of Y₂O₃ or CeO₂ decreased the strength. No grain growth was observed by one of the authors¹³⁾ when Nb₂O₅ was

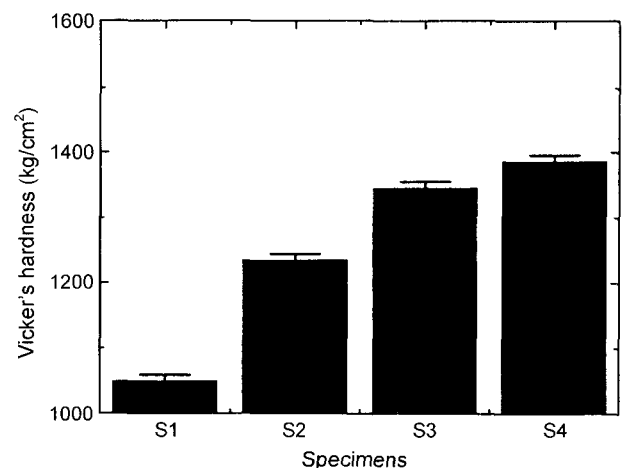


Fig. 2. Microhardness of the specimens.

alloyed to S1 up to 1.5 mol%. S2 contains 1 mol% of Nb₂O₅ and 4 mol% CeO₂, implying that the addition of CeO₂ may be attributed to grain coarsening. Small amount (0.2 mol%) of Fe₂O₃(S4) was added to S3 to show yellowish brown color close to natural human teeth, whereas it did not affect the microstructure and the grain size.⁶⁾ The strength of S3 (900 MPa) and S4 (900 MPa) was higher than the others due to the smaller grain size and the presence of rigid Al₂O₃ dispersoid. Also, the addition of the rigid Al₂O₃ particles may further impede the relaxation of the strained tetragonal ZrO₂ lattice during aging process since the relaxation is responsible for LTD and is governed by the oxygen vacancy diffusion.^{6-10,13)}

Wear resistance, which is prerequisite for artificial joints, may be affected by applied load and hardness rather than bend strength. Also, humidity and body temperature should be considered for the long-term use. However, the short-term in vivo tests have been only conducted to inspect the feasibility of the materials. In the present study, wear test was conducted at room temperature and at 250°C, respectively, to study the effect of temperature on biotribological properties. The variation of friction coefficient as a function of sliding distance was shown in Fig. 3. The friction coefficient of S1 at 250°C was higher than that at room temperature. On the other hand, the friction coefficient of other specimens was the opposite. It has been known that the friction coefficient of ceramics decreased generally with raising

temperature due to the introduction of heat. The friction coefficient of 3Y-TZP at 250°C presented a different trend as compared with the others. This is likely due to the formation of monoclinic debris caused by the tetragonal to monoclinic phase transformation at 250°C. The sliding motion of SiC ball may be hampered due to the presence of debris, resulting in the increase in friction coefficient. However, friction coefficient (0.45) of 3Y-TZP at room temperature was the lowest because of fine microstructure.

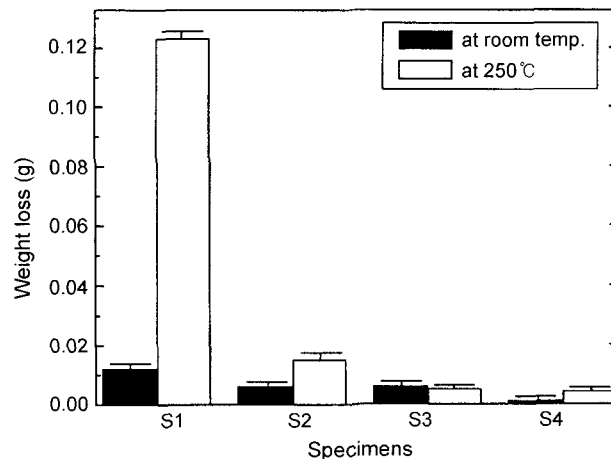


Fig. 4. Weight loss of (a) S1, (b) S2, (c) S3, and (d) S4 at room temperature and at 250°C, respectively.

