Hertzian Contact Fatigue Test of Y-PSZ and Y-PSZ/Al₂O₃ Ceramics in Hot Water

Jing-Feng LI, Masaru ONO, * Ryuzo WATANABE and Shigetaka WADA**

Department of Materials Processing, Graduate School of Engineering, Tohoku University, 02, Aza-Aoba, Aramaki, Aoba-ku, Sendai-shi 980-8579
*Graduate School, Tohoku University, 02, Aza-Aoba, Aramaki, Aoba-ku, Sendai-shi 980-8579
**Toyota Central R & D Labs., Inc., Nagakute, Aichi 480-1192

A Hertzian contact fatigue test was proposed to simulate conventional rolling wear experiments, by which the wear behavior and phase transformation of 3 mol%Y₂O₃-partially stabilized zirconia (3Y-PSZ) and 3Y-PSZ/20 mass%Al₂O₃ ceramics in water at 90°C were investigated. The Hertzian stress contact fatigue property was found to be greatly dependent on fracture strength and remarkably improved by the post-HIP treatment. The Hertzian contact stress was revealed to have minor influence on the water-assisted tetragonal-to-monoclinic phase transformation in Y-PSZ-based ceramics at temperatures as low as 90°C. The addition of Al₂O₃ into Y-PSZ effectively suppressed the low-temperature phase transformation, but it did not lead to the improvement in the contact fatigue property probably because the strength of the resultant composite was lower than the monolithic Y-PSZ; however, more work is required to completely understand the Hertzian stress contact fatigue behavior of composites. [Received May 19, 1999; Accepted June 21, 1999]

Key-words: Zirconia, Alumina, Ceramic composite, Bearing materials, Contact fatigue, Wear, Hertzian stress, Phase transformation

1. Introduction

New ceramics possess many attractive properties, such as high strength and hardness, low friction coefficient, low density and chemical stability, for bearing applications. For example, silicon nitride (Si₃N₄) ceramics have been successfully applied to the rolling elements for Si₃N₄ hybrid bearings consisting of ceramic balls and steel supports, which show superior performance in comparison with conventional all-steel bearings.1) 2) Besides Si₃N₄ ceramics, Y₂O₃-partially stabilized zirconia (Y-PSZ) ceramics also have been considered as bearing materials.3) The rolling wear properties of Y-PSZ ceramics have been studied,4) 5) 6) 7) but most of them were limited to comparing Y-PSZ ceramics with other advanced ceramics, such as Si₃N₄, SiC, SiAlON and Al₂O₃. Nevertheless, Y-PSZ ceramic may be promising materials for all-ceramic bearings to be used in severe environments containing acid or alkali solutions as it is generally more corrosion-resistant than non-oxide Si₃N₄ ceramics.

As to Y-PSZ ceramics, the wear behavior is in close relation with the tetragonal-to-monoclinic phase transformation,3) 4) which contributes high fracture toughness and strength to the PSZ ceramics. However, apart from that well-known stress-induced martensitic transformation, there exists another type of phase transformation that takes place during aging or in service within a specific temperature range.10) 11) 12) The latter aging-induced type of phase transformation is accelerated in the presence of water and responsible for the low-temperature degradation problem of Y-PSZ ceramics. The main concern is whether such phase transformation affects the applicability of Y-PSZ ceramics to bearing materials, especially for use in acid or base solutions. More work is therefore needed to explore the influence of the phase transformation on the rolling wear properties of Y-PSZ ceramics.

In the present study, we proposed a simple testing method, Hertzian contact fatigue test (see Fig. 1), to simulate conventional rolling wear experiments. The wear and fracture behaviors were investigated with an emphasis on the tetragonal-to-monoclinic phase transformation in the cyclically contacted areas in hot water. Neither acid nor alkali solution was used because the cause for the phase transformation was water, no matter where, acid or alkali solutions, it is in.11) Experiments were concentrated on ZrO₂-3 mol%Y₂O₃ (3Y-PSZ) ceramics, while 3Y-PSZ/20 mass%Al₂O₃ also was investigated for comparison because it is known that the addition of Al₂O₃ into Y-PSZ can effectively suppress phase transformation during aging in water.10) 12)
2. Experimental procedure

