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Effect of amount of magnesia on wear behavior of silicon nitride

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마그네시아 양이 질화규소의 마모거동에 미치는 영향

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Abstract The microstructure of ceramic composite has been found to be governed by the type and amount of the secondary phase, the sintering aid, and the sintering conditions such as sintering temperature, pressure and holding time. Moreover, tribological properties are strongly dependent on microstructure of composite and operating conditions. In this study, silicon nitride with various amount of magnesia as a sintering aid were prepared and sintered by a hot pressing (HP) technique. Microstructure, mechanical properties (hardness, strength, and fracture toughness), and tribological properties in different environments of Si_3N_4 (in air, water, and paraffin oil) were investigated as a funtion of MgO content in Si_3N_4. As increasing the amount of MgO in Si_3N_4, the glassy phase in the grain boundaries enlarged the β-phase elongated grains, and also degraded the Hertzian contact damage resistance. Tribological behaviors in air was seemed to be determined by fracture toughness of Si_3N_4, and those in water and paraffin oil was seemed to be determined by hardness as well as strength. Since glassy grain-boundary phase (MgO) in Si_3N_4 expected to be reacted with water during sliding, such tribochemical reaction reduced wear. In paraffin oil under a higher applied load, the initial sliding dominated wear rate because of Hertzian contact damage.

요 약 세라믹 복합체의 미세구조는 이차상의 종류 및 양, 소결 조제, 그리고 소결 조건(즉, 소결 온도, 압력, 유지시간)에 영향을 받는다. 또한, 내마모 특성은 미세구조와 작업 조건이 내마모 특성에 크게 영향을 미친다. 본 실험에서는 질화규소에 마그네시아의 양을 변화시켜 가압 소결(Hot Press) 방법으로 시편을 제조하였다. 마그네시아 양에 따른 미세구조, 기계적 특성(경도, 강도, 파괴인성), 그리고 다양한 분위기(공기, 물, paraffin oil)에서의 내마모 특성을 조사하였다. 질화규소에 마그네시아의 양이 증가하였을 때, 입계의 유리상이 β-상의 장주형 입자를 커지게 하고, 또한 Hertzian contact damage를 저하시킨다. 대기 중에서 내마모 거동은 강도뿐만 아니라 파괴인성과 관련이 있고, 물과 paraffin oil에서는 경도와 밀접하다. 물속에서 마모시험 중 많은 유리상이 물과 반응하는 것을 생각할 수 있다. 그러므로 마찰화학적 반응(tribochemical reaction)은 마모도 저하시킨다. Paraffin oil에서 높은 하중을 부하할 경우, Hertzian contact damage 때문에 초기 마모가 마모량에 지배적이다.

1. Introduction

A development of adiabatic and turbocompound engine was proposed by Kamo [1], which was highly potential with high thermal efficiency. Advantages of structural ceramics for the applicant of heat engine are high strength, high corrosion resistant, high oxidation resistant, and high thermal shock resistant materials. Currently, the structural ceramics such as silicon carbide, toughened zirconia, alumina, silicon nitride, and silicon whisker reinforced composite ceramics have been extensively examined for the application to heat engine.

Wear-resistant tribo-materials generally require higher hardness and chemical inertness than those of widely used engineering materials. Further, it has been known that wear characteristic of materials are extensively influenced by operating conditions such as normal load, sliding speed, temperature, sliding distance and grain size [2-6].

Under the sliding without lubrication, the coefficient of friction of Si_3N_4 would vary from 0.2 to 0.8 depending on the environmental conditions [7-9]. With coefficient of friction near 0.8, micro-fracture was found to be the predominant wear mechanism when sliding in dry gases [7], while the tribochemical reaction with water was the governing factor when sliding in a humid environment [8]. In the later case, a thin hydroxide film on the Si_3N_4 materials was formed resulting in a marked decrease in the coefficient of friction and in the resulting wear. Because of the complexity of wear processes, a detailed understanding of how ceramic materials react in tribological environments continues to avoid both materials and design engineers. For the abrasive wear of brittle materials, mathematical models generally express wear volume as an inverse function of the hardness and the fracture toughness of the materials [10, 11]. Amorphous silicon hydrated was formed on Si_3N_4 by reacted with water [7]. Habeeb also reported an increase in wear rate as a function of water concentration in the lubricant [12]. According to Adewaye and Page is study on the deformation mode of silicon nitride during unlubricated wear testing, it was suggested that plastic deformation mechanism was dominant [13].

