Journal of the Korean Ceramic Society
Vol. 38, No. 7, pp. 602~607, 2001.

The Effect of Nitrogen Plasma Treatment on Tribological Behaviors of Plasma-sprayed Zirconia Coatings

Jong-Han Shin, Jung-Yeob Lee, Chang-Hee Cho and Dae-Soon Lim†

Department of Material Science and Engineering, Korea University, Seoul 136-701, Korea
(Received March 9, 2001; Accepted July 3, 2001)

ABSTRACT

Zirconia powder containing 3 mol% yttria (3Y-PSZ) was coated on the cast iron substrate by plasma spraying method. Coated specimens were then heat treated at 500°C in nitrogen plasma. Wear tests were performed on nitrogen heat treated and non heat treated samples at temperatures from 25°C to 600°C. Wear results showed that the friction coefficient and the wear loss of both the treated and the non-treated samples showed maximum value at 400°C. These results were explained by low temperature thermal degradation due to the monoclinic transformation. Nitrogen plasma treatment significantly improved the tribological performance. The effect of nitrogen heat treatment on tribological behavior was explained by the increased micro-hardness and decreased monoclinic fraction.

Key words **:** ***Zirconia, Nitrogen plasma treatment, Plasma spraying, Tribology***

1. Introduction

Plasma spraying process is a surface treatment technique, which uses a high temperature source to melt the powders into a molten state and propels them by at an extremely high speed onto a base material. Plasma spraying coating has the advantage of being able to control the coating thickness easily and apply to the complex shaped parts. This technique can be applied to various materials requiring wear-resistance, corrosion-inhibition, heat-resistance and thermal insulation. Although plasma spray coating has been used for several decades in various applications due to the advantage of the process, but due to the process where each molten particle has to be coated the bonding strength between the coated layers and uniformity of the coating, existence of pores are points of disadvantage and need further research.[1)]

Zirconia has been considered to be a good candidate coating material for high temperature tribological applications because of its superior properties such as a low thermal conductivity, high thermal expansion coefficient similar to metal and high toughness.[2,3)] In particular, partially stabilized zirconia (PSZ) is one of the most attractive tribological materials because of its good combination of high toughness, strength and hardness.[4)] However, the effect of phase transformation on tribological properties of PSZ should be further studied for high temperature tribological uses, since the significant loss of fracture strength and wear resistance occurs in the temperature ranges of 200~400°C, in particular, in the environments containing water or its vapor.[5,6)]

Previous studies showed that the wear loss increased with the increase in the test temperature and reaching its maximum loss at about 400°C. This unique behavior was explained by the tetragonal to monoclinic transformation.[7-9)] Lange *et al.*, found the presence of $Y(OH)_3$ crystallites and suggested that dissolution of Y elements from the surface into H_2O was responsible for the low temperature thermal degradation.[10)]

Many researchers have tried to improve the low temperature thermal degradation. In the case of the bulk zirconia, the addition of stabilizers and the control of sintering temperature were suggested.[11-13)] However, these treatments have limitation to apply to plasma spray coating, since the control of sintering temperature is not easy in the plasma spray coating. Strength also decreases with addition of the stabilizer. Lerch *et al.* and other researchers reported that the nitrogen treatment at 1300~1500°C was effective for increase in fracture strength.[14-16)] These heat-treatment temperature ranges are too high to use for plasma spray coating on metal substrate.

Therefore in this study, relatively low temperature treatment with nitrogen plasma was tried to investigate the effects of nitrogen plasma treatment on the phase transformation and tribological performance of the plasma coating layer.