2.1 Materials preparation and characterization

Commercial ZrO$_2$-3 mol%Y$_2$O$_3$ (3Y) and ZrO$_2$-3 mol% Y$_2$O$_3$/20 mass% Al$_2$O$_3$ (3Y2OA) powders, manufactured by Tosoh Corp., Tokyo, Japan, were used as starting materials. The as-received powders were formed into pellets and plates by die pressing at 30 MPa and subsequent cold-isostatic pressing (CIP) at 300 MPa. The green compacts were sintered in air for 2 h at 1370 and 1550°C, respectively, for the 3Y and the 3Y2OA. Most of the pressureless-sintered samples were treated by cladless hot-isostatic pressing (HIP), also called post-HIP treatment, to eliminate any possible residual pores. The post-HIP treatments were performed under 200 MPa of argon gas with soaking time for 2 h, and at three temperatures (1300, 1400, 1500°C) for the 3Y and at 1500°C for the 3Y2OA.

Density was measured by the Archimedes method. Microstructures were observed by scanning electron microscopy (SEM). Grain sizes were determined using the line-intercept technique on scanning electron micrographs of polished and thermally etched (1300°C, 1 h) surfaces. Fracture strength was measured in a 4-point bending test with lower and upper spans of 20 and 10 mm, respectively. The bending tests were performed at a crosshead speed of 0.5 mm/min by using specimens of nominal dimensions 24 mm × 2.0 mm × 1.5 mm. The prospective tensile surfaces were ground and polished to achieve a mirrorlike surface finish prior to mechanical testing. Young's modulus and Poisson's ratio were measured at room temperature by a static method using a cross-shaped electrical-resistance strain gauge mounted onto a bend specimen. Vickers microhardness was measured under a load of 4.9 N. Fracture toughness was measured by the Vickers indentation microfracture (IM) technique under a load of 49 N, and the values were calculated using the equation proposed by Niihara et al.\textsuperscript{20} for Palmqvist cracks.

2.2 Hertzian contact fatigue test

As shown in Fig. 1, one well-polished surface of a disc specimen in hot water is indented cyclically by a stainless steel (JIS SUS440C) bearing ball (4.76 mm in diameter). The water was heated and kept at 90°C using a heater soaked in it. The water was heated and kept at 90°C using a heater soaked in it. The temperature was selected because at which the low-temperature aging phase transformation can be significantly induced by water, whereas at higher temperatures the thermal activation may cause the phase transformation even in the absence of water.\textsuperscript{14)-17}

Cyclic loading in the form of a triangular wave between 98 and 980 N in compression was applied to the specimen at a frequency of 10 Hz, by using a fatigue-testing machine (EHF-ED 100KN-10L, Shimadzu Corp., Japan). The minimum load was used intentionally to prevent any possible movement of the tested specimen from its initial position. The maximum load was determined because our preliminary experiments confirmed that inelastic deformation would be caused at the higher loads. Chen et al.\textsuperscript{21} also used a similar method to investigate the contact damage process in Si$_3$N$_4$ ceramics. Compared with normal ball-on-disc type rolling testing, the Hertzian contact fatigue test has the following advantages. First, the damage and fracture can easily be monitored and analyzed because the applied stresses were repeated at the same place. Second, the influence of wear debris, which usually complicates the tribological problems of ceramics, can be neglected. Finally, small sized specimens make the experiments easy.

