Journal of Korean Powder Metallurgy Institute
Vol. 8, No. 3, 2001

Microstructural Wear Mechanism of Al_2O_3-5 vol% SiC Nanocomposite and Si_3N_4 Ceramics

Doh-Hyung Riu, Yoon-Ho Kim, Soo-Wohn Lee* and Koichi Niihara****
Korea Institute of Ceramic Engineering and Technology, 153-023, Seoul, Korea
**Sun-Moon University, 336-840, Asan, Korea*
***ISIR, Osaka University, Ibaraki, 567-0047, Japan*

(Received July 12, 2001)

Abstract Through the observation of wear scar of two ceramic materials, microstructural wear mechanisms was investigated. As for the Al_2O_3-5 vol% SiC nanocomposite, the grain boundary fracture was suppressed by the presence of SiC nano-particles. The intragranular SiC particles have inhibited the extension of plastic deformation through the whole grain. Part of plastic deformation was accommodated around SiC particles, which made a cavity at the interface between SiC and matrix alumina. On the other hand, gas-pressure sintered silicon nitride showed extensive grain boundary fracture due to the thermal fatigue. The lamination of wear scar was initiated by the dissolution of grain boundary phase. These two extreme cases showed the importance of microstructures in wear behavior.

Keywords : Al_2O_3-SiC nanocomposite, Silicon nitride, Microstructure, Wear mechanism

1. Introduction

Ancient Egyptians used a lever with roller to move the heavy blocks of stone. With those tools they could save their manual forces. The modern day life still needs the relief of friction for the rotating or sliding parts of machine. Heat engines have a number of contacting or moving parts that consume dynamical force, and they drop the efficiency of engine. Even with only 0.1 point drop of friction coefficient, it will lead to the steep increase of mileage. For this purpose, sintered ceramics with low specific gravity have been used as small parts of the dynamic contact or rotation machinery of heat engine. Under such an un-lubricating and high temperature condition, the materials are prone to wear by various stages of mechanisms such as tribochemical, oxidation, micro fracture and abrasive wear.1)

In this report microstructural wear mechanism of two representing structural ceramic materials are compared and investigated with an emphasis on the microstructural aspect. One is Al_2O_3-5 vol% SiC nanocomposite that represent a solid state sintered ceramics. The other one is a gas-pressure sintered silicon nitride ceramics that involves a grain boundary liquid phase due to the addition of large amount of sintering additives. These two materials were selected to illustrate and compare the behavior of grain boundary fracture characteristics during severe wear.

The wear of polycrystalline alumina have been known to depend on (1) the microstructural variables such as mean grain size, grain size distribution, and porosity,2,3) (2) the composition such as an impurity, glass phase,4,5) and also (3) test geometry and environment.6) Most of investigations into the influence of microstructure on the wear resistance of alumina ceramics have shown that wear rate decreases as grain size decreases. This was attributed mostly to the grain boundary micro-fracture, occurrence of which determines the transition from mild to severe wear.2,3)

Cho et. al.2) investigated the wear transition behavior of various grain sized alumina ceramics and suggested a damage accumulation model, in which internal stresses associated with damage accumulated during the initial stage leads to crack initiation and propagation. The grain boundary cracking is known to occur after a prescribed period of initial stage wear, which depends on the level of stress applied and damage accumulation. When the slip arrays and twins generated by the asperity contact is accumulated in grain boundary, where they cannot be accommodated each other since the plastic flow in each grains has characteristic anisotropy with respect to their relative orientations, the grain boundaries act as sites for crack nucleation.[2)]

There is no clear evidence about the extent of the deformation region under the subsurface during grinding or polishing. But, it is generally accepted that the process defect is generally on the order of a grain with mild grinding.[7)] This is might be due to the fact that the generation of slip band and twin is limited in single grains. This residual stress damage is not strictly confined to the vicinity of the individual surface scratches or furrows produced during the initial stage of wear. Instead, the dislocations are characteristically contained within slip arrays which generally span the individual grains.[2)]

