

Tribocatalytic Reaction of Polytetrafluoroethylene Sliding on an Aluminum Surface

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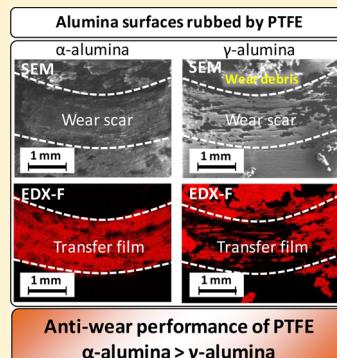
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ABSTRACT: To improve the tribological performance of polytetrafluoroethylene (PTFE) resin sliding against a metallic surface, it is important to understand the chemical behavior of PTFE in this sliding system. The tribochemical reaction of PTFE on an aluminum surface has been strenuously studied by a series of computational chemistry methods [Onodera, T., et al. *J. Phys. Chem. C* 2014, 118, 5390–5396, and Onodera, T., et al. *J. Phys. Chem. C* 2014, 118, 11820–11826]. One of the most important insights was that PTFE reacted tribochemically with the oxidized surface of aluminum as a Lewis acid catalyst, forming a fluoride on the aluminum surface. The aluminum fluoride formed was a cause of decreasing tribological performance of PTFE because of less formation of a transfer film. In regard to this tribochemical reaction, it was suggested that preventing the fluoride formation is a key to improving the tribological performance of PTFE sliding against an aluminum surface. In this study, to investigate fluoride formation by a tribochemical reaction, the catalytic effect of an oxidized aluminum surface was investigated experimentally and theoretically. Two phases of an oxidized aluminum surface, namely, the α and γ phases of alumina, were chosen for investigating the catalytic tribochemistry of PTFE. A thermogravimetric analysis showed that the γ -alumina surface potentially exhibited a stronger catalytic effect in regard to PTFE since the reaction took place at lower temperature. The effect of the catalytic reaction on the tribological performance of PTFE was then investigated by a pin-on-disk tribometer. The results of this investigation show that the amount of wear of PTFE on the γ -alumina surface was higher than that on the α -alumina surface. By observing the wear scar on alumina surfaces by a scanning electron microscope (SEM) combined with energy-dispersive X-ray spectroscopy (EDX), it was clarified that the transfer film formed on the γ -alumina surface was less abundant, while it was regularly formed and more abundant on the α -alumina surface. In other words, the antiwear performance of PTFE was decreased because a lower amount of transfer film was formed by the catalytic effect during friction. In addition, a density-functional-theory (DFT) calculation also showed a stronger catalytic effect on the γ -alumina surface because the energy barrier for the chemical reaction producing fluoride was lower than that on the α -alumina surface. On the basis of these results, it was suggested that controlling the catalytic reaction of PTFE on the sliding surface is one of the ways to improve the antiwear performance of PTFE.



1. INTRODUCTION

Polytetrafluoroethylene (PTFE) is recognized as a useful bearing material because it generates low friction when rubbed against metallic surfaces. However, its wear resistance is rather low in nature, thereby impairing its application as an engineering material. To overcome this problem, PTFE has often been used as a composite in combination with carbon,^{1,2} metal,² and ceramics^{3,4} fillers to increase its mechanical properties (such as hardness). On the other hand, the tribological performance of PTFE and its composites is strongly influenced by whether its working environment is high or low humidity.^{3,5} That is, rubbing PTFE under a low-humidity condition significantly increases the amount of wear.³

To address the above-described problem concerning use of PTFE under low-humidity conditions, a simulation method based on quantum chemical molecular dynamics (MD) has been applied to a sliding system composed of PTFE and a metal,^{6,7} and it was recently suggested that PTFE shows a unique tribochemical reaction in spite of its chemically stable nature. That is, as PTFE was rubbed against an aluminum-based material as a counter surface, the chemical bond between the carbon and fluorine atoms in the PTFE was dissociated, and aluminum fluoride was coincidentally formed on the counter

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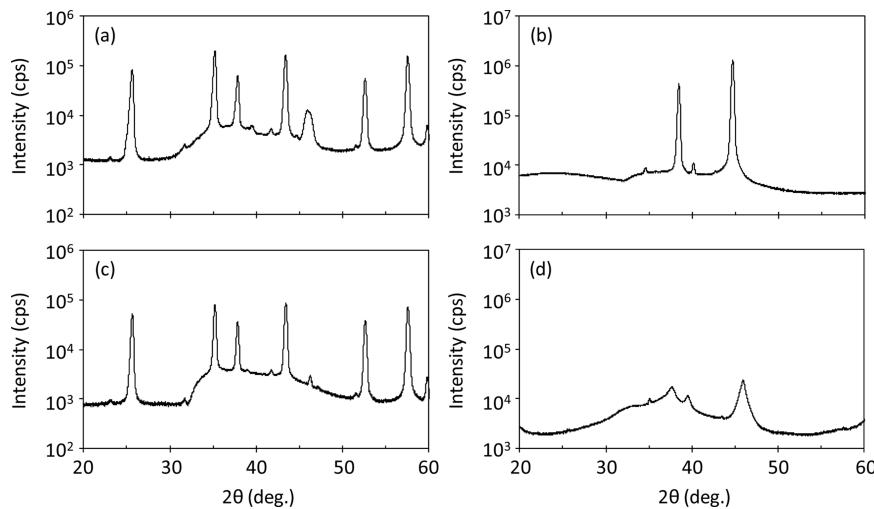


Figure 1. XRD patterns for aluminum disks treated by the (a) thermal spraying method and (b) anodizing alumite treatment. (c) and (d) are for the referential α - and γ -alumina powders. The diffraction intensity is plotted on a log scale.

