EFFECT OF ADSORBED WATER ON FRICTION OF HOT-PRESSED SILICON NITRIDE AND SILICON CARBIDE AT SLOW SPEED SLIDING

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Summary

The effect of adsorbed water on the characteristics of friction of both silicon nitride and silicon carbide was studied experimentally using a pin-on-flat-type friction apparatus at a slow sliding speed of 10 mm min^{-1}. Silicon nitride and silicon carbide powder were hot pressed under the sintering conditions of pressure, 30 MPa, and temperatures 1800 °C and 2100 °C respectively.

A continuous increase in friction during reciprocal sliding was observed for the sliding of silicon nitride in laboratory air with a relative humidity of 50% ± 5%. It was attributed to a decrease in the protective surface layer during reciprocal sliding. The effects of time intervals in reciprocal sliding, environmental humidity and temperature on the formation of the surface layer were examined. Experimental results showed that shorter time intervals, lower humidity and higher surface temperature increased the sliding friction of ceramics. These influences were also attributed to the decrease in the effect of adsorbed water on sliding friction, because the above sliding conditions prevented the formation of a protective surface layer.

1. Introduction

Material studies have indicated that chemically active environments can markedly influence the deformation of solids [1 - 6]. These effects include

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the following: strengthening by dissolution of the solid surface, the Joffe effect [1]; surface hardening, the Roscoe effect [2]; surface softening, the Rebinder effect [3]; correlation between hardness and the zeta potential [4]; the effect of adsorbed water on indentation creep [5].

Besides these chemomechanical effects [6], the presence of adsorbate on ceramics can alter the surface activity of the materials [7].

Tribological properties, such as adhesion, friction and wear of solid surfaces in contact, are extremely dependent on the adsorbed molecules. Among various kinds of adsorbates, water is one of the most important molecules which can affect the tribological properties of ceramics. These effects are quite complicated and the characteristics are dependent on the materials of the ceramics. Highly humid air reduces both the friction and the wear rate of silicon nitride [8, 9] but increases the wear rate of zirconium oxide or aluminium oxide [10, 11].

Although these effects of water vapour have not yet been fully understood, interesting explanations have been proposed by Fischer and Tomizawa [9]. Wear tracks on silicon nitride are covered by a highly hydrated silica which is obtained through a tribochemical mechanism. This surface layer may protect the silicon nitride surface from severe wear. In contrast, aluminium oxide is stable with respect to oxidation and does not form a protective layer. Alumina is subject to stress corrosion cracking which is enhanced by the presence of water vapour. In alumina, water vapour increases wear by facilitating the fracture of the material [9].

The existence of a surface layer, which is similar to that of the above study, has been reported with respect to a surface of silicon nitride which was surface finished in water [12].

The objective of the present paper is to study the effects of adsorbed water on the friction of silicon nitride and silicon carbide at slow sliding speed. A surface protective layer which reduces the friction of both ceramics will be formed through the adsorption of water and removed during sliding. Therefore the effectiveness of the adsorbed water must depend on the time intervals of reciprocal sliding, the humidity and the environmental temperature. The influences of these three factors on the sensitivities of silicon nitride and silicon carbide to humidity were studied using slow speed reciprocal sliding experiments.

2. Materials

The materials used in the investigations were hot-pressed silicon nitride and silicon carbide. Silicon nitride powder was Hermann C. Starck's H1. The average particle diameter was 0.7 μm. More than 97% of the powder was α-Si_3N_4. The powder was mixed with sintering aids and was milled with a ball mill for 24 h. After that, it was filtered and dried in an oven. Silicon carbide powder was Hermann C. Starck's B-10. The average particle diameter was 0.5 μm. Silicon carbide powder was mixed with a densification aid of

2 wt.% aluminium oxide and was prepared for hot-press sintering using the same procedure as silicon nitride. Hot-press sintering was carried out using a graphite mould along with a high frequency inductive heater. The hot-press temperatures of silicon nitride and silicon carbide were 1800 °C and 2100 °C respectively. These powders were pressed at these temperatures at a pressure of 30 MPa for 30 min. The hot-pressed ceramics were ground with a number 200 diamond whirl and polished with a diamond disk containing diamond powder of which the average diameter was 6 μm. Surface roughness values (r.m.s.) for silicon nitride and silicon carbide were 0.07 μm and 0.12 μm respectively. The mechanical properties of these ceramics are shown in Table 1. The fracture toughness K_{1C} was measured using a controlled microflaw technique. Microflaws were introduced using a Knoop indenter with a 50 N load in the centre of a surface perpendicular to the longitudinal axis of the specimens. The specimens were then polished to remove residual stresses and were fractured using three-point bending at a constant crosshead speed of 0.5 mm min^{-1}.