The easy grain pull out in alumina has been considered to be due to the residual stress that is originated from the anisotropic thermo-elastic properties of alumina and developed along grain boundaries when the sintered body was cooled from the sintering temperature to the ambient temperatures.[8)] The residual stress level is known to scale up with grain size as suggested by Coble et. al.[9)] The abrasive wear rates have been reported to increase with grain size, which have been attributed to the residual stress by Cho et. al.[2)]

For the people who have experiences in grinding alumina ceramic for the final finishing of the surface, it was difficult to obtain a mirror surface with fine grinding due to the grain pull out or pitting out phenomenon.[8)] By contrast, in the case of Al_2O_3/SiC nanocomposite, mirror surface can be readily obtained, which implies the suppression of the pullout of alumina grain compared to the monolithic alumina. This good surface finish encourages investigating into the wear behavior of the nanocomposite. However, only a few papers have described the wear behavior of Al_2O_3/SiC nanocomposites. Davidge et. al.[10)] have compared the wet erosive wear of monolithic Al_2O_3 and Al_2O_3-SiC composites. They reported 2-3 factor of decrease of wear rate for composite and attributed it to the reduced grain boundary cracking by the dispersion of SiC nano particles. More recently, Moya et. al[11)] have reported the sliding wear behavior of Al_2O_3/SiC nanocomposite. Intergranular and transgranular fracture was observed for the nanocomposite at low contact loads. At high contact loads, wear has occurred via intergranular fracture dominantly. However, their results showed that the wear resistance of the nanocomposite was order of magnitude better than the monolithic alumina when the applied load ranges was greater than 50 N. No further microstructural wear mechanism was not suggested.

In this report microstructural wear mechanism of Al_2O_3-5 vol% SiC nanocomposite is suggested. In order to reveal the microstructural mechanism the wear surface was observed with TEM with the help of diffraction analysis. Through the observation of the wear surface of the nanocomposite, the generation and accommodation of deformation damage and fracture is identified and discussed.

Silicon nitride ceramics have been used as wear parts where application of lubrication is limited. Under conditions like this, the materials suffer an extensive friction and wear due to the interaction between the two bodies or three bodies.[12)] Tomizawa and Fisher[13)] studied the effects of temperature and humidity on friction coefficient and wear rate of hot-pressed silicon nitride. They showed that the friction coefficient for the tests conducted in a dry atmosphere and in a temperature range 150-800°C was approximately 0.8. Under these conditions, wear was primarily controlled by intergranular micro-fracture. Skopp et al.[14] have reported that mechanical wear with fatigue between the grains and the amorphous grain boundaries predominates at lower velocities.

In this study, the deformation and fracture behavior of GPS sintered Si_3N_4 during the unlubricated sliding wear were investigated with electron microscopy. By observation of the cross section as well as plane surface of the wear scar, delamination process was precisely investigated and discussed. The pull out of grains is controlled by the preferential grain boundary phase sweeping out of fatigue of grain boundary by the thermo-chemical dissolution

2. Experimental Procedure

2.1. Materials

α-Al_2O_3(AKP-53, 0.3 μm, Sumitomo, Japan) was used as a matrix materials. Mixed powders of α-Al_2O_3 and β-SiC were hot-pressed at 1550°C in Ar atmosphere with an applied pressure of 30 MPa for 1 h. The particle size of silicon carbide was 100 nm on average but was widely distributed from several nanometers to several hundred nanometers. The relative density was above 99%. The alumina grains were equiaxed and were about 2 micrometer. Silicon carbide particles were distributed inside alumina grains as well as on interfaces between alumina grains. The intragranular particles are nominally smaller than the intergranular ones.