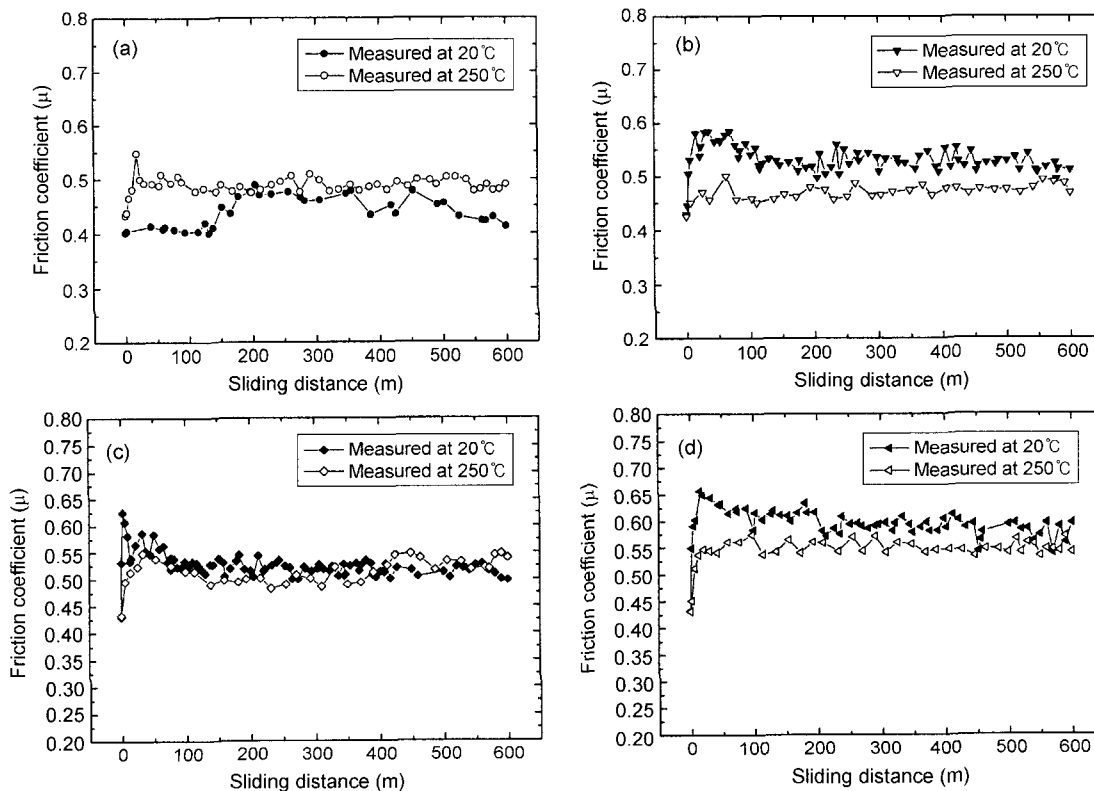


Fig. 3. Friction coefficient of (a) S1, (b) S2, (c) S3, and (d) S4 as a function of sliding distance at room temperature and at 250°C, respectively.

Weight loss, volume and rate were evaluated by measuring the weight before and after the test and the geometry of worn track after the test, which is shown in Fig. 4 and Table 2. Fig. 4 shows that a relatively large weight loss was observed for S1 worn at room temperature as compared with other specimens, however, almost null loss was found for S4. The wear loss of S1 increased significantly with raising the temperature. The observation indicated that the increase of weight loss and rate may be due to the accumulation of external stress on the surface of S1 and thermal energy for the spontaneous phase transformation at 250°C during the wear test. Monoclinic phase can be easily formed on the surface of highly transformable S1 specimen due to the repetitive external stress as a result of the sliding wear.

Table 2. Wear Rate($\times 10^{-6}$ mm³/Nm) of the Specimens at Room Temperature and at 250°C, Respectively

Specimen	Room temperature	250°C
S1	9.62	47.19
S2	2.87	23.75
S3	2.8	9.64
S4	0.34	9.45

And the isothermal degradation effect may be progressed, resulting in higher wear rate (Table 2) as verified in Fig. 5. Fig. 5(a) and (b) represented that grain pullout (dark spot) became a main wear mechanism by the intergranular microfracture, resulting in abrasive wear and microfracture. The removed monoclinic grains caused by phase transformation may act as a third body resulting in an increase of abrasive wear. Wear rate of S1 rose with increasing temperature (Table 2), indicating that the aging transformation during sliding can be an onset for higher wear rate, especially at more severe biotribological conditions. However, a smooth surface (delamination of the thin film) was observed for the S4 specimen (Fig. 5(c) and (d)), implying that they underwent adhesive wear. It may be conceivable that S1 produced higher weight loss and wear rate than the others because S2, S3, and S4 were LTD-free materials. The accumulation of debris introduced during friction, which was demonstrated by the observation of weight loss and wear rate, may induce osteoclast formation around bone,¹⁹⁾ which was deleterious for biomaterials. Human body was operated at 37°C under humid condition. Artificial saliva had a pH of 5.2, which is severely corrosive environments.²⁰⁾ The degradation of S1 may be more exacerbated in the human body

