Environmental Effects on Friction and Wear of Ceramics

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Abstract

It is well known that the characteristics of friction and wear of ceramics are extremely sensitive to the environment. It is possible to divide the mechanism of the environmental effects into three major steps: The formation of the adsorbed layers, the change of the surface properties and the formation of tribochemical reaction products. Under actual sliding conditions, the influence of tribochemical reaction plays an effective role. An attempt have been made to use this effect to activate an excellent lubrication. This work deals with the relationships between the environment and the tribological characteristics of ceramics.

1. Introduction

Friction and wear of solids are caused by phenomena which occur on material surfaces. Thus, friction and wear characteristics depend highly on the physical and chemical properties of the surfaces. One of the most important factors used for defining the properties of surfaces is the environmental effect which results in a thin surface layer. It is well known that the mechanical strength of ceramic materials is likely to be strongly affected by the surrounding atmosphere. In particular, their tribological properties are extremely sensitive to the environment. Many factors influence the usual phenomena of friction and wear simultaneously, so it is difficult to observe the environmental factor alone. Therefore, the first important step in the study of the tribology of ceramics is to single out those factors from among many factors that contribute to the environmental effect which exert a strong influence on the friction and wear characteristics and to elucidate the mechanisms of their action. If it were possible to start from this premise and construct lubricating systems which make use of the environmental effect and use this feedback of the tribology of materials as a guide for planning the development of ceramic materials, it would definitely be possible to design new sliding systems possessing properties required for applications under different environmental conditions.

2. Mechanisms of environmental effect

The elucidation of environmental effect mechanisms is much easier if the effects are classified into three major steps depending on the environmental action, as shown in Table 1.

| 1 | Formation of adsorption layers |
| 2 | Change of mechanical properties by adsorption |
| 2-1 | Chemo-mechanical effect |
| 2-2 | Stress corrosion cracking |
| 3 | Tribochemical reaction |

2.1 Formation of adsorption layers

The adhesion theory concerning the mechanism of friction between solids proposed by Bowden-Tabor is based on experimental results obtained by studying friction phenomena, mainly between metal surfaces in friction. However, this adhesion theory can also be applied to NaCl crystals and to numerous types of hard and brittle materials as was proven by King and Tabor in 1954. At present, the adhesion theory is applicable to friction between ceramic materials, excluding the controversy concerning the anisotropy of friction observed in single crystalline materials. According to the adhesion theory, the shearing stress at the junction between two solids within

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the region of an actual contact decreases with
an increase in the adsorbed molecular layer.
The formation of the adsorbed layer results in a
wear reduction through the reduction of the
friction coefficient.

2.2 Change of mechanical properties of sur-
faces with adsorption
Molecules adsorbed from the environment
cause a change in the surface properties of
solids. At present the following two main fac-
tors are related to this process.

2.2.1 Chemo-mechanical effect
The mechanical strength of a solid surface is
affected by the adsorption of extraneous mole-
cules from the surface. The changes in the
strength depend highly on the type and molecu-
lar weight of the molecules adsorbed. Rehbin-
der et. al.7 explained that these phenomena
were due to the fact that the rupture stress of
the solids is related to the surface energy
by the equation8,9:
\[ \sigma = \left[ \frac{E y P}{C} \right]^{1/2} \] (1)
where
\( \sigma \): Rupture stress of ideal brittle material
containing micro-cracks
\( E \): Young's modulus
\( P \): Surface plastic work
\( C \): Depth of micro-crack on the surface

In brittle materials such as ceramics \( y \gg P \).
Since it is believed that other variables are not
affected by the environment, is lowered with a
reduction in \( r \). The relationship between the
surface energy and the strength was established
for quartz glass10 as shown in Fig. 1. Numerous
data proving this relationship were also
reported11.

On the other hand, Westwood et al. perfor-
m a series of studies on the mechanical
strength of crystals and glass in various liquid
surroundings. They proposed the WGL
(Westwood, Goldheim, Lye) hypothesis12,13),
which states that the surface potential and
distribution of mobile charge carriers in the
near-surface region change with chemisorption
of molecules. These changes, it is suggested,
affects the ease with which kinks are generated
on, and move along, near-surface dislocations
in crystals, and hence affect line-defect mobi-
ity. For ionic solids, changes in the electron
occupancy of near-surface point defects will
also influence their interactions with disloca-
tions, and this too will affect dislocation mobi-
ity and crystal hardness. Figure 2 illustrates
one of the results obtained in the experiments
performed by Westwood et al. where the rela-
tionship between the hardness and the zeta
potential14 of alumina single crystals in a water
solution of sodium hydroxide and n-alcohol with
a number \( N_c \) of carbon atoms in a molecule can
be verified. In both solutions the maximal
hardness is observed when the zeta potential is equal
to 0. This correlation between the zeta potential
and the mechanical properties was also
observed in soda glass and \( \text{MgO}^{15} \). Numerous reports
indicating indefinite results based on the WGL
hypothesis have been published as well16.