The powder mixture was prepared by ball milling of α-Si_3N_4 (Ube E10) with 4 wt% Y_2O_3, 2 wt% Al_2O_3 and 5 mol% of La_2O_3 with respect to Si_3N_4, respectively. After shaping and cold isostatic pressing with 250 MPa, the compact was sintered by gas press sintering system at 1950°C for 2 h under 30 atm of N_2 gas pressure. The materials examined in this study have almost full density. The phases of all silicon nitride ceramics consisted of glass phase without any crystalline phase except matrix β-Si_3N_4.

2.2. Wear test

Wear test was done by ball on plate test rig. Commercial Si_3N_4 ball (NBD 100; 12.7 mm in diameter) was used as a sliding ball for all wear test in this study. The stroke length of 6.86 mm was rubbed by upper ball at a normal load of 10 N with constant frequency of 5 Hz for 1 h. The sliding distance was about 247 m with linear speed of 0.07 m/s.

2.3. Microstructure observation

The wear track was examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The cross section of the wear scar was also observed in order to get information about the fracture process just below the wear surface. Especial caution was paid to preserve the integrity of worn surface after the wear since it is on one end of edge surface that is always prone to receive damage during specimen preparation for observation. Transmission electron microscopy (TEM) was employed for characterization of the worn surface together with energy dispersive spectroscopy (EDS). Specimens for TEM were prepared by mechanical grinding from the opposite side of the wear scar. The side of wear scar was Ar-ion sputtered for 30 min with an incidence angle of 15 deg. After this short time double gun polishing, only the back side of the wear scar was sputtered down to the electron transparency. A thin carbon film was coated before observation to prevent the electron discharge during observation.

3. Results and Discussion

3.1. Damage accumulation in Al_2O_3-5 vol% SiC nanocomposite

Figure 1 shows a transmission electron microscopy of the wear surface of alumina silicon carbide nanocomposite that has been tested with 10 N at 5 Hz at room temperature for 1 h. Large SiC particles were present along grain boundaries, whereas nano-sized SiC particles were distributed inside the alumina grains. The reciprocating sliding was done in the horizontal direction. A crack is running across the sliding direction. The crack generated run through inside the alumina grains. Several researches on the wear behavior of monolithic alumina have shown that the crack generated during wear was almost intergranular crack because the grain boundary acts as a preferable site for crack initiation due to the accumulation of damages.[2-5] However, as shown in Fig. 1, the crack was generated through the alumina grain. Transgranular fracture is a common in nanocomposite system during flexure testing at room temperature and is also observed during wear test with low contact loads. This type of fracture mode suggests that the pull-out of alumina grains due to the grain boundary cracking can be significantly suppressed in this nanocomposite systems during grinding process.

Fig. 1. TEM micrograph that shows an overall morphology of wear scar. A crack is running through the alumina grain.

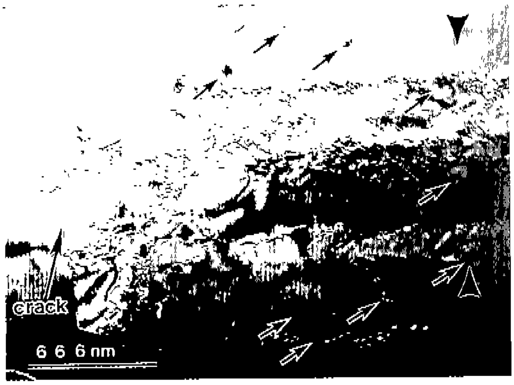

Fig. 2. TEM micrograph that shows high density of dislocations and dispersed nano sized SiC particles inside an alumina grain.