The contact areas were observed by scanning electron microscopy. The changes in surface roughness were measured with a profilometer. The phase compositions around the contact areas were analyzed with a microfocus X-ray diffractometer (30 μm beam in diameter) with Cu Kα radiation. The monoclinic intensity fraction was evaluated from the ratio between the XRD height of the two monoclinic peaks, (111)$_m$ and (111)$_m$, and the tetragonal peak (111)$_t$.\textsuperscript{21}

3. Results and discussion

3.1 Major mechanical properties

Table 1 summarizes some mechanical properties of the materials investigated in this study, including Young's modulus, Poisson's ratio, 4-point bending strength, Vickers hardness, fracture toughness and density. The bending strengths were increased remarkably after the HIP treatment from the quite high level obtained in the pressureless-sintered specimens, showing a maximum when the post-HIP was performed at 1400°C. The other properties were varied slightly after the post-HIP at the different temperatures. The addition of Al$_2$O$_3$ increased Young's modulus, hardness and fracture toughness, whereas the strength for the composite was not so improved by the post-HIP treatment as in the monolithic PSZ ceramics. The increases in Young's modulus and hardness by the addition of Al$_2$O$_3$ were simply due to the rule of mixture; Al$_2$O$_3$ is much stiffer and harder than PSZ. The fracture toughness was in-

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Process</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Young's modulus (GPa)</th>
<th>Poisson's ratio</th>
<th>Vickers hardness (GPa)</th>
<th>Bending strength (MPa)</th>
<th>Fracture toughness (MPa m$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Y (3mol% Y$_2$O$_3$/ZrO$_2$)</td>
<td>Normally Sintered (NS, 1370 °C)</td>
<td>6.02</td>
<td>184</td>
<td>0.303</td>
<td>14.8±0.4</td>
<td>1080±120</td>
<td>4.56±0.20</td>
</tr>
<tr>
<td></td>
<td>NS (1370 °C)+ HIP (1500 °C)</td>
<td>6.08</td>
<td>191</td>
<td>0.304</td>
<td>15.1±0.3</td>
<td>2096±153</td>
<td>4.65±0.22</td>
</tr>
<tr>
<td></td>
<td>NS (1370 °C)+ HIP (1400 °C)</td>
<td>6.09</td>
<td>191</td>
<td>0.305</td>
<td>15.3±0.2</td>
<td>2370±80</td>
<td>4.69±0.13</td>
</tr>
<tr>
<td></td>
<td>NS (1370 °C)+ HIP (1500 °C)</td>
<td>6.08</td>
<td>192</td>
<td>0.306</td>
<td>14.8±0.3</td>
<td>2177±96</td>
<td>4.94±0.18</td>
</tr>
<tr>
<td>3Y2OA (3Y/20mass%Al$_2$O$_3$)</td>
<td>Normally Sintered (NS, 1550 °C)</td>
<td>5.48</td>
<td>237</td>
<td>0.289</td>
<td>15.9±0.2</td>
<td>944±82</td>
<td>6.24±0.80</td>
</tr>
<tr>
<td></td>
<td>NS (1550 °C)+ HIP (1500 °C)</td>
<td>5.51</td>
<td>238</td>
<td>0.289</td>
<td>16.3±0.3</td>
<td>1800±50</td>
<td>6.28±0.22</td>
</tr>
</tbody>
</table>
creased by the addition of 20 mass% \text{Al}_2\text{O}_3, probably because of the dispersion toughening effect of \text{Al}_2\text{O}_3 particles as analyzed in our previous papers,\textsuperscript{22,23} Although high strength over 2.5 GPa was reported in \text{Al}_2\text{O}_3-dispersed PSZ composites,\textsuperscript{24} the strength of the present 3Y20A subject to the post-HIP was not high enough, probably because the pressureless sintering and HIPping temperatures were not optimized.

Figure 2 shows the representative SEM micrographs of the thermally etched surfaces of 3Y and 3Y20A specimens. Some small pores were often found on the surface in the specimens prior to the HIP treatment. Such residual pores in the pressureless-sintered 3Y sample were totally eliminated after the HIP treatment conducted at 1400 and 1500°C; however, the grain sizes became obviously larger after HIPping at the latter temperature. The zirconia matrix of the 3Y20A specimens before HIPing already had fairly larger grains than the pressureless-sintered 3Y specimens, so that post-HIP at 1500°C resulted in a coarser microstructure in the 3Y20A. The strength first increased as residual pores were eliminated, but tended to decrease when the grain growth became remarkable. That is why there existed an optimal HIPping temperature, where the strength of the 3Y showed a maximum. The effects of post-HIP on the strength improvement in Y-PSZ ceramics had also been examined by Kim et al.\textsuperscript{25} The 3Y specimen HIPed at 1400°C was mainly used for the following Hertzian contact fatigue test since it had the highest bending strength.