Norton Company has commercialized the Si_3N_4 ball bearing containing 1 wt% MgO as a sintering additive (NC132, NBD100, and NBD200) [14]. Also, Si_3N_4-4 wt% MgO was reported to be suitable for the structure component at high temperature [15]. However, the effects of the amount of MgO content in Si_3N_4 on microstructure, mechanical properties and wear properties have never been reported.

In this study, microstructure, mechanical properties as well as tribological characterization (in air, water, and paraffin oil) of silicon nitride with various amounts of MgO as sintering aid were investigated.

2. Experimental procedures

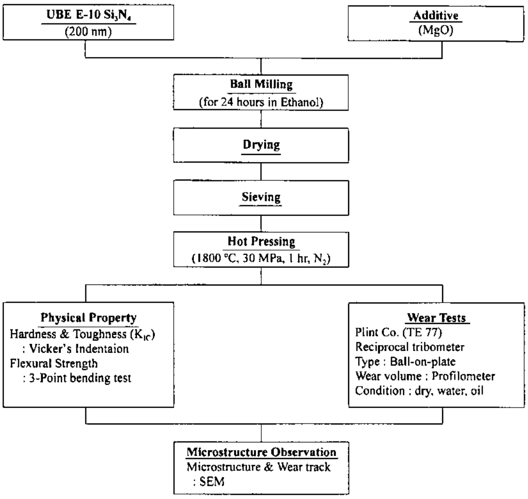


Fig. 1. Flow diagram of the experimental procedure.

The specimens were prepared by the procedure shown in Fig. 1. Si_3N_4 (UBE Industries LTD., E-10) powder with higher α-fraction was used. Average particle size of Si_3N_4 was 0.2 μm. MgO powder (first grade of Yakuri Chemicals LTD) was used a sintering additive. Si_3N_4 containing 1 wt% to 5 wt% MgO were fabricated. Fabrication processing of specimens was as followed. These powders were weighed, and mixed in ethanol. The mixtures were milled using silicon nitride ball as milling media in plastic pot for 24 hours at 250 rpm. After drying slurry, powders were sieved. The compacted powder mixture were hot pressed in graphite mold coated with BN at 1800℃ for 1 hour with 30 MPa of applied pressure in a flowing N_2 atmosphere.

For microstructure examination using SEM, plasma-etching technique was employed, and etched surface was coated with gold.

Bulk density of the hot pressed samples was measured by Archimedes method, and the relative density was calculated with the theoretical density of each powder by the mixing rule. Hardness and fracture toughness of sintered samples was measured by an indentation method using Zwick 3212 hardness tester, and indentation was performed for 15 seconds at 196N load. The value of fracture toughness calculated by Evans and Charles equation [16]. Flexural strength samples of 3 mm×4 mm×35 mm in dimension were cut and ground using sintered body. The edges of the tensile side of the fracture strength bars were chamfered at 45° using diamond wheel. All data points were averages of at least 10 samples fractured at 0.5 mm/min crosshead speed, and spans of 25 mm.

Friction and wear tests were performed using Plint Tribometer (TE 77) on a reciprocating ball-on-plate tester. Before wear and friction test, the surface of specimen was finished by 0.3 μm alumina paste. The surface of specimen was cleaned using acetone and ethanol. Used ball for friction and wear test was silicon nitride ball. The test atmospheres used in this study were unlubricated (in air) and lubricated conditions (in water and paraffin oil). The test conditions used in each environment were as follows; 10 N in air, 40 N in water, and 200 N in paraffin oil at 5 Hz of frequency (about 0.07 m/s of sliding speed), for 1 hour of test time, at room temperature. The applied loads in paraffin oil were 100 N, 150 N, and 200 N. Wear rate of Si_3N_4-5 wt% MgO sample was studied as a function of sliding time from 1min to 60 min. After wear test, a wear trace was measured by using a profilometer (Rank Taylor Hobson Company), which was used to calculate wear volume. Three times average value of the three measurements for each wear condition was adopted. SEM was employed to study surface topography of the worn area.