Figure 2 shows a magnified image of wear surface. Small arrows indicate the SiC nano particle dispersed inside the alumina grains. A high density of dislocations and defect were observed through the wear scar. Several authors have reported plastic deformation of Al_2O_3 during wear applications.[5] Considering the highly localized stress, the presence of plastic deformation is not surprising. In a substantial research, Cho et. al.[5] have showed that dislocations and twins generated inside an individual grains extended across the entire grain. They have suggested that grain boundary cracking is caused by the accumulation of intersecting slip arrays and twins. However, as shown in Fig. 2, several nano particles are contacting with dislocation line, suggesting a pinning of dislocation line extension. The generation of slip band and twin is known to be limited in single grains. However, the size and region of slip band and twin in a grain is not well known. Based on TEM observation, it was shown that slip arrays generally span the individual grains.[5] However, when nano particles are present inside a grain, they acts as a barrier for the extension of dislocations thus inhibits the formation of slip band across a entire grain. Ohji et. al. have shown in an alumina-17 vol% SiC nanocomposites that the crack front was deflected by the presence of SiC nanoparticles. They suggested a particle bridging toughening mechanism to explain the increased strength and toughness in Al_2O_3SiC nanocomposite. Also, a small crack is seen inside the grain, which intersects the grain boundary and is connected to the adjacent grain without invoking grain boundary cracking.

Figure 3 is a bright field transmission electron micrograph that shows the embedded β-SiC particles inside alumina grain and a related cavity. A lot of defects are also seen around and along the wear scar. Inset is a selected area diffraction pattern around the β-SiC particle and the matrix. The bright spot is from the matrix spot of alumina and the six folded small spot is from the SiC particle. This electron diffraction indicated that the β-SiC particle was entrapped during sintering and grain growth. Then, the observed cavity adjacent to the β-SiC particle is thought to be generated during wear process. The formation of cavity along the interface between the β-SiC particle and matrix alumina suggests the accommodation of plastic flow inside grains of alumina when nano particle is present.

The current observations on the wear scar of Al_2O_3-5 vol% SiC support: (1) transgranular fracture is still dominant fracture mode during under this sliding condition; (2) a high density of deformation such as dislocations are generated and pinned by the nano sized SiC particles embedded inside the alumina grains; (3) plastic deformation can be accommodated at the interface of intragranular SiC particle and matrix.

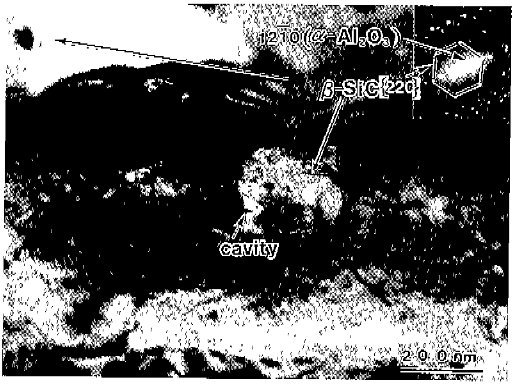

Fig. 3. Bright field transmission electron micrograph of intragranular SiC particles with cavity formation.

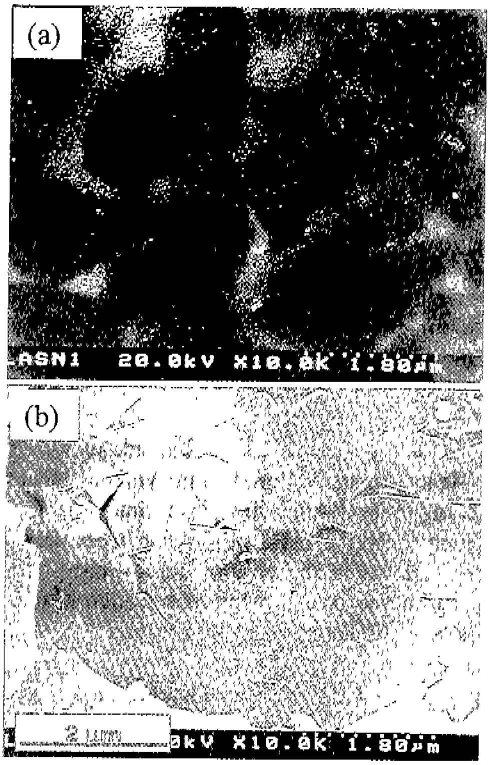

Fig. 4. Scanning electron micrographs of Si_3N_4 sintered with 5Y2A and 5 mol% La_2O_3; (a) shows the freshly polished surface and (b) is the edge of the wear scar which shows the dissolution of grain boundary phase and some part of tribo-layer formed by the wear process.