2. Experimental procedures

Coating powders used in this study were zirconia powders containing 3 mol% yittria (Tosho product 3Y-PSZ). To obtain the desired shape and size for plasma spraying, the spray-drying method was used.[17)] Scanning electron micrograph of spray-dried granules is shown in Fig. 1. Typical

†Corresponding author : dslim@mail.korea.ac.kr

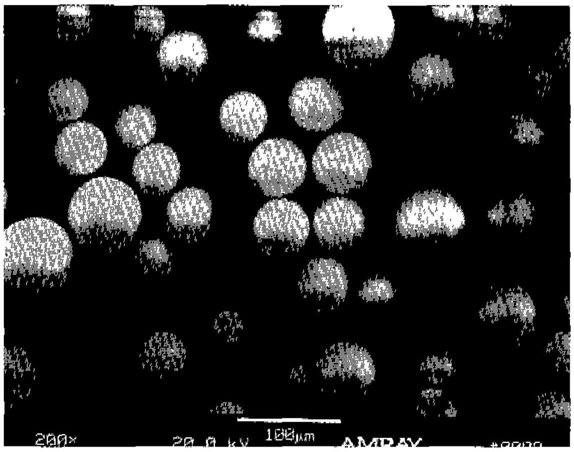

Fig. 1. The SEM image of powders made by spray drying process.

powders produced by this method are shown in Fig. 1. Powders has the spherical granules range in diameter from 40 to 50 μm.

FC25 cast iron was selected as the substrate material because it is being used as cylinder lining in heat engines. Substrate material samples were machined into rings shapes having outer diameter of 30 mm, thickness 5 mm and square shapes of width 30 mm, length 20 mm and thickness of 5 mm.

Plasma spray coating was conducted using spray-dried granules. Prior to plasma spray coating, Ni-Cr-Al composites were applied as a bond coat to enhance adhesion and reduce thermal expansion mismatch between the substrate and the coating layer. The surface of the plasma sprayed coating was very rough so in order to achieve uniform and minimum surface roughness it was ground using a diamond wheel and polished with diamond paste having 6 μm size particles.

After plasma spraying coating, the coating layer was exposed to nitrogen plasma. At 500°C, mixed gases with 90% nitrogen and 10% hydrogen were injected to make nitrogen plasma and then samples were exposed in these plasma nitrogen for 30 minutes. After the heat treatment the amount of diffused nitrogen gas into the coating layer was measured using an Auger Electron Spectroscopy (AES).

Fig. 2 shows the schematic diagram of the high temperature wear tester used to evaluate the friction and wear properties of the sprayed coating. It is capable of conducting wear tests from room temperature to 1000°C. The plate specimen was placed on a reciprocating holder moved by a D.C. motor. The specimen was loaded and slid against a ring type counterpart specimen. Both the plasma treated and non-treated coatings were prepared for the plate type specimens and non-treated coating was used for ring type specimen.

Wear tests were conducted in air and at temperatures of 25, 200, 400 and 600°C by ring on plate type high temperature wear tester. Each test was conducted for 1 hour after 30-minute stabilization at the desired temperature. The

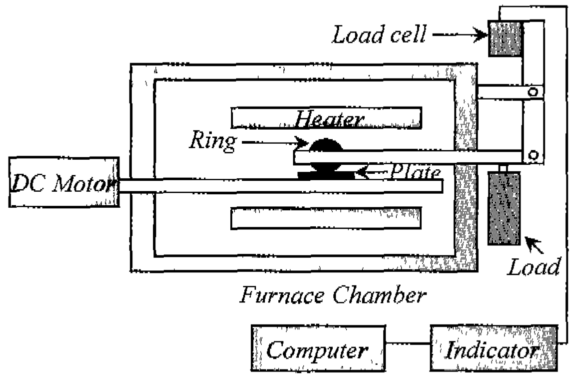

Fig. 2. Schematic diagram of high temperature wear tester.

sliding velocity and stroke length were fixed to 1×10^{-2} m/s and 8×10^{-3} m, respectively. The applied load was 15 N. The relative wear loss was measured by weight change of the plate specimen before and after the experiment. Worn surfaces were observed by using SEM (Scanning Electron Microscopy). For observing the phase transformation before and after the wear test, XRD (X-ray diffractormetry) was conducted with conditions of 30 kV, 30 mA, CuK = 1.5428 Å and from $2\theta = 27\sim33°$ by 0.01/sec step mode. The peaks of (111), $(11\bar{1})$ monoclinic planes and (111) tetragonal plane were analyzed.