It is possible to say that we are now at a stage
where the existence of chemo-mechanical effects17
is being confirmed, but a comprehen-
sive insight into their mechanisms has not yet
been reached. However, if the chemo-mechani-
cal effect is accepted as an environmental effect
on friction and wear behavior of ceramics, then
such mechanisms as the reduction of the friction
coefficient by a lowering of the yield stress in
the subsurface layers and the restricting effect
on the rupture by wear due to the avoidance of
local stress concentrations are possible.

2.2.2 Stress corrosion cracking
This phenomenon appears following adsor-
tion of polar molecules to solid surfaces. How-
ever, it is different from the chemo-mechanical effect\(^{18}\). In some types of ceramics, it is known that the crack growth speed at the surface of a material under stress is accelerated by adsorption of polar molecules such as water and ammonia\(^{19,20,21}\). This phenomenon is called stress corrosion cracking. It is attributed to the fact that the chemical reaction at the crack tip accelerates under the influence of the applied stress. Since stress corrosion cracking has an influence deep beneath the surface compared with the chemo-mechanical effect, it is likely to cause destructive wear. Figure 3 shows a model of stress corrosion cracking of partially stabilized zirconia.

2.3 Tribochemical reaction

At the sliding surface, the peculiar chemical reaction which is caused by friction is generally called a tribochemical reaction\(^{22}\). When subjected to the mechanical action of friction, surfaces are activated by the exposure of fresh surfaces which are free from any adsorbed molecules or by a change in the crystalline structure (lattice defects, dislocation, amorphous state)\(^{23}\). During friction, sites of specific reactions are initiated by high temperature, high pressure and high shear stress. The occurrence of secondary or tertiary physical and chemical phenomena, such as exoelectron (Kramer electron) radiation\(^{24}\), triboelectrification\(^{25}\), triboluminescence\(^{26}\) and tribo-plasma generation\(^{27}\) promote peculiar chemical reactions. Reactions between adsorbed molecules, reactions between adsorbed molecules and surface molecules, or reactions between atoms of solids through adsorbed molecules result in the formation of a layer of a third material which differs from the initial materials on the sliding surfaces. This tribochemical reaction is believed to promote lubrication through the formation of reaction prod-

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**Fig. 2** Relationship between hardness and zeta potential of Al\(_2\)O\(_3\)
(a) in water sodium hydroxide
(b) in n-alcohol

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**Fig. 3** A model of stress corrosion cracking
ucts at the sliding surface which reduce friction and wear in ceramics. However, removal of these reaction products leads to a slight increase in wear.

3. Friction and wear characteristics and tribochemistry

We will now attempt to establish the relationships between the actual friction and wear characteristics taking into account tribochemistry. Friction and wear in ceramics from the viewpoint of tribochemistry were analyzed by Fischer and Tomizawa who reported their studies on the friction characteristics of silicon nitride and silicon carbide in water. Figure 4 shows a typical example of friction and wear behavior of ceramics being lubricated with pure water. The friction coefficients of silicon nitride and silicon carbide have very small values even under low sliding velocity conditions, and are comparable with that of hydrodynamic lubrication. In addition, the specific wear rate of these materials decreases with an increase in sliding velocity. These phenomena of friction reduction in water are explained by the formation and the dissolution of silicon hydrates as a result of tribochemical reactions and by the simultaneous synergistic effect of the smoothing of the sliding surfaces. The form of wear in which the wear proceeds with a gradual dissolution due to tribochemical reactions is called tribochemical wear. This wear mechanism was established by Tomlinson 60 years ago; it was called “atomic wear”.