3.2 Morphology of Hertzian contact areas
The Hertzian contact fatigue tests were interrupted after

![Fig. 2. SEM micrographs of polished and thermally etched (1300°C, 1 h) surfaces of the materials investigated. (a) non-HIPed 3Y, (b) 3Y HIPed at 1300°C, (c) 3Y HIPed at 1400°C, (d) 3Y HIPed at 1500°C, (e) non-HIPed 3Y20A, (f) 3Y20A HIPed at 1500°C](image)

![Fig. 3. Change in surface roughness. (a) non-HIPed 3Y, tested for 50 h; (b-1, 2, 3) HIPed 3Y, tested for 50, 100, 200 h; (c-1, 2) HIPed 3Y20A, tested for 100 and 200 h.](image)

![Fig. 4. SEM micrographs (left: overall image, right: damaged/worn area at high magnification) of the Hertzian contact areas for the following specimens. (A-1) and (A-2): non-HIPed TZ-3Y, tested for 50 h (1.8 × 10^6 cycles) (B-1) and (B-2): TZ-3Y HIPed at 1400°C, tested for 100 h (3.6 × 10^6 cycles) (B-1) and (B-2): TZ-3Y20A HIPed at 1500°C, tested for 100 h (3.6 × 10^6 cycles).](image)
a period of time, and the resultant contact areas were observed by SEM. Figure 3 shows the profiles of the surface roughness across the contact areas, and some representative SEM micrographs of the contacted areas are shown in Fig. 4. The morphology of the contact areas can be divided into two groups by the formation of Hertzian cone cracks. The 3Y specimen before post-HIP treatment was most sensitive to the Hertzian contact fatigue test. As shown in Fig. 4(A-1), a series of circles corresponding to Hertzian cone cracks were formed in it after testing for 50 h \((1.8 \times 10^6)\) cycles. Three non-HIPed 3Y specimens were tested, but other two ones were more damaged than that shown in Fig. 4. On the other hand, the HIPed 3Y became much more resistant again the Hertzian contact fatigue test. Only a shallow depression was detected in the HIPed 3Y tested for the same 50 h by the surface roughness measurement, whereas the contact area was not so contrasted for SEM observation. Even after 100 h \((3.6 \times 10^8)\) cycles), only a slightly contrasted ring was formed on the surface of the HIPed 3Y. The SEM observation at high magnification showed that some surface grains on the ring were removed away, resulting in a considerable increase in surface roughness. Comparing Fig. 4(B-2) with Fig. 4(C-2), it seems that the surface of the 3Y2OA was more damaged than that of the 3Y. This was also confirmed by the difference in surface roughness as shown in Figs. 3(b-2) and (c-1). Eventually after testing for 200 h, although chipping was introduced in the two specimens and consequently the contact area became significantly rough, by comparing the roughness profiles shown in Figs. 3(b-3) and (c-2) it is clear that chipping was more severe in the HIPed 3Y2OA specimen. Hertzian cone cracks are known to be caused by the maximum tensile stress just outside the circumference of the contact area,\(^ {26}\) The maximum tensile stresses, \(\sigma_{\text{max}}\), corresponding to the maximum load, \(P=980\) N, were 942 and 1088 MPa, respectively, for the 3Y and 3Y2OA, according to the following equations,\(^ {26}\)

\[
\sigma_{\text{max}} = \frac{1 - 2v_1}{2} \frac{P}{\pi a^2}
\]  

where the radius of the contact area, \(a\), is given as follows:

\[
a = \sqrt{\frac{3PR}{4}} \left[ \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \right]
\]

where \(R\) is the ball radius, and \(E\) and \(v\) are Young’s modulus and Poisson’s ratio for the specimen (subscript 1) and ball (subscript 2). Young’s modulus and Poisson’s ratio are 196 GPa and 0.3 for the ball used in the present study. Hertzian cone cracks were easily formed in the 3Y specimen without post-HIP treatment, because its bending strength was lower than the maximum tensile stress at Hertzian contact. On the other hand, the maximum tensile stresses are quite lower than the bending strengths of the HIPed 3Y and HIPed 3Y2OA ceramics. Between them, the HIPed 3Y2OA had a lower bending strength than the HIPed 3Y, which may be responsible for the inferior contact fatigue property of the 3Y2OA composite. However, the Hertzian contact fatigue of composites may be more complicated due to the influence of local fatigue resulting from the different properties of the dispersion and matrix, as compared with the case of monolithic ceramics. 