3. Results and discussion

Wear tests were performed from room temperature to 600 °C to study the effects of heat treatment in nitrogen plasma atmosphere on wear properties. As shown in Fig. 3 and 4, for both non-treated and nitrogen plasma treated specimens the friction coefficient and the amount of wear loss increased from room temperature to 400°C and decreased at 600°C. The results showed that the friction coefficient and the wear loss values for the nitrogen plasma treated specimen compared with the non-treated specimen were lower

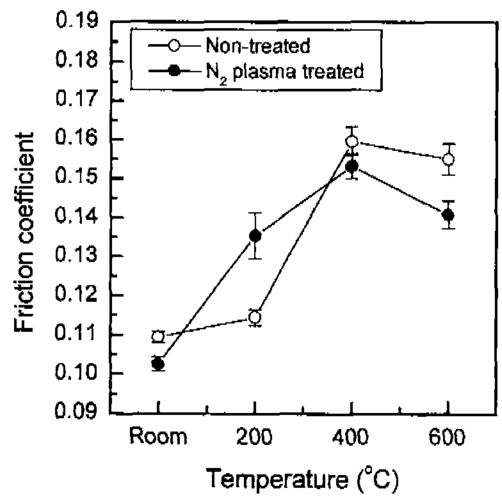

Fig. 3. The friction coefficient of 3Y-PSZ coatings as a function of nitrogen plasma treatment.

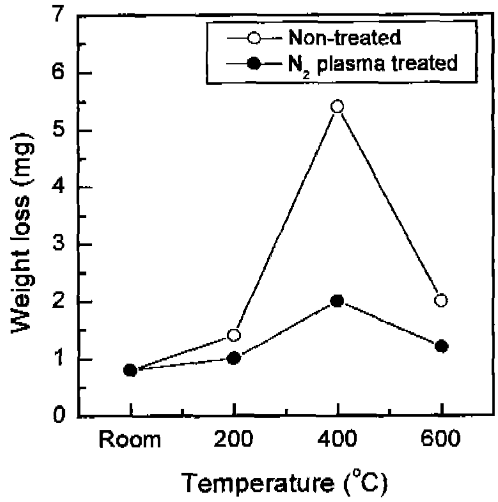

Fig. 4. The wear loss of 3Y-PSZ coatings as a function of nitrogen plasma treatment.

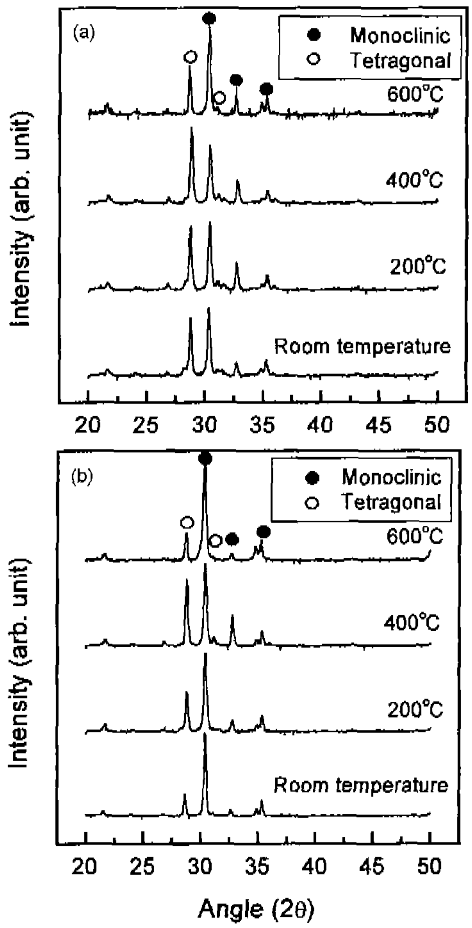

Fig. 5. XRD patterns of 3Y-PSZ coating; (a) non-treated and (b) nitrogen plasma treated.

except at 200°C. The wear loss was maximum at 400°C and the difference of wear rate at that temperature were greatest.