3.2. Delamination process in Si_3N_4 ceramics

Figure 4 show SEM micrographs of as polished surface (Fig. 4a) and the edge of the worn surface partly covered with the debris layer (Fig. 4b). From Fig. 4(a), the grain boundary phase that is appeared as white contrast in the freshly polished surface is clearly seen. In contrast, the worn surface clearly showed that the glass phase have been swept and gone out from the triple point of the grains and from two grains boundary by the wear. The cleanliness of the boundaries suggested that the removal of the grain boundary phase was occurred even without the damage of the surface grain of silicon nitride. This means that the grain boundary phase was dissolved and swept out during the first stage of sliding wear by tribochemical dissolution reactions.

The dissolution of the grain boundary phase leaves the silicon nitride grain un-supported state. When the binding phase was disappeared from the structure, the overall strength of the materials easily drops below the critical strength that stands up with the pull out of the grains. The reciprocating sliding repeatedly touches those grains during the cyclic fatigue conditions. Hence, the heat that could not be transmitted into the neighbor will stay around the grain boundary that is continuously stressed by the cyclic sliding. Therefore, the grain boundary of the silicon nitride will be cracked partially. The transition from the mild wear to the severe wear is, thus, thought to be related to the removal of the grain boundary phase.

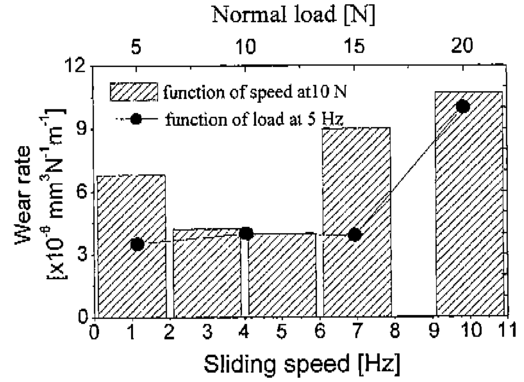

Fig. 5. Change of wear rate with the sliding speed and the load.

Figure 5 shows the wear rate as a function of load and the sliding velocity. The wear rate increases monotonically with the increase of the sliding speed and also with the sliding load. Around 10 N with sliding speed of 5 Hz the change in the wear mode occurs from the mild wear into the severe wear with showing a very steep increase in the wear rate.

Figure 6 shows the high magnification images of the cross section. The surface had some roughness resulted