TABLE 1

Sintering conditions and mechanical properties of test specimens[a]

Specimen	*Materials*	*Hot-press temperature* (°C)	*Densification aids*	*Vickers' hardness* (MPa)	*Fracture toughness* K_{1C} (MN m$^{-3/2}$)	*Density* (g cm^{-3})
SN-1	Si_3N_4	1800	MgO	17800	2.56	3.14
SiC	SiC	2100	Al_2O_3	20400	1.70	3.17

[a]Hot-press pressure 30 MPa, 30 min.

3. Experimental equipment

Friction experiments were carried out using a pin-on-flat-type friction apparatus which is shown schematically in Fig. 1. The tip radius of curvature of the pin specimen was 0.2 mm. The sliding speed of the flat specimen was 10 mm min^{-1}. Load was applied by placing a dead-weight of 0.25 N on the top of the pin specimen holder. These sliding conditions were selected so that the friction characteristics of the ceramics would not be affected by frictional heat during sliding. The frictional forces were sensed by strain gauges which were cemented on parallel leaf springs. The apparatus was housed in a plastic box to maintain atmospheric control (Fig. 2). The plastic box had a capacity of 0.08 m^3 and an air pump, which supplied dry or wet air to the box, which had a flow rate of 0.01 m^3 min^{-1}. Specimens were kept in a hot oven at a temperature of 80 °C for 1 h and then set on the friction apparatus. After being kept in the box at a given humidity for 1 h, the friction experiments were conducted.

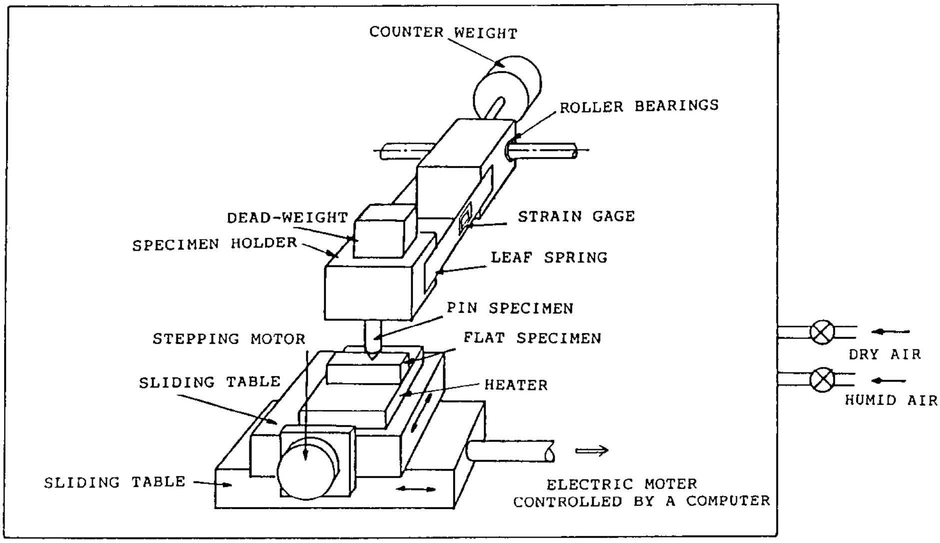

Fig. 1. Schematic representation of friction apparatus.

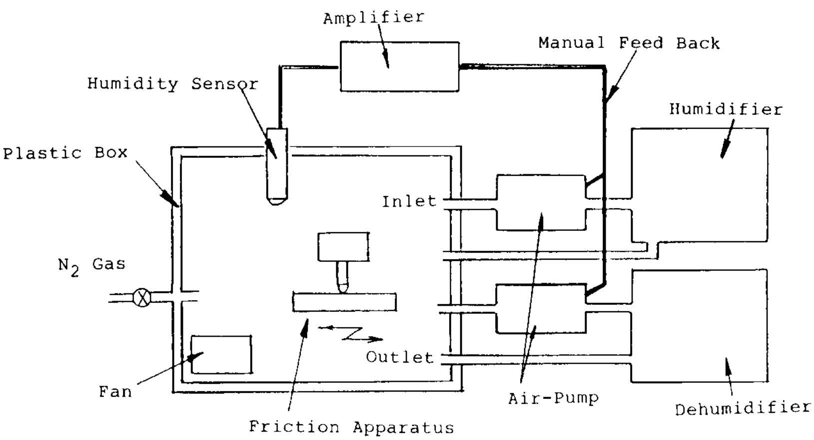

Fig. 2. Schematic representation of system of humidity control.