The surface of the specimens tested for wear from room

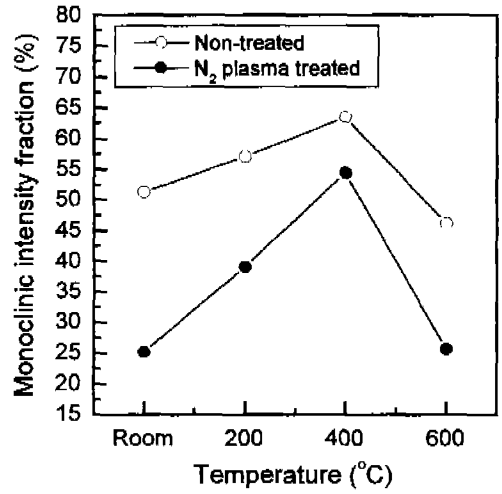

Fig. 6. The changes of monoclinic intensity fraction in non-treated and nitrogen plasma treated samples, tested at various temperatures.

temperature to 600°C were analyzed by using XRD for phase transformation to investigate the relation between phase transformations and wear loss. Fig. 5 shows that the peak intensity of monoclinic or tetragonal phase changes with the testing temperature, and that the peak intensities of monoclinic phase in the plasma treated samples are lower than those in the non-treated samples. The monoclinic intensity fraction was calculated from the following equation,[18]

$$[(11\bar{1})_m + (111)_m]/[(11\bar{1})_m + (111)_m + (111)_t] \times 100 \quad (1)$$

where $(11\bar{1})_m$ is the intensity of monoclinic $(11\bar{1})$ peak, $(111)_m$ is the intensity of monoclinic (111) peak and $(111)_t$ is the intensity of tetragonal (111) peak. The calculated fraction for both group of samples as a function of testing temperature are shown in Fig. 6. The proportion of the monoclinic phase was greatest for both non-treated and nitrogen plasma treated specimen at 400°C. The fraction of the monoclinic phase was lower for the nitrogen plasma treated specimen in the tested temperature range. The degrees of phase transformations coincide with the changes of the friction coefficient and wear loss.

The similar behaviors of phase transformation, friction coefficient and wear loss can be explained by the low temperature thermal degradation of partially stabilized zirconia.[5,6] Low temperature thermal degradation of partially stabilized zirconia is related to the phase transformation phenomena from tetragonal to monoclinic phase at temperatures below 400°C. There is about 3% volume increase from tetragonal to monoclinic phase transformation and microcracks appear around the monoclinic phase. It is reported that this phenomena in the case of repeated friction and wear increase the wear loss whereas in the case of uniaxial stress the micro cracks inhibit the growth of cracks and increases the toughness.[7] The phase transformation to monoclinic increases up to 400°C and the friction coefficient and wear loss gradually increase due to the generation of microcracks. Above 400°C the tetragonal phase is stabilized and the friction coefficient and wear loss decreases.

The nitrogen plasma treated specimens showed lower friction coefficient and wear loss values than non-treated specimens. The nitrogen diffused into the coating acted as stabilizers as suggested by Lerch *et al.*,[14-16] suppressing the phase transformation into monoclinic phase and thus stabilization of the coating led to the decrease in the friction coefficient and wear loss.

The degree of the nitrogen diffusion into the plasma treatment specimen measured by AES is shown in Fig. 7. The average thickness of the coating was approximately 200 μm. Nitrogen contents was maintained to be 1~3 atomic % in plasma coating layer without forming nitride layer on the coating surface.

SEM micrographs of the wear track of 3Y-PSZ coatings after nitrogen plasma treatment are shown in Fig. 8. Fig. 8 reveals that delaminated layers due to the frictional sliding were most frequently observed in sample tested at 400°C. As shown in Fig. 9, more frequent delaminated surfaces were observed in non-treated samples compared to nitrogen plasma treated sample. This observation supports indirectly the explanation of suppressing phase transformation due to nitrogen diffusion.

