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Mechanical and tribological characterization of Si_3N_4-ZrO_2 composites

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질화규소-지르코니아 복합체의 기계적 및 내마모 특성

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Abstract In this study, the effects of the content of ZrO_2 in Si_3N_4 on mechanical and wear properties were investigated. Si_3N_4 based composites containing 0~40 wt% ZrO_2 powders were fabricated using hot isostatic pressing (HIP), at 1750℃, 172 MPa for 1 hour in N_2 gas. Mechanical properties and wear properties of composites were examined. Mechanical properties (hardness, strength, and fracture toughness) of Si_3N_4-ZrO_2 composite were decreased with increasing the amount of ZrO_2, but relative density of composites were increased. Further, the increase in amount of ZrO_2, reduced wear rates in air. It was found that wear behaviors in air were related to microcracking.

요 약 본 연구에서는 질화규소에 지르코니아 첨가량에 따른 효과를 조사하였다. 0 wt%~40 wt%의 지르코니아를 포함하는 세라믹 복합체 재료를 토대로 하는 질화규소를 1750℃에서 172 MPa의 질소가스압으로 한 시간동안 유지하는 조건으로 hot isostatic pressing(HIP)하였다. 소결된 시편의 기계적 특성과 마모 특성을 조사하였다. 질화 규소-지르코니아 복합체는 지르코니아 양이 증가함에 따라 경도와 굽힘강도는 감소하였으나 밀도는 증가하였다. 그리고, 지르코니아 첨가량이 증가함에 따른 공기 중에서의 마모량은 감소하였으며, 공기 중에서의 마모 거동은 microcracking에 유관하였다.

1. Introduction

Wear problem of mechanical components has been raised as an important issue in the application of structural ceramics, although the following parameters such as the coefficient of thermal expansion, fracture toughness, thermal shock resistance, and density have been significantly considered to define the characteristic properties of the mechanical components. The application of structural ceramics such as Si_3N_4 has been listed to pump, chute, and pipe liner used in industry delivering abrasive slurry and dry slurry due to it's high fabrication cost as well as it's characteristics of brittle fracture. Ceramic composites have been developed to produce tough, mechanically reliable ceramic materials for advanced structural applications at elevated temperature [1]. It has been expected that Si_3N_4 is one of promising wear-resistant tribo-materials because of it's high hardness and chemical inertness compared with widely used engineering metals and plastics. Currently, structural ceramics are commerciallized for wear resistant components, such as automotive engine component, metal working mold die, high spindle and high vacuum ceramic bearing, high speed and precision cutting tool [2].

It should be noted that wear and tribological characteristics of materials are more closely contributed to system properties rather than material properties. It has been known that wear mechanisms depend on the contact type (rolling, sliding, etc.), the operating conditions, the environment, the material characteristics of the test material, and the mating material [3]. For the sliding of brittle solid, brittle fracture generally was caused by a combination of contact and thermal stresses. It is obvious that the frictional heating induced by sliding is an important parameter in wear of materials [4].

It has been reported that fracture toughness of Si_3N_4 could be improved with adding second phase in the form of particle, platelet, whisker, fiber, etc [5-6]. It has been known that the fracture toughness of Si_3N_4 was improved by a microcracking mechanism in Si_3N_4/ZrO_2 composites containing up to 30 vol% of ZrO_2 [7]. Furthermore, small additions of ZrO_2 could promote the densification of Si_3N_4. The densification of Si_3N_4 powder with ZrO_2 and Al_2O_3 is more effective than with ZrO_2 alone [8].

In this paper, mechanical properties and wear behavior of Si_3N_4 are investigated as a function of ZrO_2 content in order to design the optimum microstructure of Si_3N_4 for wear resistance.

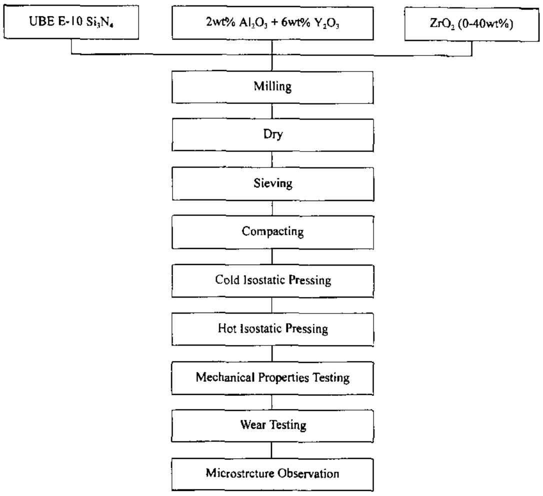

Fig. 1. Flow chart of experimental processing for Si_3N_4-ZrO_2 composites.