3. Results and discussions

3.1. *Mechanical properties*

Figure 2 shows the variation of mechanical properties of Si_3N_4 as a function of the amount of MgO. It reveal that mechanical properties of Si_3N_4 are relied on the contents of MgO. When increasing the amount of MgO, relative density, hardness and flexural strength were decreased, but aspect ratio of the elongated Si_3N_4 grain and fracture toughness was increased. As increasing the amount of MgO, hardness was seems to be decreased because of increase of glassy grain boundary phase. Furthermore it has commonly been accepted that hardness (HV) generally increases with decreasing grain size (G), due to Hall-Petch type effects on the associated plastic flow. It can be suggested that hardness was decreased with increasing amount of MgO in Si_3N_4 which is associated with the enlargement of grain size as shown in Fig. 3.

It has been reported that anisotropic grains in Si_3N_4 deflect cracks propagating, which causes the increase in the fracture toughness of ceramics [17, 18]. The aspect ratio of grains and consequently the fracture toughness of hot pressed materials are proportional to the α content in the starting powder [19, 20]. High α content of Si_3N_4 powder develops anisotropic and large gains during hot pressing [20-26]. When increasing the amount of MgO, the amount of liquid phase in grain boundary was increased. Grain growth of the elongated Si_3N_4 was accelerated by liquid phase. Based on liquid-phase sintering of Si_3N_4 α grains dissolve and α grains are precipitated. In this reason, the elongated β-phase grains were increased with increasing the amount of MgO. Therefore, aspect ratio and fracture toughness were increased, but hardness and flexural strength were decreased. The increase of fracture

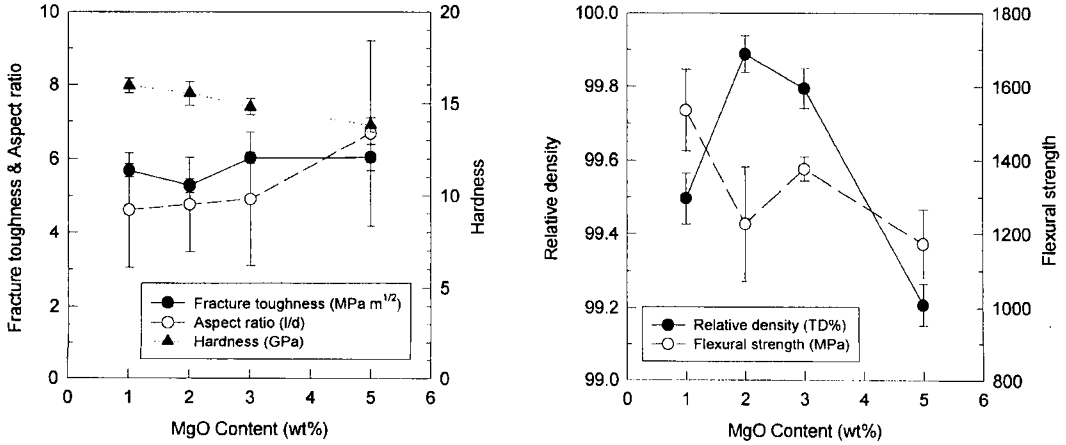
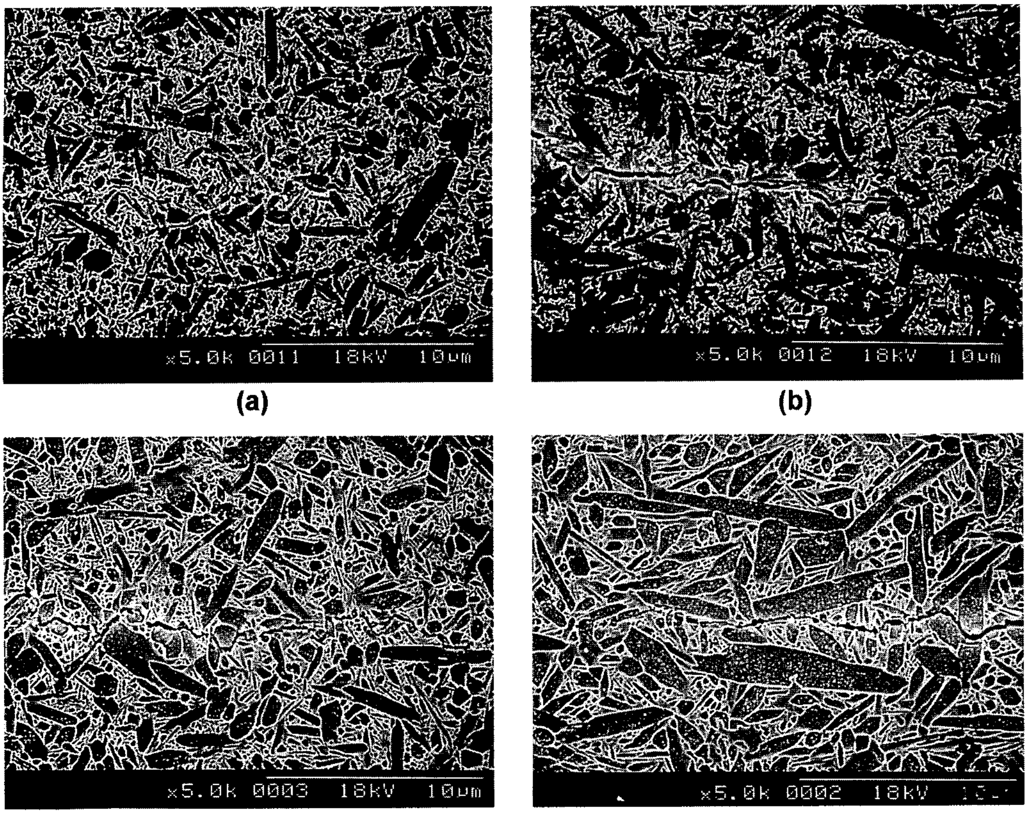