surface. This chemical reaction was caused by not only the effect of friction but also the catalytic effect of the aluminum surface playing a role as a Lewis acid. The resultant product of this chemical reaction, viz., aluminum fluoride, affected the formation of a transfer film on the counter surface (which is the most important phenomenon that reduces wear). The transfer film inhibits direct contact between the PTFE and metallic surface despite its nanometric-scale thickness,³ i.e., 10 nm. The coverage and morphology of the transfer film on a metallic surface are also important in regard to the self-lubrication mechanism of PTFE.⁴ However, PTFE cannot easily be transferred to a counter surface with aluminum fluoride owing to the electrostatic repulsive interaction between the two materials; thus, the tribological performance of the PTFE/aluminum interface is decreased. Furthermore, under the low-humidity condition, the fluoride is easier to form on a metallic counter surface than under a high-humidity condition because the catalytic center is always exposed during the friction process.⁷

The above theoretical findings suggest that preventing fluoride formation, especially under a low-humidity condition, is the key factor in improving the tribological performance of PTFE rubbed against a metallic surface. To address the issue of fluoride formation, the tribocatalytic effect of the metallic surface should be focused on because it depends strongly on the chemical property and microstructure of the surface. One of the ways to control the tribocatalytic effect is to precoat the metallic surface with a covalent material. As for the tribocatalytic reaction of aluminum with fluorocarbon gases, Mori et al. showed that the tribocatalytic effect of aluminum oxide was much stronger than aluminum nitride (which exhibits greater covalency).^{8–10} Another way is to add some particles to a PTFE matrix as a composite. If the tribocatalytic effect of a metallic surface was significantly weakened by effective additives, decreasing the tribological performance by fluoride formation would be inhibited.

Accordingly, the control of tribocatalytic effect is the first step to improve tribological performance of a system in which PTFE and aluminum are rubbing together (hereafter, “PTFE/aluminum rubbing system”). In this study, the influence of the tribocatalytic effect on fluoride formation and the resultant tribological performance of PTFE were thus investigated by an

experimental method coupled with a theoretical approach. Two surfaces with different crystal structures, namely, α -alumina and γ -alumina (which is more catalytically active than α -alumina), were compared in order to study their tribocatalytic effect in relation to PTFE. Since the catalytical difference between these two materials has been tested in regard to a fluorine-based lubricant,¹¹ they are also suitable for first analyzing the focus of this study: the tribocatalytic reaction of PTFE on a metallic surface.

2. METHODS

2.1. Thermal Analysis. To investigate the fluoride formation in the chemical reaction of PTFE with alumina and compare the reactivities of fluoride formation in terms of the difference between alumina crystal phases, a thermal analysis was first conducted using a Seiko Instruments 6200 thermogravimetric/differential thermal analyzer (TG/DTA). Two mixed-powder samples were prepared: α -alumina with PTFE and γ -alumina with PTFE. The α - and γ -alumina powders used (produced by Kojundo Chemical) had average particle sizes of about 3 μm . The PTFE powder (produced by SynQuest) had an average particle size of about 0.5 μm and average molecular weight of 5×10^4 . All samples were prepared with the same mass ratio of 50% PTFE and 50% alumina. The sample chamber was purged by dry nitrogen gas with a flow rate of 200 cm^3/min . The samples were then heated for 360 min from room temperature to one of three maximum temperatures (723, 748, or 773 K) to observe the distinct effect of reaction temperature.

After the sample chamber cooled to room temperature, the residue was collected and analyzed by X-ray photoelectron spectroscopy (XPS), an Ulvac-Phi PHI5600, to detect the chemical products in the heated powders. A focused monochromatic Al $\text{K}\alpha$ X-ray (14 keV) beam was scanned over an 800 μm diameter spot on the residue. The photoelectron takeoff angle (relative to the sample normal) was 45°.

2.2. Friction Test. To evaluate the tribocatalytic effect on the friction and wear performances of the PTFE/alumina rubbing system, a friction experiment was then conducted by using a pin-on-disk tribometer (Bruker UMT-3) with a rotary drive. In the friction test, 1/4 in. PTFE ball was contacted with

a pure aluminum disk (99% purity, 30 mm diameter, and 10 mm thickness). A normal load of 3 N was applied, while rotation speed was set as 100 rpm (equivalent to a sliding speed of 0.0523 m/s). The test was conducted under laboratory air (temperature of 293 K and relative humidity of 35%) for 60 min. After the test, the sliding surface of the aluminum disk was observed by a scanning electron microscope (SEM) (Hitachi SU1510) combined with energy-dispersive X-ray spectroscopy (EDX) (Horiba EMAX).

Since our purpose is to investigate the tribocatalytic effect, two types of surface coating were prepared on aluminum disks (α -alumina by thermal spraying and γ -alumina by anodizing alumite treatment) and used for the above-described friction test. The thickness of the alumina coatings was about 50 μm , and the surface of each sample was carefully polished so as to reproduce the arithmetic mean roughness of $R_a = 0.4 \mu\text{m}$. X-ray-diffraction (XRD) patterns of two coated samples and those of pure α - and γ -alumina powders (for reference) are shown in Figure 1. It is clear that the peak position of the sample prepared by thermal spraying agrees fairly well with that of the referential powder of α -alumina. Moreover, the peak position of the alumite-treated sample almost matches that of the referential powder of γ -alumina. These results confirm that the two sample coatings were successfully prepared—with different crystal phases—on the aluminum disks.