2. Experimental process

In this study, the specimens were prepared by the procedure as shown in Fig. 1. Si_3N_4 (UBE Industries LTD., E10) powder with higher α-fraction was used. Average particle size of Si_3N_4 was 0.2 μm. Sintering additives were 2 wt% Al_2O_3 (HP-DBN grade of Leynold) and 5 wt% Y_2O_3 powder (fine grade of Hermann C. Starck, Berlin). ZrO_2 powder as a second phase was used to TZ-3YS powder of Tosoh Cooperation. The amount of ZrO_2 into Si_3N_4 was varied from 0 to 40 wt% ZrO_2. Fabrication process of specimens was as followed. Each powder was weighed, and mixed in isopropyl alcohol (IPA). The mixtures were milled with silicon nitride ball as milling media in plastic pot for 24 hours at 250 rpm. The dried mixtures were sieved. Green body for sintering was prepared by cold isostatic pressing (CIP) under 200 MPa, and then was sintered by hot isostatic pressing (HIP) at 1750°C for 1 hour, under 172 MPa in N_2.

Bulk density of the hot isostatic pressed samples was measured by Archimedes immersion technique in water, and the relative density was calculated with the theoretical density of each powder by the

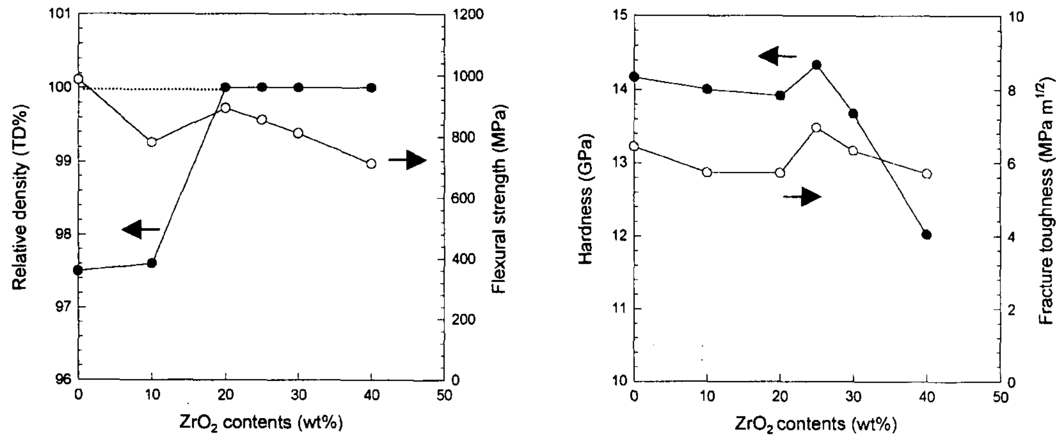

Fig. 2. Variation of mechanical properties of Si_3N_4-ZrO_2 composites with different content of ZrO_2.

mixing rule. The samples were polished using diamond paste down to 1 μm. Hardness and fracture toughness of sintered samples was measured by an indentation method with a load of 196 N. Test pieces for flexural strength were cut and ground into rectangular bar specimens (3 mm × 4 mm × 35 mm). The fracture strength was measured using the three point bending test under the conditions of crosshead speed 0.5 mm/min, and spans of 25 mm at room temperature.

Plint Tribometer (TE 77) was utilized to carry out wear tests. Friction and wear tests wear performed on a reciprocating ball-on-plate tester. The surface of sample for friction and wear test was