### 3.3 Phase transformation

To clarify the influence of Hertzian stress on the phase transformation in the presence of hot water, the following four points on the surface of the tested specimen were examined by the micro-focused XRD technique: (a) the center of contact area, (b) the worn ring, (c) just outside the ring, and (d) a place far from the contact area, as schematically illustrated in Fig. 5. It should be mentioned that point (d) was stress-free and points (a) through (c) were subject to different stresses when the applied load was cyclically varied between the minimum (98 N) and maximum (980 N) load. The stress at point (b) changed between compression and tension, whereas point (c) received only tension with a variation in magnitude.

Figure 6 shows the XRD results for the HIPed 3Y specimen subject to the Hertzian contact fatigue test for 100 h, and the amounts of monoclinic phases formed at the different points were shown in Fig. 7. It is interesting that almost no monoclinic phases were detected at the center of the contact area (point a) in the two specimens. The center was prevented from the influence of water since it was not detached from the surface of the ball, and was impressed at least under a minimum compressive load (98 N). On the other hand, certain amounts of monoclinic phases were formed at the surface far from the contact area (point d). This result confirmed the influence of water on the low-temperature phase transformation in Y-PSZ ceramics. In addition, the fact that the 3Y2OA specimen had smaller amount of monoclinic phases again indicated the suppression effect of \(\text{Al}_2\text{O}_3\) addition on the low-temperature phase transformation in Y-PSZ ceramics.\(^ {16,10}\) The monoclinic
phases formed at point (d) were totally induced by water and heat, whereas at point (b) normal stress-induced martensitic phase transformation also probably occurred due to the wear-related microfracture, in addition to the water-assisted isothermal phase transformation. The difference in monoclinic intensity fraction between points (c) and (d) was thought to be due to the influence of the maximum (Hertzian) tensile stress. Considering that the amounts of monoclinic phases were not so different at points (b) through (d) in spite of their different histories, it appears that Hertzian contact stresses have minor influence on the low-temperature isothermal phase transformation of Y-PSZ during aging in water, or in other words, such a type of phase transformation is not further stimulated by repeated Hertzian contact stress.

The present experiments were conducted in water at 90°C to intentionally accelerate the phase transformation and to investigate any possible influence of Hertzian contact stress on it. At temperatures lower than 80°C, the phase transformation in the present Y-PSZ ceramics becomes exceptionally difficult even in water. Although a post-HIP treatment is necessary for the strength improvement, the Y-PSZ-based ceramics may be a candidate for bearing materials in acid or alkali solutions at least at ambient temperature.

4. Conclusion

(1) Post-HIP treatment can remarkably increase the Hertzian stress contact fatigue properties of Y-PSZ ceramics through the significant improvement in strength; therefore, post-HIP treatment seems indispensable for ceramic bearing elements, particularly, those made of Y-PSZ ceramics.

(2) Although the experiments were conducted under some specified conditions, the present study revealed that the low-temperature aging phase transformation in Y-PSZ ceramics, which can be induced in water at temperatures as low as 90°C even without any aids of external stresses, is not further accelerated by repeated Hertzian contact stresses.

(3) The addition of Al2O3 into Y-PSZ can effectively suppress the low-temperature aging phase transformation, but more work is needed to determine if Al2O3-containing Y-PSZ composites are more resistant against Hertzian stress contact fatigue.

Acknowledgment The authors wish to thank Mr. H. Kohno, Toyota Central R & D Labs., Inc., for his assistance in conducting the microfocus X-ray diffraction experiments.

References