Fig. 2. Variation of mechanical properties with MgO contents in Si_3N_4.



(a) (b)

(c) (d)

Fig. 3. SEM micrographs of the etched surface of Si_3N_4 with various MgO contents; (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 5 wt%.

toughness has been attributed to crack deflection by the large grains [17, 18].

3.2. Wear characteristics

Figure 4 shows comparison of tribological properties of Si_3N_4 with various amount of MgO as sintering aid in air, water and paraffin oil, respectively. In air, wear volume of Si_3N_4 is a minimum at the content of 1 wt% MgO, and a maximum at the content of 2 wt% MgO. For Si_3N_4 with 3 wt% of MgO or more, the wear volume has decreased gradually. Figure 5 shows that wear debris cover the wear tracks, but some wear debris layer was removed and grain pull-out was observed. It has been reported that wear of ceramics in dry contact is supposed to be dependent upon fracture toughness [25]. In this study, it seems that the lower fracture toughness causes the higher wear volume. A lack of lubricant at the high speeds could raise the contact temperature, which produces a thermal stress and then enhance fracture of brittle ceramics. In this study, the sliding speed is relatively lower, which

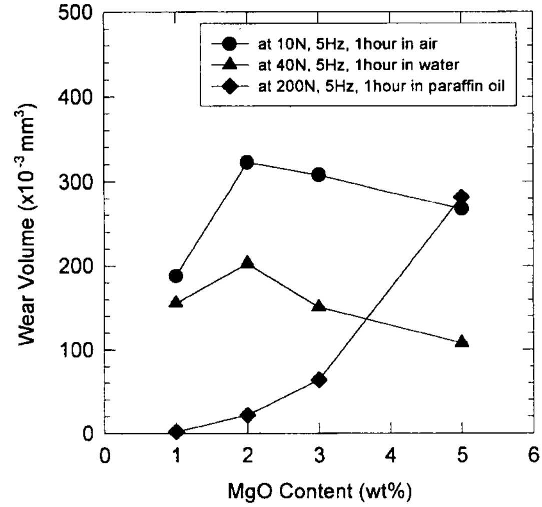
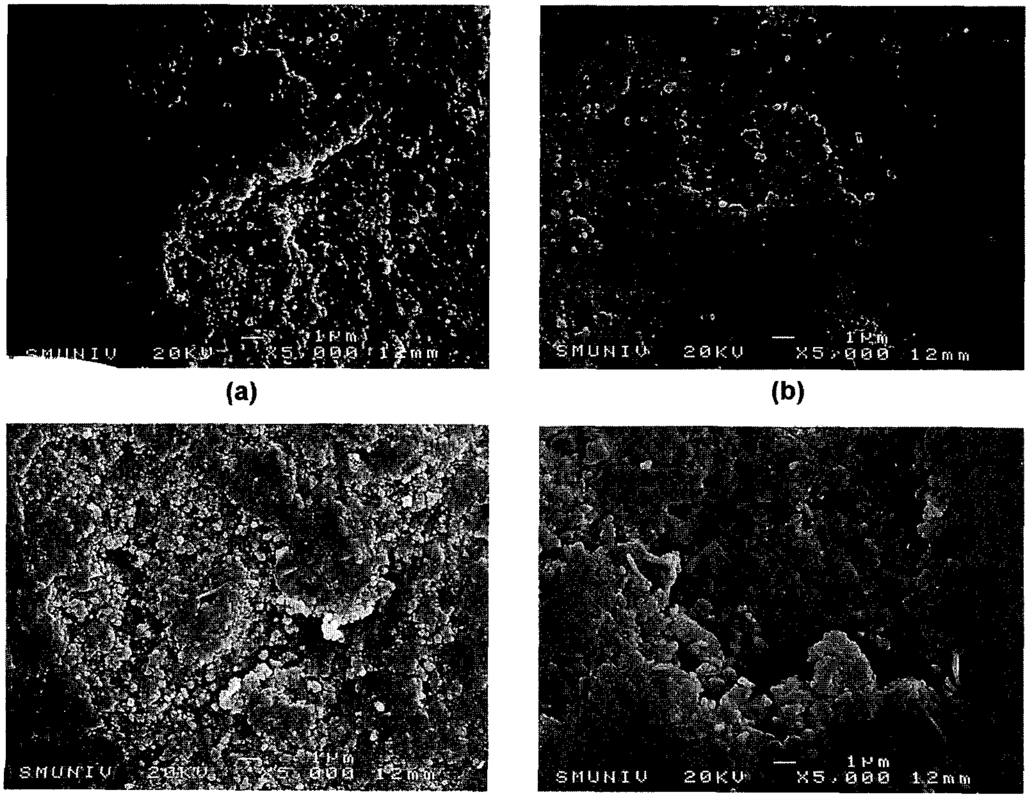