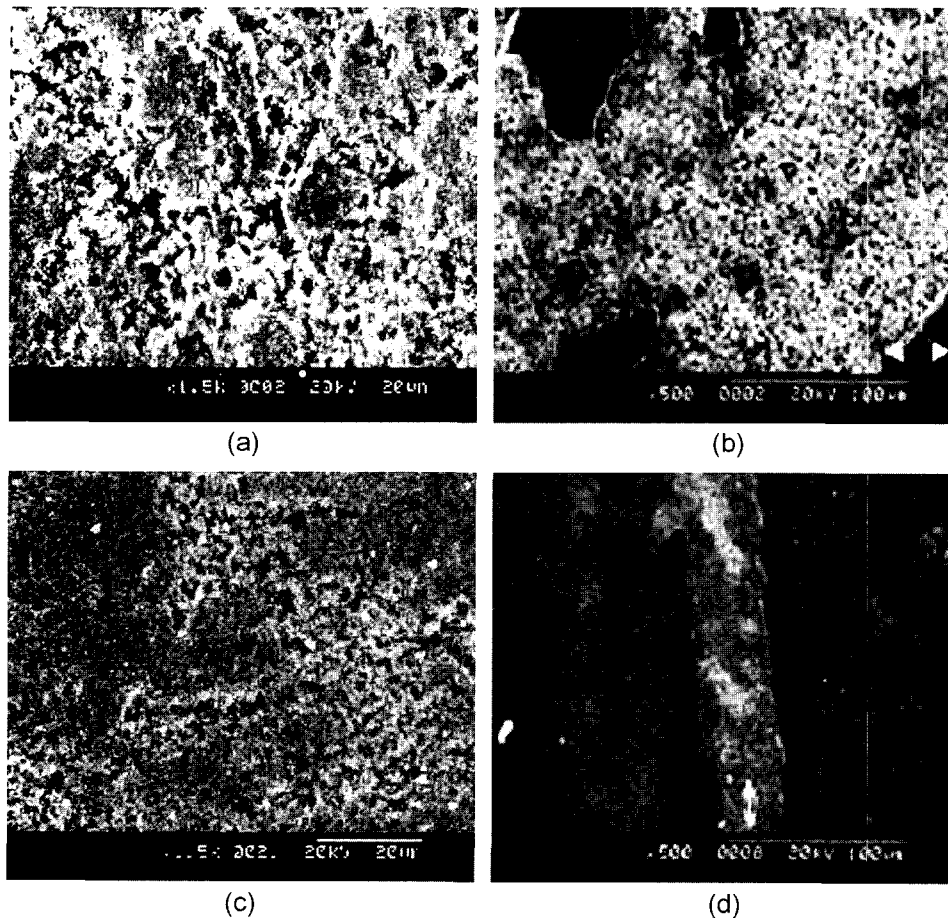


Fig. 5. SEM micrographs of S1 and S4 after sliding test in air at room temperature(a and c) and at 250°C(b and d), respectively. Abrasive wear(a and b) of S1 caused by grain pullout and adhesive wear(c and d, S4) as a result of delamination of the thin layer were shown on the contact surface. Arrow indicates the direction of the reciprocal sliding.

due to the complicated mechanics of concentrated forces. Therefore, S1 was not adequate for biomaterials being implanted in human body, whereas S2, S3, and S4 may be applicable to biomechanical applications such as artificial joints due to excellent phase stability and biotribological properties.

4. Conclusions

The worst wear loss and rate were in the present study observed for S1 tested at room temperature and at 250°C in air due to the debris of monoclinic grains as a result of the spontaneous phase transformation. Although S1 had several advantages due to the fine grain size, it may not be applicable to implant materials being operated in the human body due to osteoclast. On the contrary, S2, S3, and S4 were prospected as the candidate materials of choice for biomechanical applications such as THRs because of their excellent LTD-free properties and wear properties.

Acknowledgement

This work was supported by a grant from Research Institute of Engineering & Technology at Kyung Sung University.