4. Experimental results and discussion

4.1. Repeated reciprocal sliding experiments

Reciprocal sliding experiments were carried out using the pin-on-flat apparatus in a laboratory atmosphere with a relative humidity of 50% ± 5%. Figure 3 shows the relationship between the repeated number of reciprocal slides and the coefficient of friction. The average normalized standard deviation of these data was about 8%. The material of both the pin and the flat specimens used here was hot-pressed silicon nitride.

In cases in which the pin slides the same trace of the surface of the flat specimen during reciprocal sliding, which will be called "repeated sliding" in

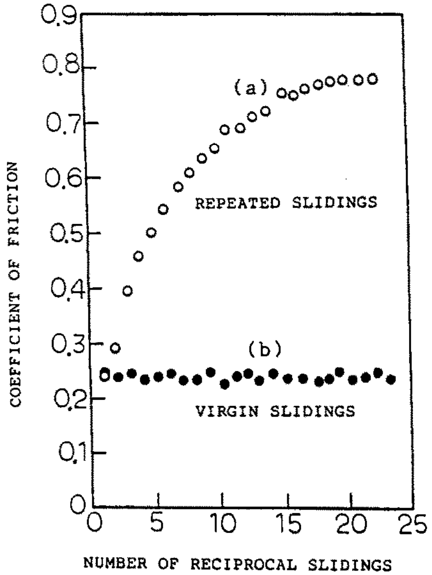

Fig. 3. Relationship between the number of reciprocal slides and the coefficient of friction: flat specimen, silicon nitride; pin specimen, silicon nitride; sliding speed, 10 mm min^{-1}; load, 0.25 N; relative humidity, 50% ± 5%.

this paper, the coefficient of friction increases as the number of slides increases. In cases in which the pin specimen slides a different trace on each reciprocal slide, which will be called "virgin sliding" in this paper, the number of reciprocal slides has little effect on the coefficient of friction. In both experiments, the surface of the pin specimen had been kept in contact with the flat specimens.

Although the former result represents a change in the adhesive properties of the contacting surfaces of both the pin and the flat specimens during reciprocal sliding, which indicates an increase in the coefficient of friction, the latter result means that a change in the surface of only the pin specimen is not enough to increase the coefficient of friction. The increase in the coefficient of friction in the former case is not so drastic but it is continuous, *i.e.* the change in the adhesive properties of the contacting surfaces is continuous. Therefore the surface layer, which is removed from the surface during sliding and affects the frictional properties of silicon nitride, cannot be considered to be a monoatomic layer.

For comparison, similar experiments with repeated slides were carried out using silicon carbide in a laboratory atmosphere with a relative humidity of 50% ± 5%. Figure 4 shows experimental results in which the silicon carbide surfaces do not experience drastic changes during sliding so as to affect the coefficient of friction.

These results show that the increase in friction during reciprocal sliding is a material-dependent phenomenon.

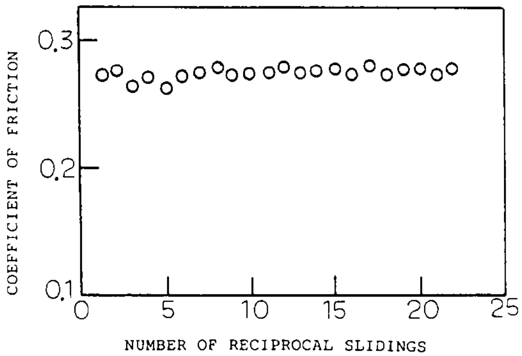

Fig. 4. Coefficient of friction *vs.* the number of reciprocal slides for silicon carbide: flat specimen, silicon carbide; pin specimen, silicon carbide; sliding speed, 10 mm min^{-1}; load, 0.25 N; relative humidity, 50% ± 5%.

4.2. Effect of holding time in each reciprocal slide

Reciprocal sliding experiments of the repeated sliding type were carried out with a silicon nitride specimen in a laboratory atmosphere with a relative humidity of 50% ± 5%. In the experiments, the sliding table was held for a period of time at the end of each slide. Figure 5 shows the relationship between the numbers of reciprocal slides and the coefficient of friction as a function of the holding time.