Fig. 4. Variation of wear volume in different lubricants with MgO contents in Si_3N_4.

may not affect thermal shock, therefore, mechanical stress causes wear by a mode of brittle fracture. According to early works, for a polycrystalline ceramics such as Si_3N_4, grain boundary seems to be the site for crack propagation because of its relatively low fracture energy and voids, or impurities at grain boundary could also lead to intergranular fracture giving "grain pull-out". Once cavities have been produced on the surface, "edge-spalling" [26] can account for continued formation of wear debris that is a characteristic of ceramics wear in the brittle regime. In this case, wear is mainly associated with microcracking, grain pull-out, and chipping. Wear debris came off from the wear track and accumulated at the edge. Surface cavity appeared, edge-spalling like that described by Thouless *et al.* [26] enlarged it on successive passes, giving fine wear-debris, and a slowly increasing wear rate. These micrographs (Fig. 5) reveal the generation of debris as fracture proceeds by lateral crack propagation, and the agglomeration of the debris to form platelets that are physically attached to the groove surface. Wear track looks smooth after removing the wear debris from the wear track. Different types of worn surfaces were a surface formed by agglomeration of wear particles. When sliding against silicon nitride ball, the coefficient of friction was below 1. Most of wear was generated in the beginning of sliding, which can be expected to indicate the early stage of fracture on wear track. When this sliding condition may not raise temperature significantly, it seems that wear is caused by brittle fracture, with or without some limited plasticity [27].

In water, wear volume is a maximum at the content of 2 wt% MgO at sliding speed of 0.07 m/s under a load of 40 N. Wear volume of Si_3N_4-5 wt% MgO was lower than that of Si_3N_4-1 wt% MgO. Figure 6 (a) and (d) show that the wear debris is attached on the worn surface. As shown in Fig. 6 (c), cracks



(a) (b) (c) (d)

Fig. 5. SEM micrographs of the worn surface of Si_3N_4 with various MgO contents in air; (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 5 wt%.