For the effects of the nitrogen plasma treatment on the mechanical properties. The micro-hardness was investigated and the results are shown in Fig. 10. The micro-hardness for non-treated coatings was 650 kg/mm^2. As the heat treatment temperatures increased, the value of micro-hardness increased. The micro-hardness for the sample treated at 600°C was roughly 750 kg/mm^2. For the specimens treated with nitrogen plasma within the whole temperature range the micro-hardness values showed 12% increase compared to the non-treated specimens. The reason for the

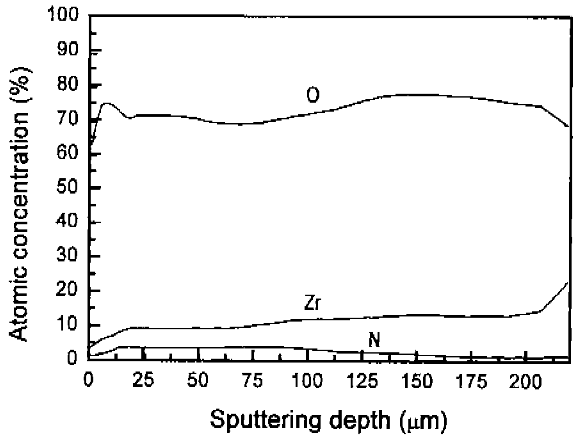

Fig. 7. Atomic concentration of nitrogen in coating after nitrogen plasma treatment.

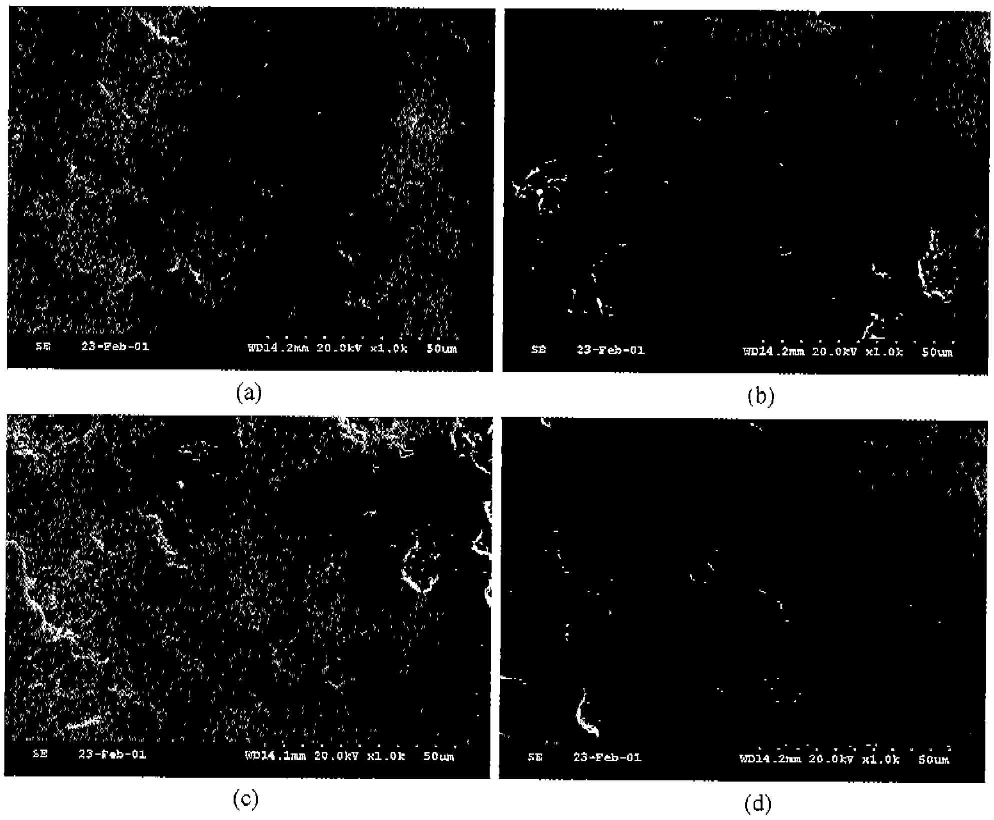

Fig. 8. SEM micrographs of worn surface of nitrogen plasma treated sample at various test temperature; (a) room temperature, (b) 200°C, (c) 400°C and (d) 600°C.