2.3. Density Functional Theory. A calculation of density functional theory (DFT) was also performed for studying the mechanism on the chemical reaction of PTFE molecules adsorbing on α - and γ -alumina. DFT calculation was performed by the DMol³ program implemented in Accelrys Materials Studio Version 4.3. In the calculation by the DMol³ program, all core electrons were represented by effective core pseudopotentials^{12,13} to reduce the computation cost. Double numerical basis sets with polarization were employed, and a generalized gradient approximation in terms of Perdew–Burke–Ernzerhof (PBE) exchange-correlation functionals^{14,15} was used to optimize geometries and evaluate energies. Transition state was searched with the complete LST/QST method, where the linear synchronous transit (LST) maximization was performed for the coordinates interpolated between a reactant and a product, followed by repeated conjugated gradient minimizations and the quadratic synchronous transit (QST) maximizations until a transition state has been located.^{16,17} This searching method has been successfully validated to find the TS structure for a catalyst,^{18,19} metallic surface,²⁰ and organic systems.^{21,22} The supposed chemical reaction and calculation model are described in Section 3.3. All models used were visualized by Accelrys Materials Studio Visualizer.

To show the accuracy of the DFT method, a normal vibration mode was analyzed for a simple molecule of fluorocarbon. Table 1 shows the DFT-obtained and experimental vibrational frequency (described in ref 23) of the CF_2 stretching mode for the CF_4 molecule. Our DFT calculation reproduces the experimental vibrational frequency with an error of 3.3%, while the result by Ignatieva et al.²³ is more accurate (2.3% error) because of the DFT calculation with hybrid functional which is suitable for organic molecules. In the table, a bond distance between carbon and fluorine atoms is also shown, and the result of our DFT calculation agrees fairly well with the experimental one. In our work, the bond energy between carbon and fluorine atoms in the fluorocarbon molecule is important since the bond dissociation reaction

Table 1. Calculated and Experimental Values of Vibration Frequency and Geometric Parameters for the CF_4 Molecule

	this work: DFT with PBE functional	DFT with hybrid functional ²³	experiment
vibrational frequency for CF_2 stretching mode (cm^{-1})	1240	1254	1283 ²⁴
C–F bond distance (nm)	0.134	0.133	0.132 ²⁴
C–F bond energy (kJ/mol)	573.1	477.0	485.3 ^{25,26}

has taken place on the alumina surface. The calculated bond energy by DFT is 573.1 kJ/mol which is higher than the experimental one (485.3 kJ/mol) with 18.1% error. It can be concluded that the DFT calculation reproduces well the vibration mode and structure of the fluorocarbon molecule, while it overestimates the bond energy. The influence of this overestimation is to be mentioned in Section 3.3.

3. RESULTS AND DISCUSSION

3.1. Catalytic Effect by Alumina. TG/DTA tests using a mixed powder of PTFE and alumina were first conducted to investigate the difference in the catalytic effects of the α - and γ -alumina surfaces. Typical thermograms obtained at a temperature of 748 K for the mixed powder of PTFE with either α - or γ -alumina are shown in Figure 2(a) and (b), respectively. At time zero, the weight 100% equals PTFE mass plus alumina mass. In the figure, the thermogram for pure PTFE powder without alumina is also shown for the reference. These curves probably trace the thermal decomposition of PTFE, including formation of gaseous molecules such as small fragments of fluorocarbon and hydrogen fluoride. Comparing the curves for PTFE with and without alumina, it can be seen that the thermal decomposition of PTFE is accelerated by the existence of both α - and γ -alumina. Moreover, the decomposition by γ -alumina was significant.

To detect the chemical products generated by the thermal reaction between PTFE and alumina, XPS analysis was subsequently done for a residue of the heated powder obtained in the TG/DTA tests. Fluorine 1s XPS spectra for the residue of mixed powder heated at 723, 748, and 773 K are shown in Figure 2(c) and (d). In the figures, the XPS spectra for nonheated samples are shown for reference. In the case of the nonheated samples, only one distinct peak can be seen at the binding energy of 689.3 eV, which is assigned to the bond between carbon and fluorine atoms in PTFE. In Figure 2(c), the peak is shifted in the case of the heated samples including α -alumina. That is, the peak of the carbon and fluorine bond is slightly shifted to a lower binding energy at 723 K. This chemical shift is caused by an intermediate formation which includes a carbon double bond in the PTFE backbone. The formation of a carbon double bond was seen in an experiment for PTFE degradation²⁷ and our previous simulations.^{6,7} At 748 K, a new peak can be seen at a binding energy of 686.4 eV corresponding to formation of aluminum fluoride. Moreover, at 773 K, the peak of the carbon–fluorine bond has vanished, and only aluminum fluoride is detected. This result indicates that PTFE thermochemically reacts with α -alumina to produce aluminum fluoride. In the case of the sample with γ -alumina (see Figure 2(d)), on the other hand, the peak is already shifted to the binding energy around 686 eV at the temperature of 723 K, meaning that the aluminum fluoride is formed at a lower