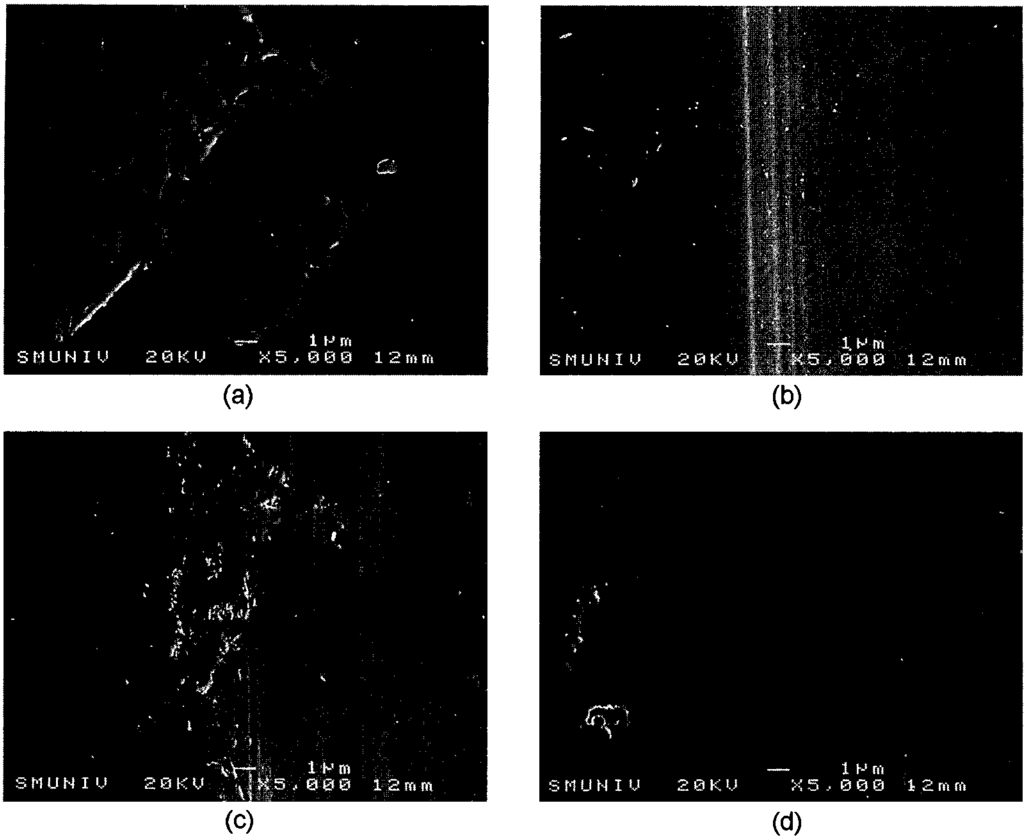
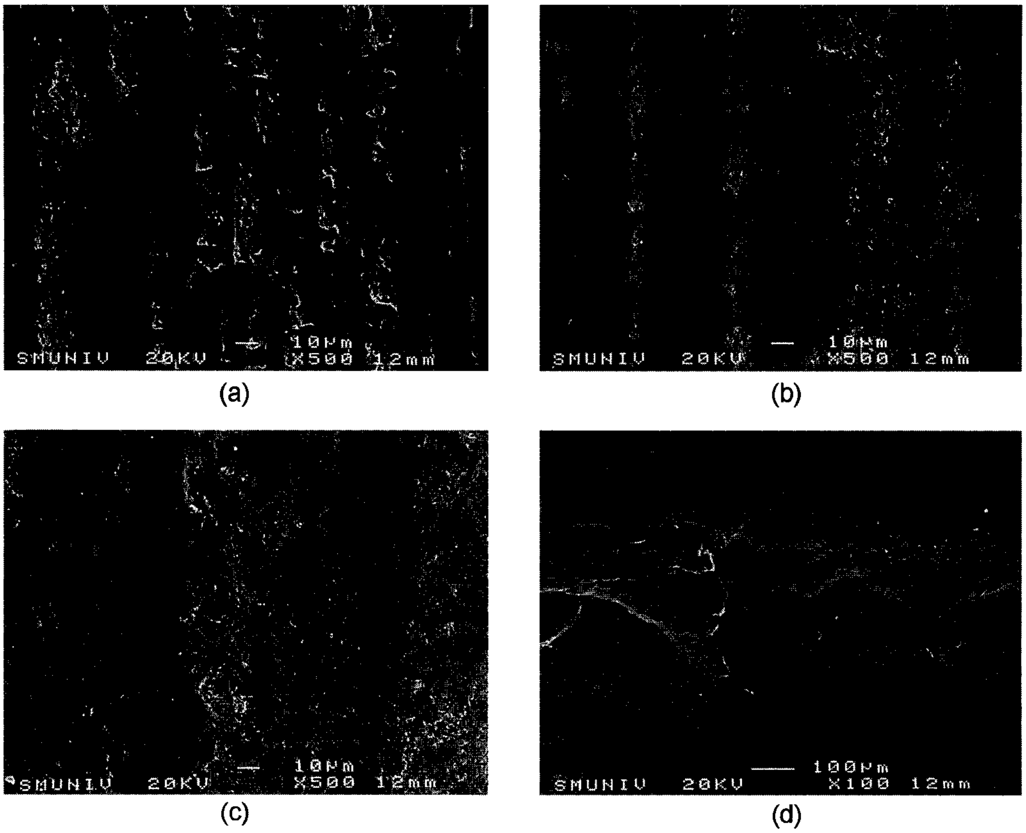