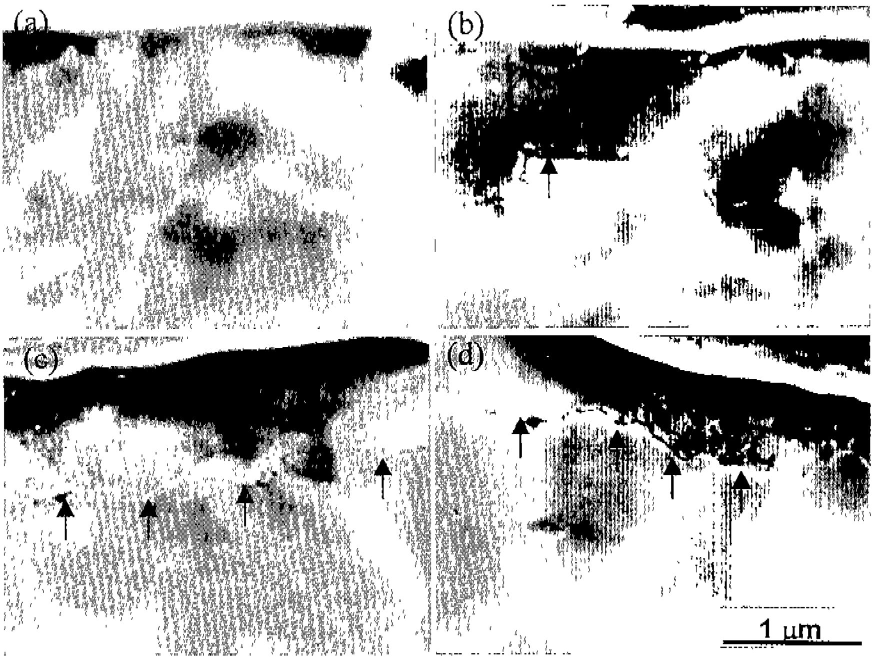

Fig. 6. High resolution scanning electron micrographs of cross section of wear scar; (a) unworn region, (b) debonding of interface on the order of one grain of Si_3N_4, (c) extension and combination of the crack and (d) opening of cracks.

from the polishing process as shown in Fig. 6(a). No crack or deformation was observed below the polished surface. After the wear process, however, debonding of grain boundary was observed at the 0.5 μm depth from the surface as is shown in Fig. 6(b), which was about the same length with one grain. As indicated by the arrows, intergranular fracture was observed to start at from the interface of the silicon nitride grain and the grain boundary glass phase. Fig. 6(c) is a more advanced state of the crack propagations, which shows the extension and combination of the crack generated by the debonding of interface. It is also noted that grain in the center part of the micrograph shows pitting out, which is thought to result from the fatigue. Fig. 6(d) shows an open crack that was resulted from the further extension of the combined crack to the level of lateral crack by adhesive sliding wear.

In order to clarify the characteristics of the crack generated by the wear process during sliding wear, the interface was observed by TEM. Fig. 7(a) is a dark field image that shows the presence of amorphous phase through grain boundary and in the pocket. A closer look at the interface showed that a crack, which was seen as a white line, was developed along the boundaries as shown in Fig. 7(b). A black contrast on the both side of the Si_3N_4 grain suggested a fatigue nature of the crack.

The crack generated during sliding wear test is generally considered by the brittle fracture crack. However, under the present condition, the crack generated has its character of non-brittle but fatigue type of thermal crack. The driving force of the wear crack generation is the frictional force. Since the friction coefficient of this system was approximately 0.8-0.9 which is still higher for the transmission of the shear stress. When the transmission of the heat and stress is assumed to be on the order of one grain of silicon nitride, the wear of fine-grained materials would be small compared to that of large grain sized materials.

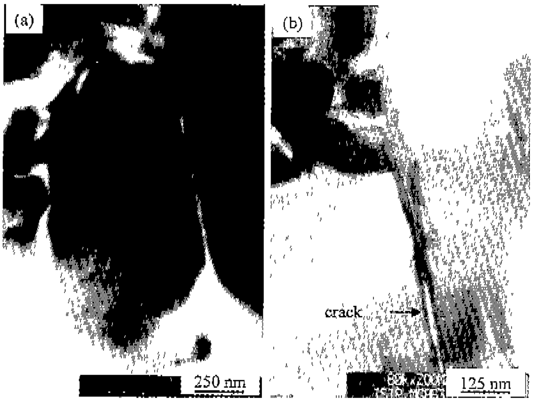

Fig. 7. Transmission electron micrograph of worn surface of Si_3N_4, (a) dark field image by diffracted beam from the glass phase and (b) bright field image that shows a crack along grain boundary.

Through the above result and discussions, it was thought that unlubricated sliding wear was dominated by the thermo-mechanical fatigue with delamination with abrasive/adhesive wear. Under this wear condition, the respect of the microstructural effect on the wear resistance was considered.