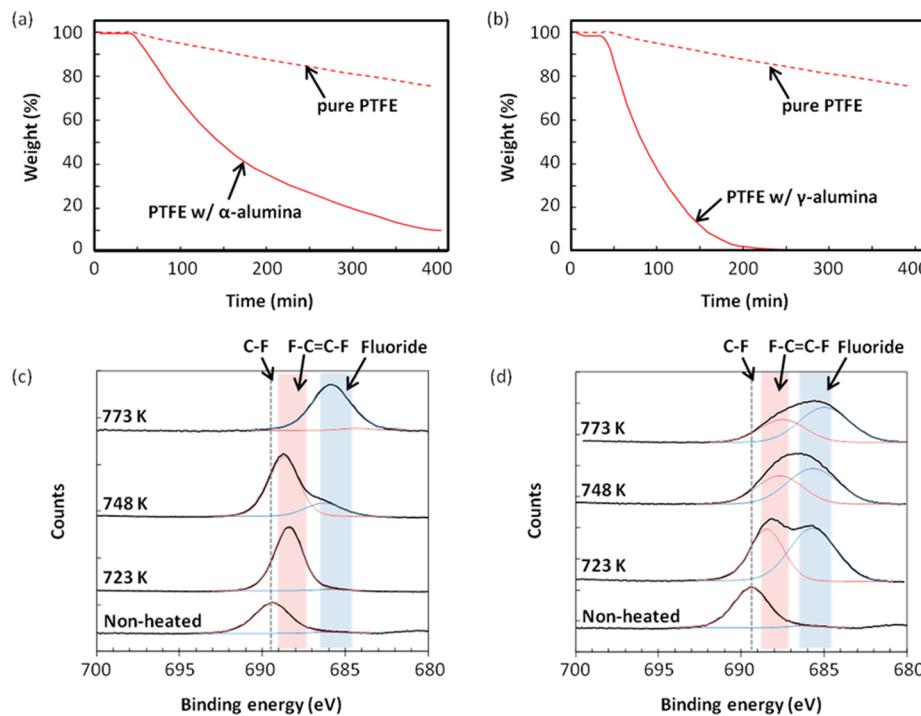


Figure 2. Typical thermograms obtained by TG/DTA at a temperature of 748 K for PTFE powder mixed with (a) α -alumina and (b) γ -alumina. Fluorine 1s XPS spectrum for the residue of PTFE with (c) α - and (d) γ -alumina powder heated at temperatures of 723, 748, and 773 K.

temperature than in the case of α -alumina. The TG/DTA and XPS experiments described above suggest that the chemical reactivity of PTFE with γ -alumina is higher than that of PTFE with α -alumina. Because the aluminum fluoride formed at lower temperature, γ -alumina thus acts as a stronger Lewis acid catalyst for PTFE decomposition than α -alumina. Simultaneously, the fact of fluoride formation on the PTFE/aluminum rubbing system successfully supports our previous theoretical results^{6,7} describing tribochemical reaction between PTFE and alumina.

3.2. Effect of Catalytic Reaction on Tribological Performance. On the basis of the result of the above-described thermal analysis, it is suggested that the alumina surface activates the chemical reaction of PTFE which forms aluminum fluoride, and the catalytic effect of γ -alumina is stronger than that of α -alumina. The effect of the formation of aluminum fluoride was previously studied by a classical MD simulation.⁷ The simulation result showed that a PTFE transfer film hardly forms on the fluorine-terminated alumina surface due to the electrostatic repulsive interaction on the sliding interface. From this result, it was inferred that the tribological performance of the PTFE/alumina rubbing system is significantly decreased because formation of a transfer film is suppressed. Therefore, a catalytic reaction by a counter surface would be one of the key processes to improving the tribological performance of PTFE.

To investigate the effect of a catalytic reaction on the transfer-film formation and the tribological performance of PTFE, friction tests on α - and γ -alumina coated disks contacted with a PTFE ball were performed. As described in Section 2.2, α - and γ -alumina coated disks were prepared by thermal spraying and anodizing alumite treatment, respectively. During the friction test, two systems showed completely different wear behaviors. The amount of wear of the PTFE ball with increasing friction time is plotted in Figure 3(a). In the figure,

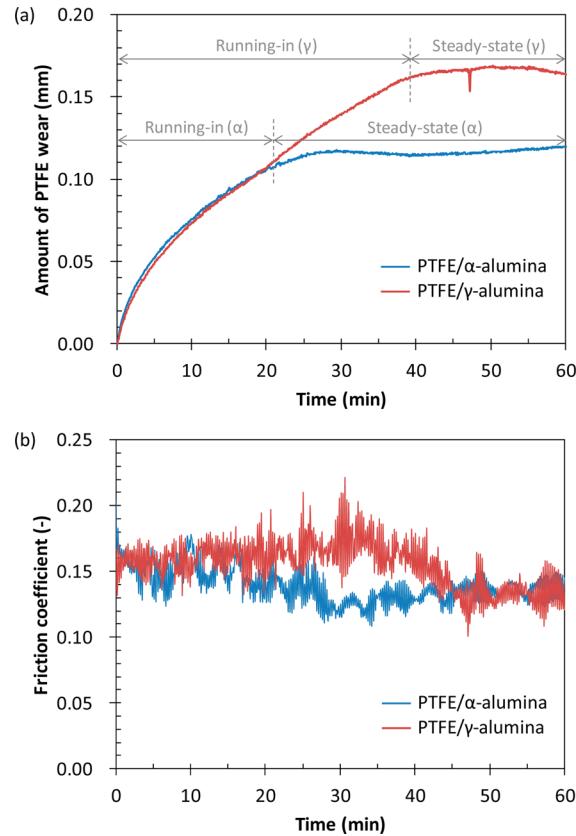


Figure 3. (a) Wear amount of PTFE ball and (b) friction coefficient on the PTFE/ α -alumina and the PTFE/ γ -alumina sliding systems.

the downward displacement of the PTFE ball, which was continuously monitored during the test, was employed as a representative wear amount. From the figure, the final amounts