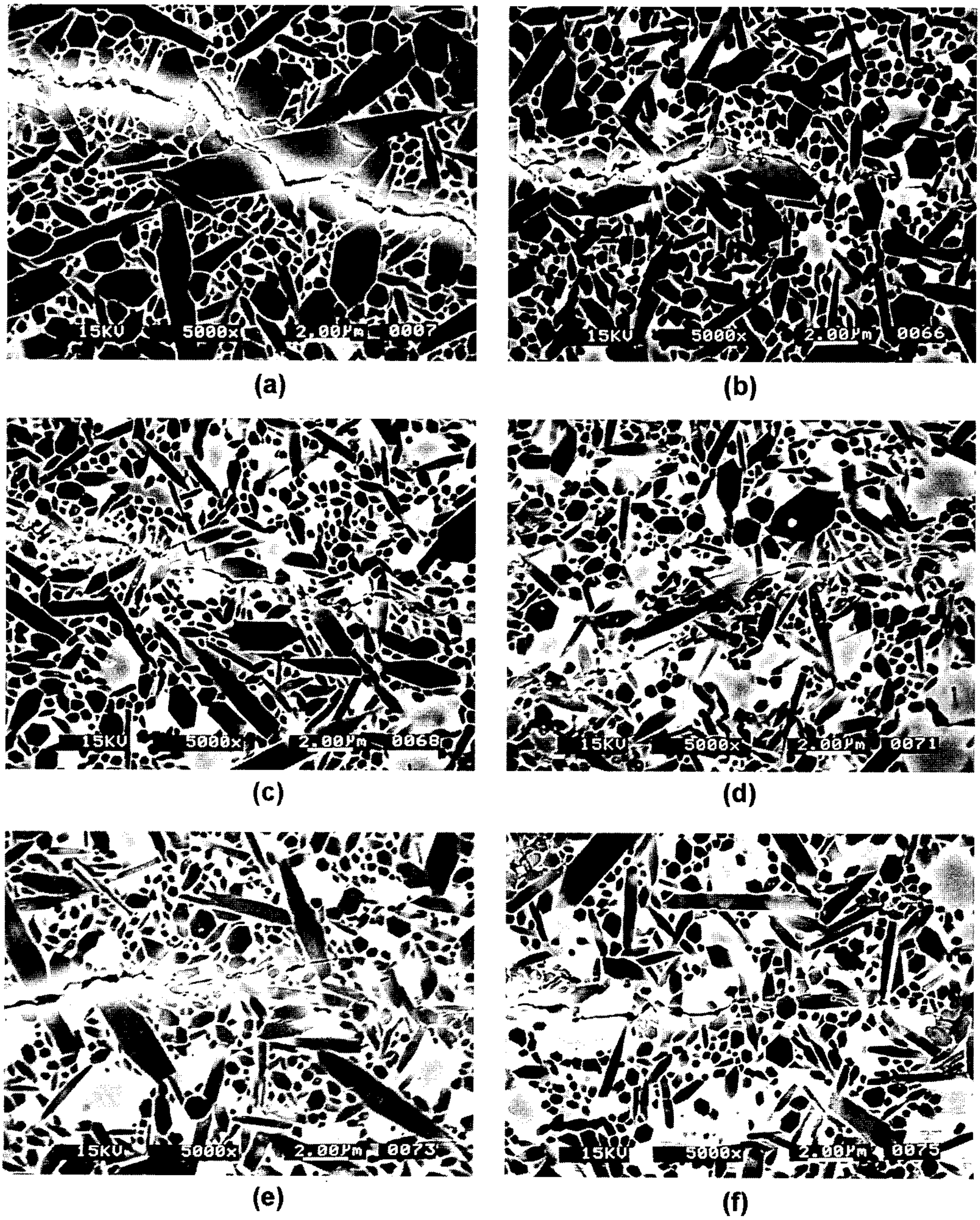

Fig. 3. Scanning electron micrographs of the etched surface of Si_3N_4-ZrO_2 composites with different content of ZrO_2; (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 25 wt%, (e) 30 wt%, (f) 40 wt%.

finished by 1 μm diamond paste. The upper ball was commercial Si_3N_4 ball (12.3 mm in diameter; NBD 100). The test conditions in air were fixed at 10 N and 0.07 m/s of sliding speed for 1 hour of test time at room temperature. After completing wear test, wear volume was measured by using a profilometer (Rank Taylor Hobson Company). Profilometer was utilized to measure a wear track, and planimeter was used to calculate wear area. Average value of the three measurements for each wear condition was used in the results. SEM was employed to examine the worn area on the surface of Si_3N_4-ZrO_2 composites.

3. Results and discussions

3.1. *Mechanical properties*

Figure 2 shows the variation of mechanical properties as a function of ZrO_2 content in Si_3N_4. As increased the amount of ZrO_2, grain size of Si_3N_4 did not change much, from which it can be deduced that the presence of ZrO_2 in Si_3N_4 can not contribute to the increase of the toughening parameter [7-10], but densification of Si_3N_4 was enhanced. As the amount of ZrO_2 increased, mechanical properties of Si_3N_4 were degraded, except composite with at 25 % ZrO_2. Figure 3 shows the SEM microstructures of Si_3N_4-ZrO_2 composites with variation of ZrO_2. As shown in Fig. 3, cracks propagated through the interface mainly between Si_3N_4 and ZrO_2. As increased the amount of ZrO_2, however, cracks had shown the transgranular propagation in Si_3N_4 grains. Although ZrO_2 had high fracture toughness, fracture toughness of Si_3N_4-ZrO_2 composites was decreased compared to that of Si_3N_4.