Figure 5 shows the effect of humidity on the friction and wear properties. Under such dry conditions, especially in low humidities, the distractive wear dominates the wear properties. The friction coefficient decreases with an increase in relative humidity for all ceramics, but the wear rates show no such definite tendency. For example, while the wear rates of alumina and silicon carbide decrease as the relative humidity increases, the highest wear rate of partially stabilized zirconia appears at 20% relative humidity. In the case of silicon nitride, the lowest wear rate is obtained at 50% relative humidity. The increase in humidity restrains the distractive wear, but it accelerates the tribochemical reaction of silicon nitride with water, resulting in the formation of reaction products, silicon hydrates.

Figure 6 shows the influence of an organic compound atmosphere on the friction and wear behavior of alumina. Both friction and wear in these organic compounds are very low as compared to those in nitrogen. In hexane and benzene, the formation of reaction products similar to friction polymers can be observed on the sliding surfaces as shown in Figure 7. These reaction products are highly viscous grease-like substances, and have lubricating effects. Such lubricating effect of the reaction products can also be observed for alumina being lubricated with a water solution of fatty acid sodiums as shown in Figure 8. The friction and wear of oil
Friction coefficient, $\mu$  
Specific wear rate, mm$^{3}$/N

| Compound | Friction Coefficient | Specific Wear Rate |
|----------|----------------------|--------------------|
| $\text{H}_2\text{O}$ | 0.2 | $10^{-11}$ |
| $\text{C}_2\text{H}_6\text{OH}$ | 0.4 | $10^{0}$ |
| $\text{CH}_3\text{COOH}$ | 0.6 | $10^{-10}$ |
| $\text{C}_2\text{H}_4\text{CO}$ | 0.8 | $10^{-9}$ |
| $\text{C}_4\text{H}_8$ | 1.0 | $10^{-8}$ |

- lubricated ceramics are likely to be strongly affected by the formation of reaction products which result from tribochemical reactions that contribute to the lubrication effect of a particular introduced additive$^{34}$. Studies on the formation of friction polymers by Hermance and Egan$^{35}$ were first published more than 30 years ago$^{36}$, but mechanisms of their formation still remain unclear in many aspects.

When the surfaces of different materials are mated, a reaction through the surrounding atmosphere between them occurs. For example, when sliding alumina and iron surfaces, the formation of a spinel-type solid solution occurs between the iron oxide and alumina. This is attributed to the process of wear$^{37}$. The characteristics of friction and wear for silicon nitride and alumina in water are shown in Fig. 9$^{38}$. On

**Fig. 6** Influence of organic compounds on friction and wear of $\text{Al}_2\text{O}_3$: load 10N, sliding velocity 0.4m/s, total sliding distance 1256m.

**Fig. 7** Example of friction polymer like reaction product on alumina disk surface in atmosphere of benzene vapor.

**Fig. 8** Optical micrograph of $\text{Al}_2\text{O}_3$ in water with lauric acid sodium.

**Fig. 9** Friction and wear characteristics in water when mating silicon nitride and alumina; Pin-on disk, load 50N, sliding velocity 0.4m/s, total sliding distance 1256m.
the other hand, when the wear process proceeds with the dissolution resulting from the reaction between silicon nitride and alumina, the dis­
tructive wear of silicon nitride is restrained. In this case the friction characteristics are signifi­
cantly improved. The improvement of the lubrica­tion characteristics using the reactions between mated surfaces of different materials is one of the important methods for future tribo­
systems.

Figure 10 shows the wear characteristics of alumina particles dispersed zirconia and par­
tially stabilized zirconia (PSZ) in water. This composite material was developed to improve the mechanical properties of PSZ; it raised the stress level required for the martensitic trans­
formation of tetragonal phase to a monoclinic phase and restrained the stress corrosion crack­ing. The wear rates of both PSZ (ZYM, ZYH) increase with the sliding velocity. On the other hand, the specific wear rate of the composite materials (ZYS) decreases slightly with sliding velocities of over 0.2 m/s, and is found to be less than 1/10 that of ZYM and ZYH. A larger superiority in the wear characteristics of ZYS is obtained in organic liquids as shown in Fig. 11. Such an excellent tribological property is believed to be strongly related to the chemical activity of alumina, in addition to an improve­
ment in the mechanical strength.

4. Conclusion

Efficient applications of tribochemical reac­tions in lubricating processes require a quanti­tative estimation of the reactions at specific stages and the possibility of controlling them. One of the methods to achieve this objective is to clarify the tribochemical reactions that are necessary, giving a deeper insight into the tribo­
chemical activation and development of mater­i­als while taking their tribology into account. Therefore, fundamental approaches to the tribochemical reactions will be more and more important with the sophistication of analytical equip­ments.

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