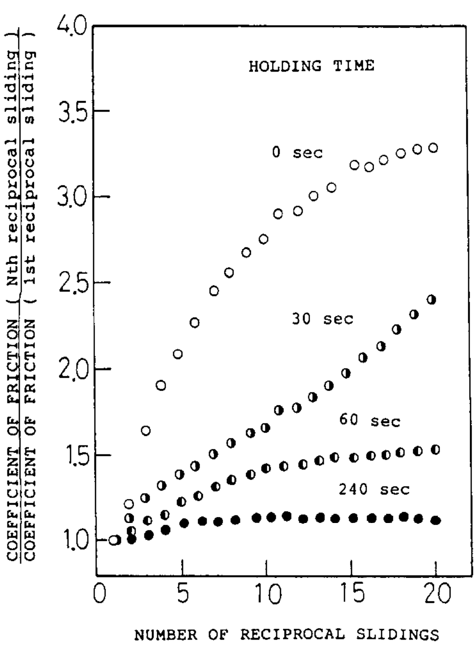

Fig. 5. Effect of the holding time between each reciprocal slide on the coefficient of friction: flat specimen, silicon nitride; pin specimen, silicon nitride; sliding speed, 10 mm min^{-1}; load, 0.25 N; relative humidity, 50% ± 5%.

As the holding time increases the increment of the coefficient of friction becomes smaller. The coefficient of friction at a holding time of 240 s is almost constant even after 30 reciprocal slides. The surface of silicon nitride has a protective layer which is removed gradually by each sliding contact but is repaired when the surface is exposed to the atmosphere.

The results show that the protective layer is repaired even more sufficiently as the holding time increases and, in the case of the holding time of 240 s, the protective layer is almost stable during reciprocal sliding.

Because the formation of a protective layer takes more than several tens of seconds, the formation is not just the physical adsorption of a monolayer. To understand the factors which affect the formation of the protective layer, friction experiments were carried out in an atmosphere consisting of more humid air.

4.3. Effect of humidity on friction

Figure 6 shows the relationship between the number of reciprocal slides and the coefficient of friction for repeated sliding in an atmosphere with a relative humidity of 80% ± 2%. No increase in friction can be seen in the figure during reciprocal sliding.

Although the sliding conditions of the experiment were quite similar to those of curve (a) in Fig. 3, except for the atmospheric humidity, the results in Fig. 6 show a completely different tendency than that of curve (a) which shows an evident increase in friction during reciprocal sliding. This means that the formation of a protective layer is a phenomenon which is related to adsorption of water.

Concerning silicon carbide, although hot-pressed silicon carbide shows no evident increase during reciprocal sliding, as shown in Fig. 4, the frictional characteristics of silicon carbide may also be affected by the atmospheric

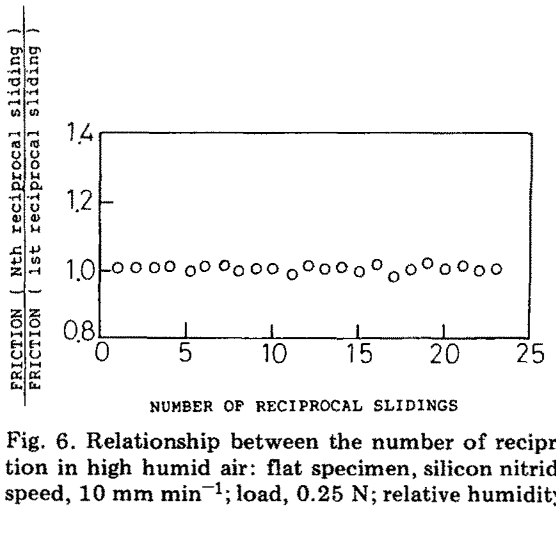

Fig. 6. Relationship between the number of reciprocal slides and the coefficient of friction in high humid air: flat specimen, silicon nitride; pin specimen, silicon nitride; sliding speed, 10 mm min^{-1}; load, 0.25 N; relative humidity, 80% ± 2%.

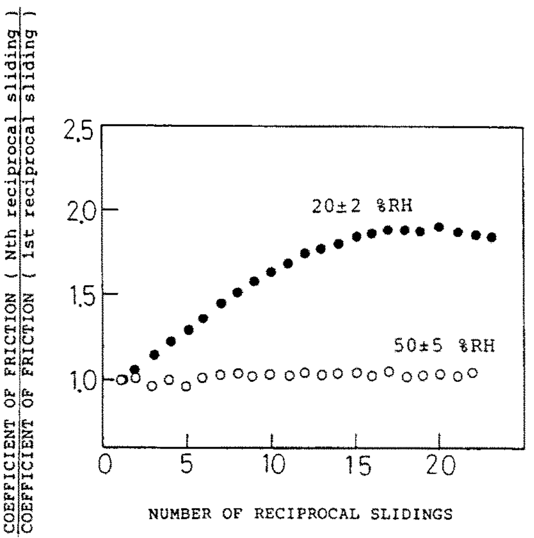

Fig. 7. Relationship between the number of reciprocal slides and the coefficient of friction in low humid air: flat specimen, silicon carbide; pin specimen, silicon carbide; sliding speed, 10 mm min^{-1}; load, 0.25 N; relative humidity, 20% ± 2%.

humidity. Therefore the undetectable increase in friction may depend on the humidity.