REFERENCES

1. K. Tsukuma, K. Ueda, and M. Shimada, "Strength and Fracture Toughness of Hot Isostatic-pressed Y₂O₃-partially Stabilized ZrO₂-Al₂O₃ Composites," *J. Am. Ceram. Soc.*, **68** C4-C5 (1985).
2. D.-J. Kim, M.-H. Lee, D. Y. Lee, and J.-S. Han, "Mechanical Properties, Phase Stability, and Biocompatibility of (Y,Nb)-TZP/Al₂O₃ Composite Abutments for Dental Implant," *J. Biomed. Mater. Res. (Appl. Biomater.)*, **53** [4] 438-43 (2000).
3. J. Chevalier, J. M. Drouin, and B. Cales, "Low Temperature Aging Behaviour of Zirconia Hip Joint Heads," *Bioceramics*, **10** 135-37 (1977).
4. P. Christel, "Zirconia: The Second Hip Generation of Ceramics for Total Hip Replacement," *Bull. Hosp. Joint Dis. Orthop. Inst.*, **49** [2] 170-79 (1989).
5. B. R. Lawn, "Ceramic-based Layer Structures for Biomechanical Applications," *Current Opinion in Solid State and Mater. Sci.*, **6** 229-35 (2002).
6. D. Y. Lee, D.-J. Kim, and Y.-S. Song, "Chromaticity, Hydrothermal Stability, and Mechanical Properties of t-ZrO₂/Al₂O₃ Composites Doped with Yttrium, Niobium and Ferric Oxides," *Mater. Sci. & Eng. A*, **A289** 1-7 (2000).
7. D. Y. Lee, J.-W. Jang, and D.-J. Kim, "Raman Spectral Characterization of Existing Phases in the ZrO₂-Y₂O₃-Nb₂O₅ System," *Ceram. Intl.*, **27** 291-98 (2001).
8. D. Y. Lee, D.-J. Kim, and D.-H. Cho, "Low-temperature Phase Stability and Mechanical Properties of Y₂O₃ and Nb₂O₅ Co-doped Tetragonal Zirconia Polycrystal Ceramics," *J. Mater. Sci. Lett.*, **17** 185-87 (1998).
9. D. Y. Lee, D.-J. Kim, J.-W. Jang, D.-W. Choi, and S.-J. Lee, "Phase Stability of (Y,Nb)-TZP/Al₂O₃ Composites under Low Temperature Hydrothermal Conditions," *Mater. Lett.*, **39** 221-26 (1999).
10. J.-W. Jang, D.-J. Kim, and D. Y. Lee, "Size Effect of Trivalent Oxides on Low Temperature Phase Stability of 2Y-TZP," *J. Mater. Sci.*, **36** 5391-95 (2001).
11. P. Kumar, J. Shimizu, and M. Oka, "Biological Reaction of Zirconia Ceramics," *Bioceramics*, **1** 341-46 (1989).
12. P. Christel, A. Meunier, M. Heller, J.-P. Torre, B. Class, and C. N. Peille, "Mechanical Properties and Short-term in vivo Evaluation of Yttrium Oxide Partially Stabilized Zirconia," *J. Biomed. Mater. Res.*, **23** 45-61 (1989).
13. D.-J. Kim, H.-J. Jung, J.-W. Jang, and H.-L. Lee, "Fracture Toughness, Ionic Conductivity, and Low Temperature Phase Stability of Tetragonal Zirconia Co-doped with Y₂O₃ and Nb₂O₅," *J. Am. Ceram. Soc.*, **81** [9] 2309-14 (1998).
14. D.-J. Kim, D. Y. Lee, and J.-S. Han, "Low Temperature Stability of Zirconia/Alumina Hip Joint Heads," *Key Eng. Mater.*, **240-242** 831-34 (2003).
15. D. Y. Lee, D.-J. Kim, and B.-Y. Kim, "Influence of Alumina Particle Size on Fracture Toughness of (Y,Nb)-TZP/Al₂O₃ Composites," *J. Eur. Ceram. Soc.*, **22** 2173-79 (2002).
16. H. S. Kim, "Mechanical Properties and Low Temperature Phase Stability of (Y,Nb,Ce)-TZP/Al₂O₃," Master Thesis, Yonsei University (1998).
17. D. Y. Lee and D.-J. Kim, "Strength and Fracture Toughness of Isostatically Hot-pressed (Y,Nb)-TZP/Al₂O₃ Composites," *J. Mater. Sci. Lett.*, **19** 1233-35 (2000).
18. M. J. Mendelson, "Average Grain Size in Polycrystalline Ceramics," *J. Am. Ceram. Soc.*, **74** [2] 431-32 (1991).
19. C. D. Hummer, R. H. Rothman, and W. J. Hozack, "Catastrophic Failure of Modular Zirconia Ceramic Femoral Head Components after Total Hip Arthroplasty," *J. Arthr.*, **10** [6] 848-50 (1995).
20. D. Y. Lee, S.-J. Lee, I.-S. Park, D.-J. Kim, and B.-Y. Kim, "Strength Degradation from Contact Fatigue in Dental Crown Composites," 105th Annual Meeting of American Ceramic Society, Nashville, USA, 2003.