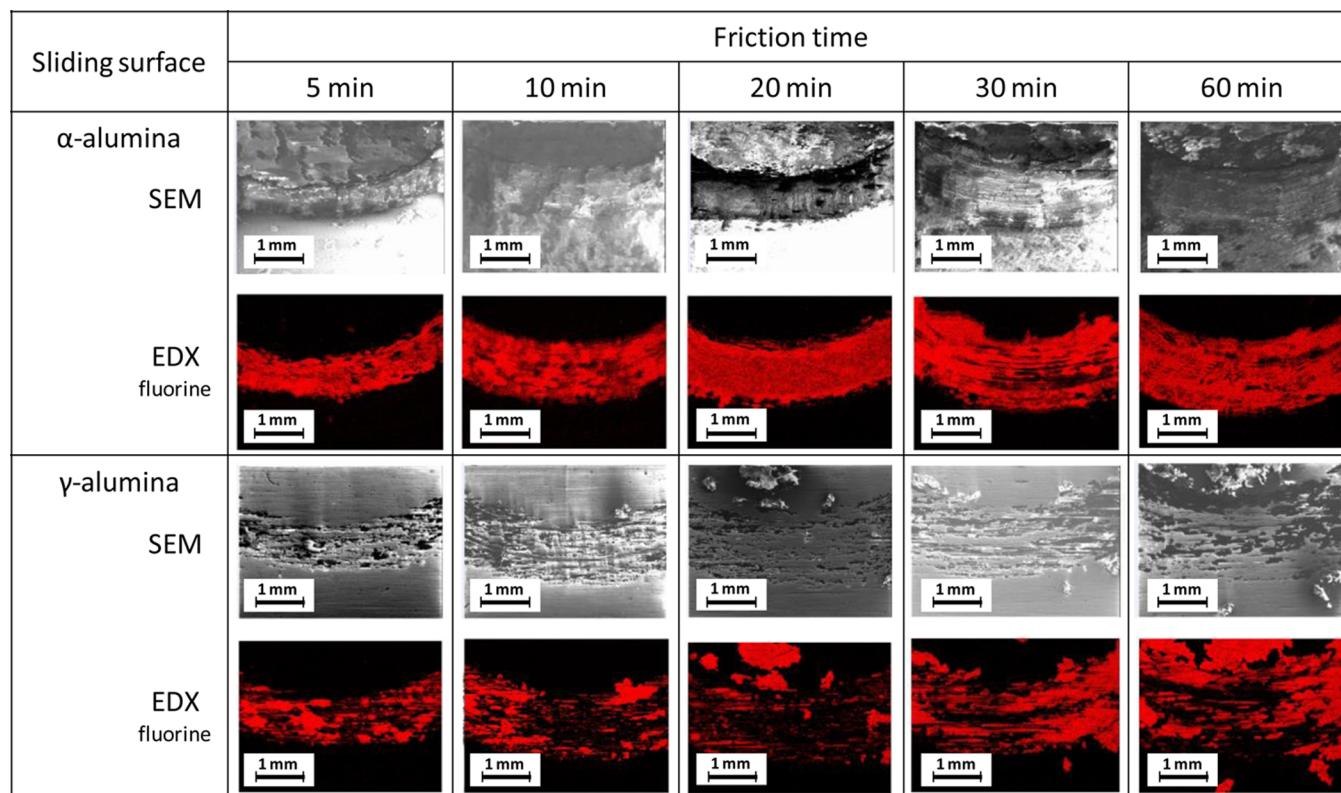


Figure 4. SEM and EDX images of a wear scar on α - and γ -alumina sliding with the PTFE ball. In the EDX images, red color means the existence of fluorine species.

of PTFE wear at a friction time of 60 min are significantly different, namely, 0.12 mm for the PTFE/ α -alumina system and 0.17 mm for the PTFE/ γ -alumina system. This result confirms that the wear performance of PTFE is influenced by the crystal structure of alumina as a counter surface. It should be noted that this difference could also result from different coating methods: thermal spraying for α -alumina and anodizing alumite treatment for γ -alumina. The wear behavior may be related to the adhesion between coating and the substrate. Although the adhesion strength of the coating has not been measured yet, γ -alumina must show a stronger adhesion than α -alumina because the alumite itself is originated from the substrate. Therefore, there is a possibility that strong adhesion of γ -alumina on the substrate affects the wear of PTFE.

In Figure 3(a), two unique periods can be defined on the basis of the wear rate (gradient of wear amount), viz., the running-in and the steady-state periods. In the running-in period, the surface of the PTFE ball may be delaminated roughly by the surface asperity of alumina. Thus, the wear rate was the largest in the initial stage of this period (up to the friction time of 3 min). The wear rate was then decreased slightly because the PTFE transfer film began to attach on the alumina surface. After forming the transfer film, the wear behavior shifted to the steady-state period at the friction time of 21 min for the PTFE/ α -alumina sliding system. The PTFE/ γ -alumina sliding system also shows a similar tendency, but the steady-state period started at the friction time of 39 min. It took two times longer for the PTFE/ γ -alumina system to shift to the steady-state period. The reason for the difference in wear behavior of PTFE should be explained by the catalytic reaction. That is, according to the above-described thermal analysis, the γ -alumina surface more easily reacts with PTFE than the α -

alumina. The aluminum fluoride as the reaction product is abundant on the γ -alumina surface which potentially prevents transfer-film formation.⁶ Therefore, the steady-state period in the PTFE/ γ -alumina system starts later than the PTFE/ α -alumina system.

The friction performance was also influenced by the period of friction. The friction coefficient of the PTFE/ α -alumina and PTFE/ γ -alumina systems is shown in Figure 3(b). The PTFE/ α -alumina system shows the average friction coefficient of 0.151 in the running-in period and 0.132 in the steady-state period. Similarly, the average friction coefficient of 0.164 in the running-in period and 0.138 in the steady-state period were obtained for the PTFE/ γ -alumina system. Hence the friction was slightly lowered by shifting to the steady-state period as well as the wear behavior of the PTFE ball discussed above.