Fig. 6. SEM micrographs of the worn surface of Si_3N_4 with various MgO contents in water; (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 5 wt%.

are generated primarily within the wear track along the sliding direction, with removal of little subsurface material. Similarly hardness and flexural strength were decreased with increasing the content of MgO as shown in Fig. 2. It can be suggested that wear of Si_3N_4-MgO system in water is related to the plastic deformation, which is accelerated by increasing the glassy phase. This result indicates that the higher glassy phase of MgO (at 5 wt% MgO) reduces the coefficient of friction. Furthermore, it can be also suggested that formation of tribochemical products, such as $Mg(OH)_2$, reduce the coefficient of friction. This tribochemical reaction is required to be determined.

In paraffin oil under a load of 200 N, wear volume of Si_3N_4 increases gradually with increasing the amount of MgO, but dramatically above 3 wt%. In this study, it was proved that wear volume of silicon nitride in paraffin oil is strongly related to flexural strength and hardness. Figure 7 shows SEM micrographs of the worn surface of Si_3N_4 in paraffin oil. The severe damage along sliding direction in paraffin oil was occurred. Grain boundary fracture is the predominant mode of failure in Fig. 7 (a) - (c). It is known that the glassy grain boundary phases in silicon nitride are the primary cause of fracture. These figures show that wear has occurred by a submicrometer chipping mode in materials. Figure 7 (d) shows pullout grains produced a greater wear volume loss than submicrometer chipping. It is apparent that wear occurs by fracture. Wear of Al_2O_3 in paraffin oil [28] suggested that the brittle fracture by the subsurface damage results in dislocation pile up in the preferred orientation in single grains and shear stress generates a microcrack at the grain boundary and the crack propagates through several grain boundaries. Finally the crack reaches to surface and big flakes of wear debris of several grains were removed. In the silicon nitride lubricated with paraffin oil, it is not



(a) (b)

(c) (d)

Fig. 7. SEM micrographs of the worn surface of Si_3N_4 with various MgO contents in paraffin oil; (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 5 wt%.

clear that the wear transition by subsurface damage occurs. The appearance of debris on the worn surface is able to interpret the wear behavior of silicon nitride lubricated in paraffin oil.