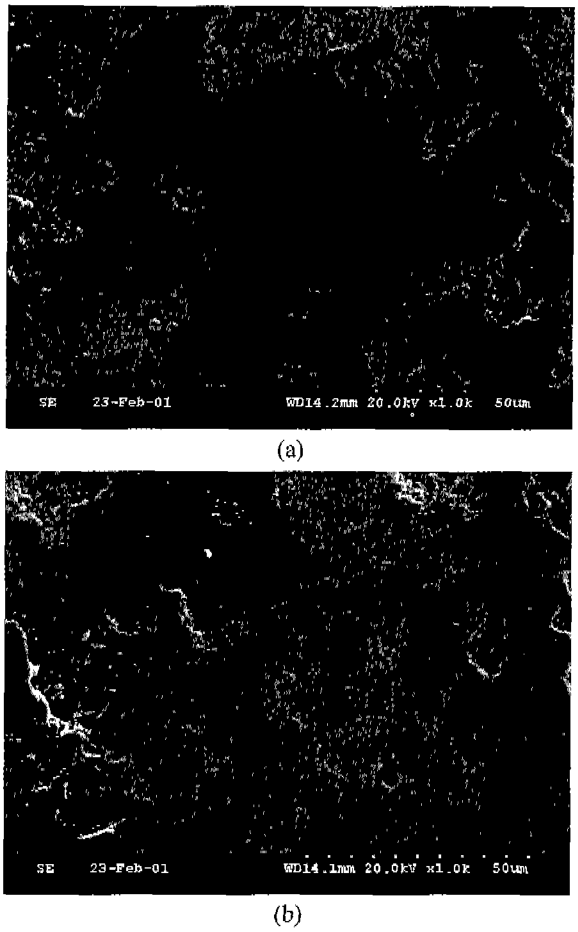

Fig. 9. SEM micrographs of worn surface at 400°C; (a) non-treated and (b) nitrogen plasma treated.

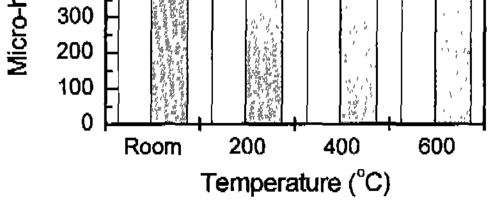

Fig. 10. The micro-hardness changes of 3Y-PSZ coatings at various heat-treated temperature.

increase in micro-hardness is thought to be due to the stabilization of the tetragonal phase by plasma treatment. The results also showed that micro-hardness increased with increasing heat treatment for nitrogen plasma treated and non-treated specimen. This tendency might be due to the removal of residual stress within the coating layers. Previous study showed that heat treatment released the tensile residual stress that induced by plasma spraying process.[19] Both increased micro-hardness and decreased monoclinic fraction due to suppressing phase transformation contribute to the improvement of the high temperature tribological performance for nitrogen plasma treated zirconia coatings.

4. Conclusion

The friction coefficient and wear loss for all the non-treated and nitrogen plasma treated specimens showed a gradual increase from room temperature to 400°C and decreased at 600°C. The cause for such results was explained by the low temperature thermal degradation phenomena of the zirconia that is the phase transformation from monoclinic to the tetragonal phase. The diffused nitrogen stabilized the tetragonal phase in the coating and resulted in lowering the friction coefficient and wear loss of the nitrogen plasma treated coatings. The nitrogen plasma treatment increased the micro-hardness of the coating by heat treatment and nitrogen diffusion. Significant improvement of the wear degradation at 400°C was explained by the maximization of the suppressing the phase transformation.

Acknowledgements

This research was supported by the special research support fund from Korea university. Also the authors would like to thank Dr. Gi-Suk Nam and Dr. Eung-Sun Byun in the thin film process group in the surface technique research department of KIMM for their help in the nitrogen plasma heat treatment of the specimens.