Under the wear condition similar to this study, debonding of silicon nitride grain from the interface is considered to be the most important.$^{14)}$ Therefore, the bond strength of the interface is required to be kept at any instance of the test. However, unlubricated sliding condition produces a relatively high temperature around or at the asperity of contact. The bond strength at the interface is not only determined by the chemical strength but also by the high temperature strength of this system. Since the thermal conductivity of silicon nitride grains is generally higher than that of the grain boundary glass phase, the end of heat conduction path, in other words, the barrier for high thermal diffusion path, should be the glass phase that surrounds the silicon nitride grains. In accompanying with this, the lower melting or glass transition point makes the grain boundary weakening at the wear track so that debonding of interface occurs.

Although the plastic deformation including dislocation formation and fracture of the silicon nitride grains itself affects the wear behavior, the most important variable is believed to be the fatigue crack generated at the interface by the increased asperity temperature and accompanying thermal stress that could not be relieved effectively when the sliding load and speed increase above a critical region.

It is thus concluded that grain boundary phase which has a high thermal conductivity with high refractoriness is required in order to reduce the thermal stress at the boundary. Therefore, when this sliding pairs will be used in a practical application, usage of materials below the critical region or microstructural and chemical design of grain and grain boundary structure are required.

4. Summary and Conclusion

The wear surfaces of the two representative ceramic materials of Al_2O_3-SiC nanocomposite and gas pressure sintered Si_3N_4 ceramics were observed. Through the observation of wear scar of two ceramic materials, the microstructural wear mechanism was investigated. As for the Al_2O_3-5 vol% SiC nanocomposite, the grain boundary fracture was suppressed by the presence of SiC nano-particles. The intragranular SiC particles have inhibited the extension of plastic deformation through the whole grain. Part of plastic deformation was accommodated around the SiC particles leaving cavity at the interface between SiC and matrix alumina. On the other hand, for gas-pressure sintered silicon nitride the crack occurred due to the thermal fatigue, not to a brittle fracture. The lamination of wear scar was initiated by the dissolution of grain boundary phase.

References

1. A. Skopp, M. Woyde and K. H. Habig: Wear, **181-183** (1995) 571.
2. S. J. Cho, H. Moon, H. J. Hockey and S. M. Hsu: Acta Metall., **40** (1992) 185.
3. S. J. Cho, B. J. Hockey, B. R. Lawn and J. Bennison: J. Am. Ceram. Soc., **72** (1989) 1249.
4. C. A. P. Dogan and J. A. Hawk: Wear, **225-229** (1999) 1050.
5. C. A. P. Dogan and J. A. Hawk: Wear, **181-183** (1995) 129.
6. F. Xion, R. R. Manory, L. Ward, M. Terheci and S. Lathabai: J. Am. Ceram. Soc., **80** (1997) 1310.
7. M. Oden and T. Ericson: J. Am. Ceram. Soc., **79** (1996) 2134.
8. C. A. P. Dogan, A. H. Heuer, M. J. Readey and K. Mieeian: J. Am. Ceram. Soc., **74** (1991) 646.
9. J. E. Blendell and R. L. Coble: J. Am. Ceram. Soc., **65** (1982) 174.
10. R. W. Davidge, P. C. Twigg and F. L. Rieley: J. Eur. Ceram. Soc., **16** (1996) 799.
11. J. Rodriguez, A. Martin, J. Y. Pastor, J. Llorca, J. F. Bartomome and J. S. Moya: J. Am. Ceram. Soc., **82** (1999) 2252.
12. A. Zutshi, R. A. Haber, D. E. Niesz, J. W. Adams, J. B. Wachtman, M. K. Ferber and S. M. Hsu: J. Am. Ceram. Soc., **77** (1994) 883.
13. T. E. Fisher and H. Tomizawa: Wear, **105** (1985) 29.
14. A. Skopp, M. Woydt and K. H. Habig: Trobi. Int., **23** (1990) 189.