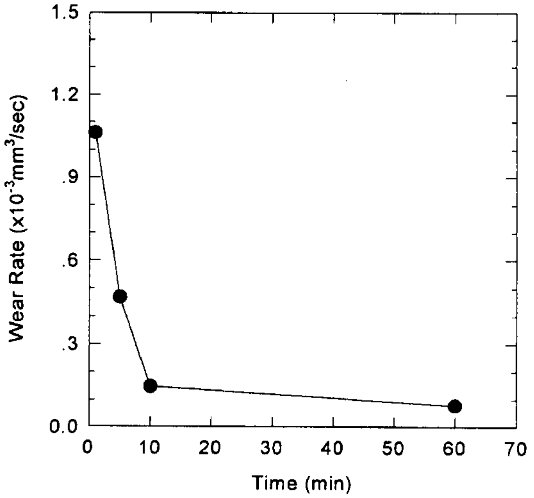
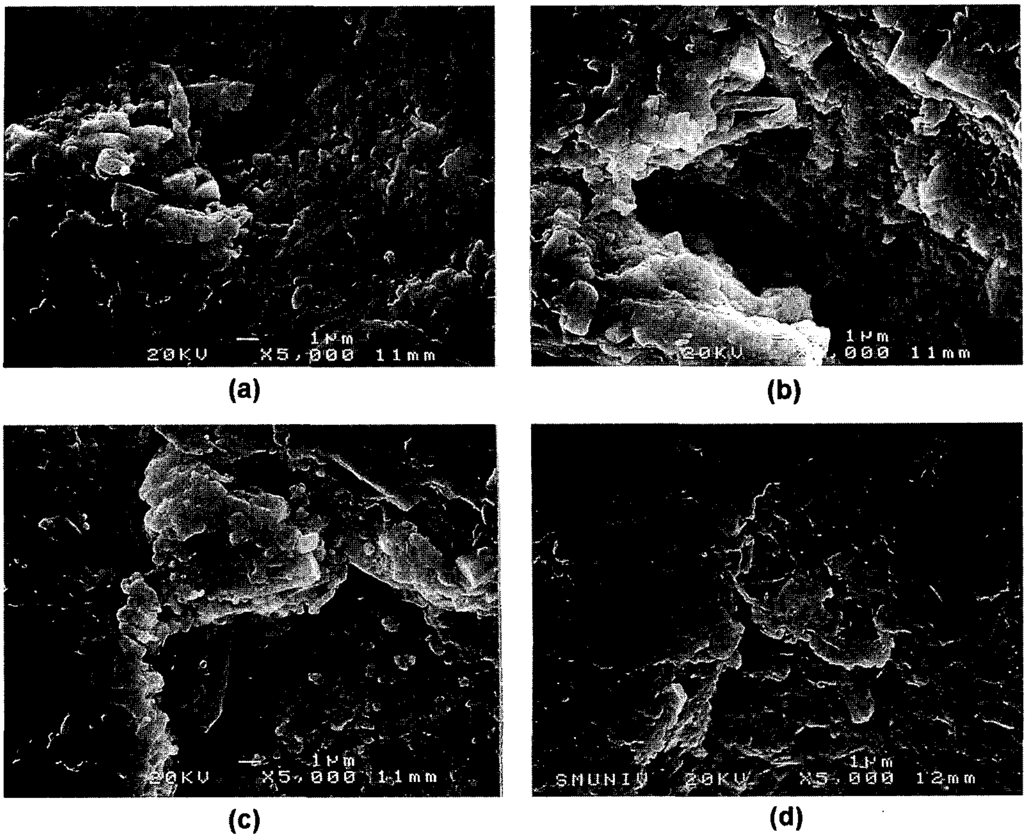


Fig. 8. Variation of wear rates for 5 wt% MgO-Si_3N_4 in paraffin oil with sliding time.

Figure 8 shows wear rates of Si_3N_4-5 wt% MgO sample with various sliding times in paraffin oil. Wear seems to be mostly affected at the initial sliding time. Up to 10 min, wear rate is rapidly dropped and then it decreases gradually. Figure 9 shows SEM micrographs of wear surface of Si_3N_4-5 wt% MgO sample in paraffin oil for different sliding times. Figure 9 (b) and (c) indicate grain boundary fracture, grain pullout, and chipping. Close observation with SEM revealed intergranular fracture, which is believed to be due to weak interphase boundaries with higher glassy phases.

4. Conclusions

Silicon nitride hot pressed with various amount of MgO as sintering aid, which is formed as glassy grain boundary phase, was investigated to find out



(a) (b) (c) (d)

Fig. 9. SEM micrographs of the worn surface of Si_3N_4 with 5 wt% MgO in paraffin oil; (a) 1 min, (b) 5 min, (c) 10 min, (d) 60 min.

the influence of amount of MgO on microstructure, mechanical properties, and tribological behavior. When increasing the content of MgO, the elongated β-phase of Si_3N_4 forms same grains. Also, when increasing MgO, hardness decreases due to increasing grain size. Relative density decreases with increasing the amount of MgO, which is caused by the steric hindrance with the enlarged elongated grain as well as the increment of the microporosity. The tribological behaviors of Si_3N_4 with various amount of MgO come to conclusions as following;

1) In air, wear of Si_3N_4-MgO ceramics was dominated by grain pull-out, micro-fracture and the agglomerations of the debris in wear track were observed.

2) In water, the worn surface exhibited relatively a smooth surface and wear debris was smeared-out even though some grains were chipped out. Wear volume decreased with increasing the amount of MgO, which indicated that the more glassy phase was reacted with water and the tribochemical products reduced the friction as well as wear volume.

3) In paraffin oil, the coefficient of friction was much lower than in dry and water environments. The wear behavior of Si_3N_4 with higher amount of MgO (5 wt%) was related to the Hertzian contact damage. The initial sliding was predominated wear rate.

Acknowledgement

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