To discuss deeply the relationship between the formation of transfer film and the tribological performance, the sliding surface of alumina was observed using a combined SEM/EDX instrument. SEM and EDX-obtained fluorine mapping images for the sliding surfaces of α - and γ -alumina at certain friction times are shown in Figure 4. At all friction times, a wear scar is clearly seen in the SEM images; nevertheless, the surfaces of both the α - and γ -alumina disks must be harder than the PTFE ball typically. In the EDX mapping images, the fluorine was clearly detected inside the wear scar on the α -alumina surface, and its distribution is likely continuous. This observation means that the transfer film of PTFE was regularly formed on the α -alumina surface during the friction test. On the other hand, by comparing the EDX mapping images of the α - and γ -alumina surfaces at the initial stage of friction, the distribution of fluorine is discontinuous on the γ -alumina surface, meaning that the transfer-film formation was suppressed. Furthermore, large

wear debris of PTFE (approximately 1 mm size) began to form then because the fluorine is also located outside the wear scar at a friction time of 20 min. At 30 and 60 min, the distribution of fluorine is still discontinuous, and much wear debris can be observed. Therefore, the formation of PTFE transfer film was not relatively easier on the γ -alumina surface than on the α -alumina surface.

According to the results presented in Section 3.1, the surface of γ -alumina plays a role as a strong catalyst to PTFE. This effect produces a lot of aluminum fluoride on the γ -alumina surface, which suppresses the transfer film of PTFE attaching to the surface; consequently, the system was not easy to shift to the steady-state period because less transfer film was formed. It can be concluded that the wear behavior and also self-lubrication property of PTFE is definitely influenced by the catalytic effect of its counter surface. If the catalytic effect of the surface was enhanced, the wear of PTFE contacting the surface could be increased. Also the friction could not be lowered until forming the transfer film stably. The catalytic property of a metallic surface must be understood to improve the antiwear property of PTFE resin through stable formation of the transfer film.

3.3. Energetics for Fluoride Formation on the Alumina Surface. DFT calculation was also applied to study the detailed mechanism of the chemical reaction between PTFE and alumina. The simulation model to be used was first constructed by the following assumption. The alumina surface is usually passivated by the hydroxyl group in the atmospheric condition. However, during the friction process, the surface hydroxyl group is thermochemically²⁸ or mechanochemically²⁹ detached, and a bare aluminum atom will be found on the surface. On the basis of this assumption, the aluminum atoms should be exposed in the surface of the DFT model to be used, namely, a fully dehydrated model. Note that the effect of humidity (water vapor) was not explicitly considered in the following DFT calculation, while the friction experiment in Section 3.2 was done under atmosphere. According to our previous simulation,⁷ the process of transfer-film formation, which follows our focused catalytic reaction, is influenced by water vapor. The water molecule reacts with the terminal of the PTFE polymer chain to form a carboxyl group and thus improves adhesion strength of the transfer film.

The model of the α -alumina (0001) surface, which is well-known as a stable facet in that crystal phase,³⁰ is shown in Figure 5(a). Moreover, the γ -alumina surface, shown in Figure 5(b), was modeled on the basis of atomic positions defined by Digne et al.³¹ The simulated γ -alumina surface was defined as (100) because that facet showed the lowest energy as a fully dehydrated surface.³¹ Comparing the two surfaces reveals that all sites at the acid center, i.e., aluminum atoms, have similar structures in the case of α -alumina (0001) but different ones in the case of γ -alumina (100).

Four possible types of acidic sites can be detected on the γ -alumina (100) surface—labeled “Al_A”, “Al_B”, “Al_C”, and “Al_D” in Figure 5(b)—and each shows different chemical activities. Normally, the most effective acidic site for reaction of the PTFE molecule should be determined first. It was reported by Christiansen et al.³² that water and several organic molecules are likely to be adsorbed strongly on the Al_A site, meaning that the Lewis acidity of that site is probably the highest of the four sites. It can be thus assumed that the adsorption and reactivity of the PTFE molecule on the Al_A site is predominant as well as other molecules tested by Christiansen et al.³² Accordingly, in

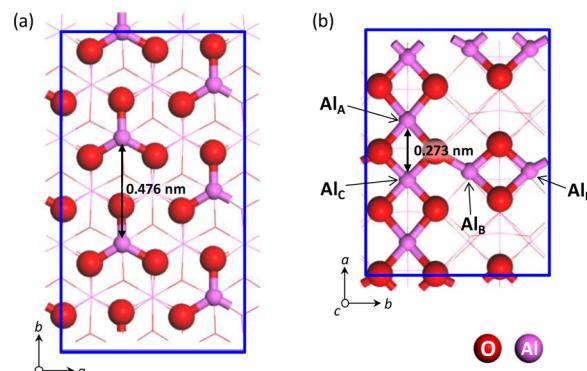


Figure 5. Models for (a) α -alumina (0001) and (b) γ -alumina (100) surfaces used for DFT calculation. Atoms on the topmost surface are expressed with large balls. The size of surface area is (a) $a = 0.824$ nm and $b = 1.428$ nm (totally 90 atoms). Similarly, (b) $a = 1.117$ nm and $b = 0.841$ nm (totally 80 atoms).

this report, the chemical reaction on the acidic site Al_A only was simulated and discussed in relation to the chemical reactivity on the γ -alumina (100) surface. The simulations for other sites Al_B, Al_C, and Al_D are now performed and will be reported in our next paper.

The chemical reaction energy of PTFE on the two prepared surface models was estimated. The DFT-optimized structures of a C₅F₁₂ molecule, which is a model compound of PTFE, adsorbed on α -alumina (0001) and γ -alumina (100) surfaces are, respectively, shown in Figure 6(a) and (b). These

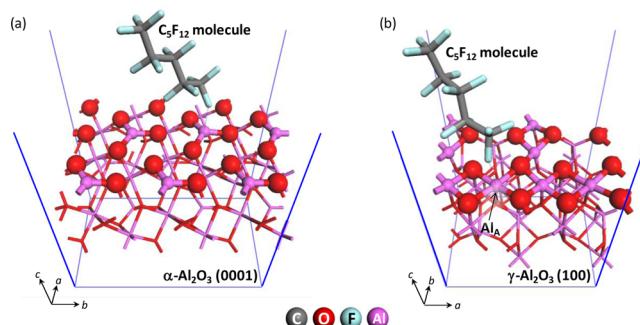


Figure 6. DFT-optimized structure for the C₅F₁₂ fluorocarbon molecule adsorbed on (a) α -alumina (0001) and (b) γ -alumina (100) surfaces.