Friction experiments were then carried out with silicon carbide in an atmosphere with a relative humidity of 20% ± 2% which is lower than that in Fig. 4. The results are shown in Fig. 7. The ratio between the coefficient of friction of the Nth number of reciprocal slides and that of the first slide increases as the number of reciprocal slides increases. This increase is similar to that of silicon nitride in laboratory air with a relative humidity of 50% ± 5%. Hot-pressed silicon carbide has similar friction characteristics with respect to the effect of water vapour but the speed of formation of the protective layer is higher than that of silicon nitride. The higher speed of formation prevents the friction at the silicon carbide surface from increasing during reciprocal sliding, as shown in Fig. 4.

From the above discussion, it is clear that the friction of both silicon carbide and silicon nitride was affected by the formation of a protective layer which was connected with the speed of adsorption of water vapour. Following this line of thought, the suspicion that the surface temperature would affect the adsorption speed and this in turn would affect the friction of ceramics is prevalent. For this reason, friction experiments were carried out with silicon carbide in laboratory air with a relative humidity of 50% ± 5% at a temperature of 200 °C.

4.4. Effect of temperature on friction

Figure 8 shows the relationship between the number of reciprocal slides and the coefficient of friction for hot-pressed silicon carbide. Although the

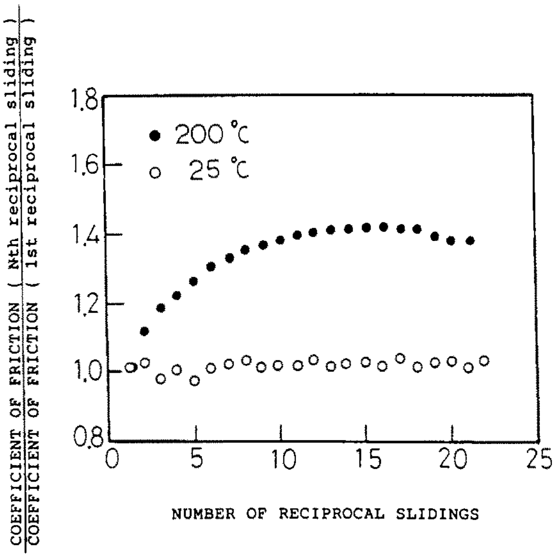

Fig. 8. Effect of surface temperature on the increase in friction: flat specimen, silicon carbide; pin specimen, silicon carbide; sliding speed, 10 mm min^{-1}; load, 0.25 N; relative humidity, 50% ± 5%.

sliding conditions in Fig. 8 are the same as those in Fig. 4, except for the surface temperature, the friction characteristics in reciprocal sliding are not the same, meaning that the results in Fig. 8 show an evident increase in the coefficient of friction during sliding.

The effect of the increase in temperature on the friction characteristics is similar to that of the decrease in humidity which is shown in Fig. 7. The higher surface temperature decreases the rate of adsorption of water on the silicon carbide surface and then reduces the speed of formation of the protective layer and, in turn, increases the friction coefficient during reciprocal sliding.

Concerning the chemical composition of the protective layer and the mechanism of the reduction of friction, many possibilities should be considered such as the occurrence of multilayered water vapour adsorption, formation of hydrated amorphous material [12] and chemomechanical effects.

Microscopic observation using a scanning electron microscope showed no evident traces of plastic grooving or occasional fracture throughout all of the experiments. This means that the thickness of the removed layers during the sliding experiments was much less than a micrometre.

Although further studies must be carried out to understand the protective layers themselves, it was made clear that these layers are removed from the surfaces during reciprocal sliding and their repair is prevented by the following three sliding conditions: the shorter time interval of each reciprocal sliding movement; lower atmospheric humidity; higher temperature. They reduce the adsorption rate of water vapour and prevent repair.

This is followed by an increase in friction for both silicon carbide and silicon nitride during reciprocal sliding.

5. Conclusions

Experimental studies were carried out to examine the effect of adsorbed water on the friction of silicon nitride and the following conclusions were drawn.

(1) A protective layer is removed from the surface during reciprocal sliding if repair is not sufficient.

(2) The rate of formation of the protective layer depends on the time interval of each reciprocal sliding movement, the atmospheric humidity and the surface temperature. A shorter time interval, lower humidity and higher surface temperature prevent the formation of the protective layer and increase sliding friction.

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