3.2. *Wear characteristics*

Figure 4 shows tribological properties of Si_3N_4-ZrO_2 composites in air. As the amount of ZrO_2 increased in Si_3N_4-ZrO_2 composites, wear volume was decreased dramatically above 20 wt% of ZrO_2. Wear properties have been known to be clearly dependent on the microstructure and mechanical properties of materials such as the grain size, grain shape, grain boundary phase, and grain boundary chemistry [11-13]. Wear rates of brittle ceramic materials was proposed to be proportional to the inverse of hardness and fracture toughness based on the assumption that wear occurred by brittle cracking [14]. In this study, it was found experimentally that wear resistance of Si_3N_4-ZrO_2 composites was improved, but mechanical properties of Si_3N_4-ZrO_2 composites were degraded.

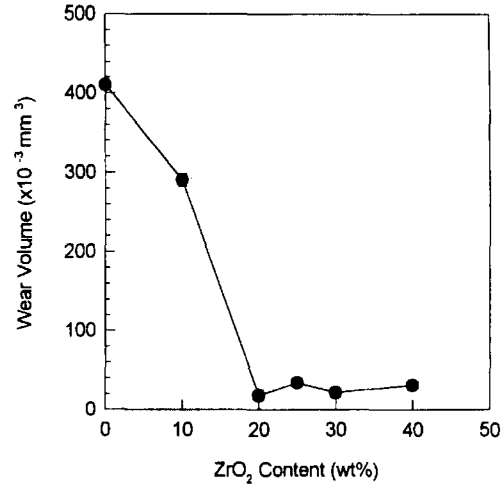

Fig. 4. Variation of wear volume of Si_3N_4-ZrO_2 composites in air with different content of ZrO_2.

Figure 5 shows SEM micrographs of wear surface for Si_3N_4-ZrO_2 composites. As increments of the amount of ZrO_2, the amount of off particles on wear surface was gradually reduced. Wear volume up to 10 wt% ZrO_2 was decreased slightly, but above 20 wt% ZrO_2 it was not changed much. It seems to be due to the full densification of Si_3N_4. In this study, wear rate was found to relate to closely sinterability. In dry contact, however, the wear rates are governed by fracture mode of materials. According to the early works [15], for a polycrystalline ceramic grain boundaries are known to preferred sites for crack propagation because of their lower fracture toughness and voids or impurities can also lead to intergranular fracture giving grain pull-out. Also, as shown in worn surface, crack propagation occurred at the edge of wears track. These micrographs reveal the formation of wear debris as fracture proceeds by lateral crack propagation, and the agglomeration of the debris to form platelets is physically attached to the groove surface. Also, a lack of lubricant and the high-speed cause to raise the contact flash temperature as well as contact stress, which produce thermal and mechanical stress and then enhance fracture of brittle