structures were defined as a reactant, and to estimate the reaction energy, the chemical reaction shown in Figure 7 was considered. According to the elucidated chemical reaction between PTFE and alumina,^{6,7} two fluorine atoms are removed from the PTFE backbone, while two chemical bonds between aluminum and fluorine are formed. The chemical products therefore include both partially fluorinated alumina and C₅F₁₀ with a carbon double bond. It is worthy to note again that this defluorination reaction is found in our XPS analysis (see Section 3.1) and also an electrochemical degradation with alkaline metals.²⁷ The geometries of a product were also constructed and optimized by DFT. The TS structure was then obtained by the complete LST/QST method, which has been well validated to find a transition state.

The DFT-obtained structures for C₅F₁₂ reacted with the α -alumina (0001) and γ -alumina (100) surfaces are shown in Figure 8(a) and (b), respectively. In the figure, the structures of

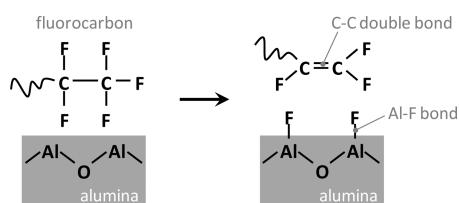


Figure 7. Schematic illustration of the catalytic chemical reaction of a fluorocarbon molecule on an alumina surface.

reactant, product, and TS are shown for each model. To discuss the reactivity of C_5F_{12} as a model compound of PTFE, the TS structure is focused on as follows. In both TS structures, one bond between aluminum and fluorine atoms can be seen. Additionally, on the α -alumina surface, one bond between carbon and fluorine atoms is extended to 0.246 nm (initial bond distance is 0.135 nm), and a fluorine radical is formed as a result. No radical formation is observed in the case of the γ -alumina surface, although the interatomic distance between carbon and fluorine atoms was slightly increased from 0.135 to 0.153 nm. The reason for the difference between the TS structure of two models is probably explained by the atomic

arrangement of the acid center on the topmost surface of alumina. In the case of the γ -alumina (100) surface, the distance between an acid center (Al_A site) and its nearest neighbor (Al_C site) is 0.273 nm (see Figure 5(b)). On the other hand, two acid centers are separated by 0.476 nm on the α -alumina (0001) surface (see Figure 5(a)). Therefore, on the α -alumina surface, moving to a distant acid center is required for the reacting fluorine atom in the C_5F_{12} molecule. This may cause the radical formation in the reaction of C_5F_{12} on the α -alumina surface.

The energy diagram for each model is shown in Figure 9. In the figure, the energy values are relative to each reactant, and the energy of the TS structure corresponds to the reaction barrier. By reflecting the radical formation described above, the TS energy involved in the reaction of C_5F_{12} on the α -alumina (0001) surface is higher than that on the γ -alumina (100) surface by nearly 100 kJ/mol. The chemical reaction with forming aluminum fluoride is thus easier to take place on the γ -alumina than on the α -alumina surface, which is the same trend with the experimental results in the previous section. Here it can be seen that the obtained TS energies are quite a large value (more than 200 kJ/mol). In the real contact area of PTFE and