REFERENCES

1. L. Pawlowski, The Science and Engineering of Thermal Spray Coatings, John Wiley & Sons Ltd, Chichester, 1st edn, p. 28, 1995.
2. R. J. Bratton and S. K. Lau, "Zirconia Thermal Barrier Coatings," *Advances in Ceramics*, **3**, 226-240 (1981).
3. E. C. Subbarao, "Zirconia-an Overview," *Advances in Ceramics*, **3**, 1-24 (1981).
4. T. A. Taylor and D. L. Applrby, "Plasma-sprayed Yttria-Stabilized Zirconia Coatings; Structure-property Relationships," *Surf. Coat. Tech.*, **43-44**, 470-480 (1990).
5. T. Sato and M. Shimada, "Crystalline Phase Change in Yttria-partially-stabilized Zirconia by Low Temperature Annealing," *J. Am. Ceram. Soc.*, **68**, C212-C213 (1985).
6. T. Sato, Ohtaki and M. Shimada, "Transformation of Yttria-partially-ptabilized Zirconia by Low Temperature Annealing in Air," *J. Mater. Sci.*, **20**, 1466-1470 (1985).
7. J. Y. Kim and D. S. Lim, "The Effects of the Annealing Temperature and Environments on the Room Temperature Wear Behavior of Plasma Sprayed Partially Stabilized Zirconia Coatings," *J. Kor. Cer. Soc.*, **31**(10), 1176-1180 (1994).

8. K. Y. Oh and S. D. Jang, "Phase Transformation and Mechanical Properties of Reaction Sintered Mullite-zirconia (Yttria) Composite," *J. Kor. Cer. Soc.*, **28**(7), 549-555 (1991).
9. H. J. Jung and Y. J. Oh, "Some Physical and Electrical Properties of Zirconia Solid Electrolyte Contained Yttria," *J. Kor. Cer. Soc.*, **23**(1), 13-20 (1986).
10. M. Yoshimura, T. Noma, K. Kawabata and S. Somiya, "Role of H_2O on the Degradation Process of Y-TZP," *J. Mater. Sci. Lett.*, **6**, 465-467 (1987).
11. W. M. Kriven, "Possible Alternative Transformation Toughers to Zirconia : Crystallographic Aspects," *J. Am. Ceram. Soc.*, **71**(12), 121-130 (1988).
12. N. Claussen, "Stress-induced Transformation of Tetragonal ZrO_2 Particles in Ceramic Matrices," *J. Am. Ceram. Soc.*, **61**(1-2), 85-56 (1978).
13. M. Li and Z. Chi, "Transformation from Metastable Tetragonal Structure into a Monoclinic in Zirconia Powder, in Science and Technology of Zirconia," Advances in Ceramics, **24**, 143-250 (1988).
14. M. Lerch, "Nitridation of Zirconia," *J. Am. Ceram. Soc.*, **79**(10), 2641-2644 (1996).
15. Y. B. Cheng and D. P. Thompson, "Nitrogen-containing Tetragonal Zirconia," *J. Am. Ceram. Soc.*, **74**(5), 1135-1138 (1991).
16. Y. B. Cheng and D. P. Thompson, The Nitriding of Zirconia; pp. 149-162 in Special Ceramics, Vol. 9. The Institute of Ceramics, Stoke-on-Trent, U. K., 1992.
17. R. Kamo and W. Bryzik, "High Temperature Lubrication of Adiabatic Engine," *Int. Tribology Conf.*, 1231-1236 (1995).
18. R. C. Garvie and P. S. Nicholson, "Phase Analysis in Zirconia System," *J. Am. Ceram. Soc.*, **55**(6), 303-305 (1972).
19. J. H. Shin, D. S. Lim and H. S. Ahn, "Effect of Annealing and Fe_2O_3 Addition on the High Temperature Tribological Behavior of the Plasma Sprayed Yttria-stabilized Zirconia Coating," *Surf. Coat. Tech.*, **133-134**, 403-410 (2000).