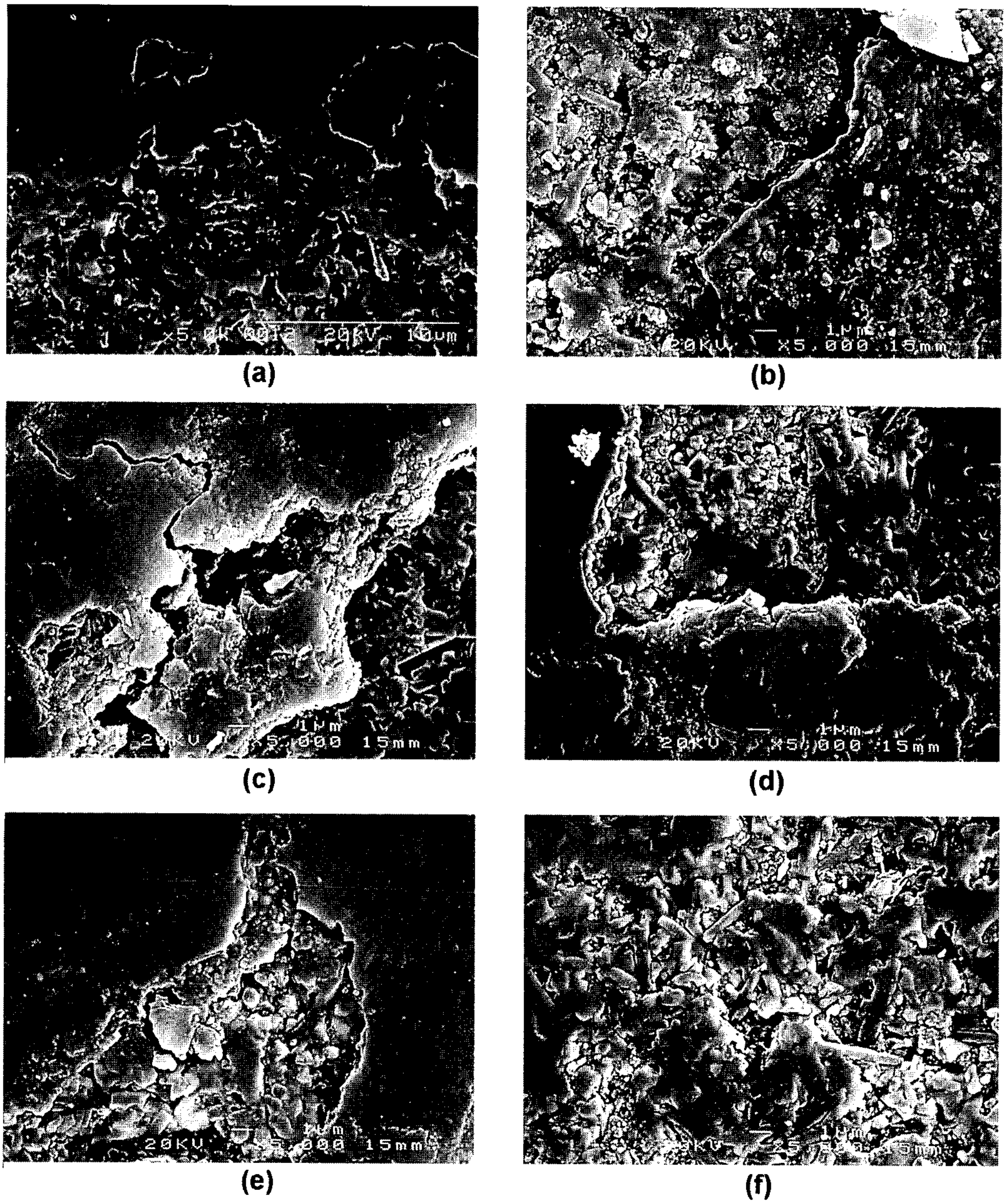

Fig. 5. Scanning electron micrographs of the worn surface with of Si_3N_4-ZrO_2 composites with different content of ZrO_2; (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 25 wt%, (e) 30 wt%, (f) 40 wt%.

ceramics. In this study, wear is mainly associated with microcracking, grain pullout, and chipping. When the amount of ZrO_2 was increased, wear resistance of Si_3N_4-ZrO_2 composites was improved due to toughening mechanism such microcracking, short crack toughness and stress induced phase transformation during sliding wear testing. Also wear behavior was improved because Si_3N_4 grain act as short fibers into Si_3N_4-ZrO_2 composites. Crack propagation occurs at the interfaces between Si_3N_4 and ZrO_2 or Si_3N_4 grain boundaries. It is important to be noted that grain pullout occurs at loads lower than the critical value required to maintain equilibrium [16].

As shown in Fig. 6, when sliding against silicon nitride ball, the coefficient of friction was below 1.