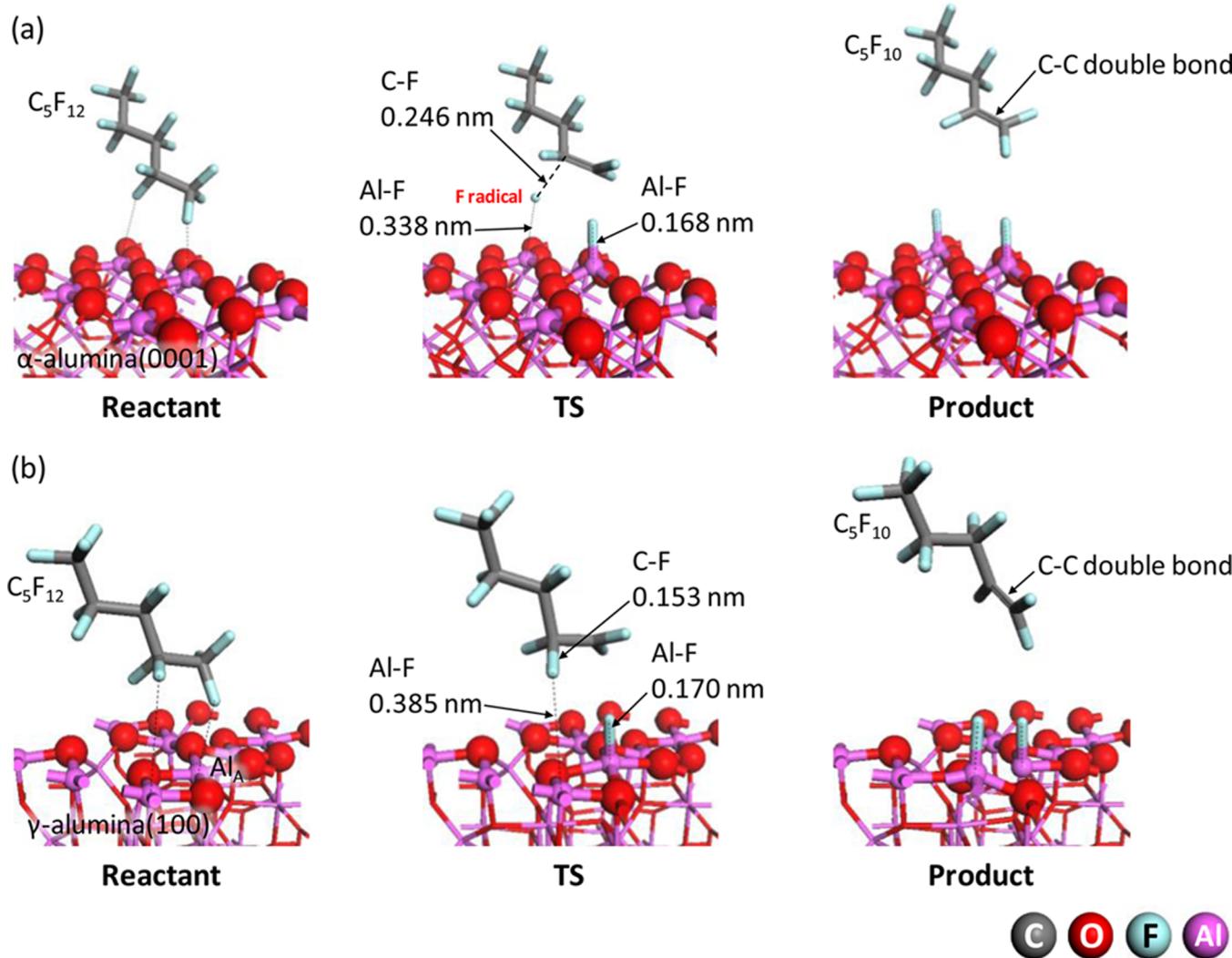


Figure 8. DFT-obtained structure of the C_5F_{12} fluorocarbon molecule adsorbed on (a) α -alumina and (b) γ -alumina surfaces. The optimized structures of reactant, product, and TS are shown for each model.

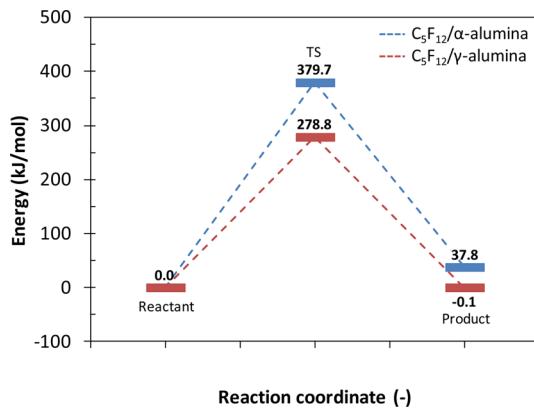


Figure 9. Energy diagram for the chemical reaction of the C_5F_{12} fluorocarbon molecule adsorbed on α - and γ -alumina surfaces. The energy of each reactant was set to zero.

alumina, an extreme pressure (over 100 MPa) and sliding speed are given. It is worth mentioning that these tribological effects may be the main driving force to overcome a high energy barrier because the PTFE molecule is forcedly pressed and moved to the alumina surface. That is, by applying an extreme pressure, the interatomic distance between the reaction pair, viz., aluminum and fluorine atoms, is shortened, while the atoms are forcedly moved to the catalytic reaction site by a sliding effect. The PTFE molecule probably overcomes a high reaction barrier by these tribological effects. In fact, the fluoride formation was certainly observed in the present friction test and also a previous quantum chemical MD simulation⁶ which explicitly considers effects of a pressure and a sliding. It should also be noted that the bond energy between carbon and fluorine atoms was overestimated by our DFT calculation (see Section 2.3). This may also cause a large value of TS energy because the bond dissociation between carbon and fluorine atoms processes the chemical reaction with forming aluminum fluoride.

The result of this DFT calculation also shows that the catalytic effect in which aluminum oxide is converted into fluoride is much stronger on the γ -alumina surface than on the α -alumina surface. The mechanism of catalytic activity of two crystal structures of alumina originated from the arrangement of a Lewis-acid center which relates to the formation of a fluorine radical in the defluorination process of the fluorocarbon molecule.

4. CONCLUSIONS

The catalytic effect of an alumina surface in regard to the formation of a PTFE transfer film and its tribological behavior was demonstrated both experimentally and theoretically. To investigate the catalytic tribochemistry of PTFE material, α - and γ -alumina were chosen as counter surfaces. A TG/DTA experiment using mixed powder samples of PTFE and alumina was performed to investigate the chemical reactivity of α - and γ -alumina. The results showed that the γ -alumina surface potentially exhibited a stronger catalytic effect for PTFE degradation than the α -alumina surface because it removes fluorine atoms from the PTFE backbone under lower temperature. The effect of a catalytic reaction on tribological performance was evaluated by using a pin-on-disk tribometer. α - and γ -Alumina coated disks were, respectively, prepared by a thermal spraying and an anodizing alumite treatment. A pure PTFE ball without any additives was contacted with each disk.

The amount of wear of PTFE on the γ -alumina surface was larger than that on the α -alumina surface. SEM and EDX images indicated that the transfer film formed on the γ -alumina surface was discontinuous and less abundant, while it was regularly formed and more abundant on the α -alumina surface. DFT calculation was also performed to discuss energetics of catalytic reaction. It showed that the energy barrier of γ -alumina for the reaction in which fluorine atoms are removed from a fluorocarbon molecule was lower than that of α -alumina. This difference is probably caused by the atomic arrangement of the Lewis-acid site on the surface. The simulation result well explained the experimentally observed difference between α - and γ -alumina concerning chemical reaction and tribological performance.

The antiwear performance and self-lubrication property of PTFE is decreased by the aluminum fluoride formed as the product of a catalytic reaction. Accordingly, preventing the catalytic effect of a surface sliding against PTFE is one way to improve the tribological performance of PTFE. Seeking a surface treatment for an aluminum surface will be the next step in achieving good tribological performance of PTFE-based material.

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Notes

The authors declare no competing financial interest.

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