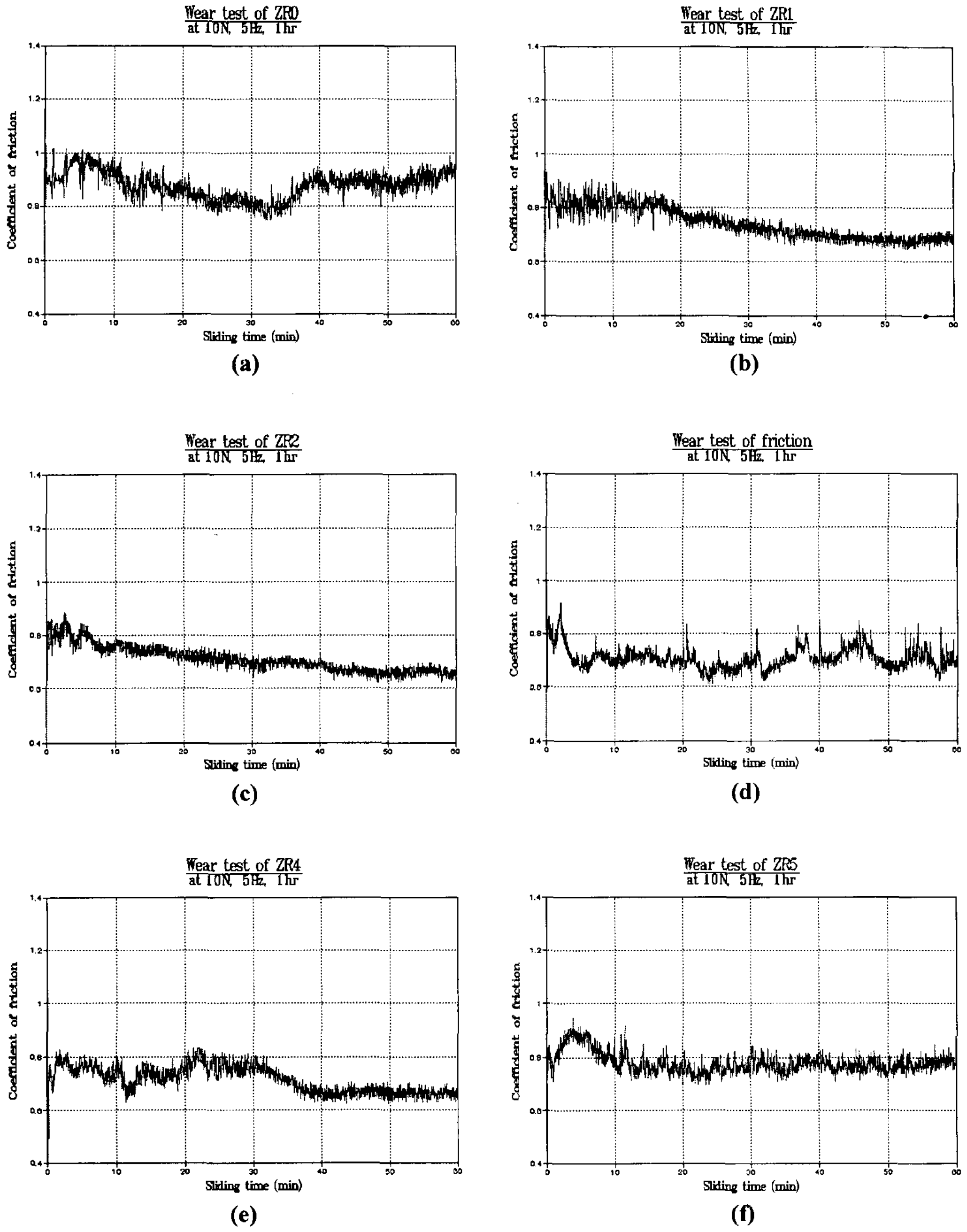

Fig. 6. Variation of friction coefficient of Si_3N_4-ZrO_2 composites in air with different content of ZrO_2; (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 25 wt%, (e) 30 wt%, (f) 40 wt%.

For Si_3N_4 without ZrO_2 and Si_3N_4-10 wt% ZrO_2 specimens, coefficient of friction were relatively lower value rather than those of other specimens. Also, high wear volume was caused by higher fluctuation of frictional coefficient. Other composites were relatively lower frictional coefficient and fluctuation of frictional coefficient. However, for composites above 20 wt% ZiO_2, increment of wear volume were caused by frictional peaks rather than other composites above 20 wt% ZiO_2. Therefore, as the coefficient of friction was rapidly stablized and a few peaks, the wear rates were decreased. Finally, factors influencing the wear rates may be considered as microcracking.

4. Conclusions

In this study, as added ZrO_2 into Si_3N_4, microstructure, mechanical properties and wear behaviors of Si_3N_4-ZrO_2 composites were investigated as a function of the amount of ZrO_2. As the amount of ZrO_2 increased, sinterability of Si_3N_4-ZrO_2 composites were enhanced. However, grain size of Si_3N_4 was unchanged, and mechanical properties were degraded. On the other hand, wear resistance with increasing the amount of ZrO_2 increased. Improvement of wear resistance may be was caused by toughening mechanism such as microcracking of ZrO_2 in Si_3N_4 during sliding wear testing.

Acknowledgement

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