MOLECULAR SCALE MECHANISM ON EVAPORATION AND REMOVAL PROCESS OF ADHERENT MOLECULES ON SURFACE BY BURNT GAS

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ABSTRACT–The interaction between adherent molecules and gas molecules was modeled in the molecular scale and simulated by the molecular dynamics method in order to understand evaporation and removal processes of adherent molecules on metallic surface using high temperature gas flow. Methanol molecules were chosen as adherent molecules to investigate effects of adhesion quantity and gas molecular collisions because the industrial oil has too complex structures of fatty acid. Effects of adherent quantity, gas temperature, surface temperature and adhesion strength for the evaporation rate of adherent molecules and the molecular removal mechanism were investigated and discussed in the present study. Evaporation and removal rates of adherent molecules from metallic surface calculated by the molecular dynamics method showed the similar dependence on the surface temperature shown in the experimental results.

KEY WORDS : Molecular dynamics method, Surface treatment, Adherent molecules, Evaporation, Burnt gas

NOMENCLATURE

L   : quantity of adherent molecules : kg/m^2
r   : distance between particles : m
R   : root mean square of molecular trajectories of adherent molecules : m
T_g : temperature of upper boundary in a gas region : K
T_s : temperature of lower boundary in a surface region : K
q   : electric charge parameter of OPLS potential
ε : energy parameter of Lennard-Jones potential : J
σ : length parameter of Lennard-Jones potential : m
$\phi(r)$: Lennard-Jones potential function : J
ϕ_{ab} : OPLS potential function between molecule a and b : J

1. INTRODUCTION

A surface degreasing method with premixed flame has been used as the removal process of adherent impurities on materials. From an ecological point of view, a dry-type "degreasing" method by flames is proposed and developed recently. In a practical use, a surface cleaning process by premixed flame is used in many production processes like the surface cleaning process of an automobile body. Such a dry-type degreasing method by using flames can be considered as a thermal treatment in molecular scale because after such surface treatments, the adsorption of paints on base materials has been improved remarkably. Mechanisms of such improvement by flame treatments are not known clearly though some suppositions are proposed based on experimental observations. It may be true that chemical species in burnt gas at high temperature have removed almost all the adherent molecules on the materials in such processes. Therefore, these flame treatment processes involve fundamental problems of heat and mass transfer between gas molecules and adherent molecules and also between adherent molecules and surface molecules. These processes seem to be very complex interfacial phenomena where various polyatomic molecules on a metallic surface are decomposed thermally or evaporated by chemical reactions or collisions of various chemical species in burnt gas (Lee and Kim, 2001; Kim *et al.*, 2002; Shudo *et al.*, 2003).

Molecular dynamics method can be useful to predict an optimal surface temperature control for complete surface cleaning process or an optimal surface state

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control by favorable evaporation rate or removal rate of adherent molecules (Shibahara *et al.*, 1999).

In order to understand relationships between molecular behaviors at a very thin adherent molecular layers and physical conditions such as gas temperature (T_g), surface temperature (T_s) and thickness of adherent molecular quantity (L_a), evaporation processes of adherent molecules by gas collisions were simulated by the molecular dynamics method in the present study. Evaporation rates of adherent molecules and molecular behaviors in the vicinity of surface were investigated and discussed from molecular dynamics point of view. Removal mechanisms of adherent molecules on the surface were investigated with changing the gas temperature, surface temperature and adhesion strength, respectively. A simple simulation system was employed for the numerical calculation shown in Figure 1. The calculation domain consists of a surface region, an adherent molecular region and a gas region.

Methanol molecules, as the adherent molecules, were employed to investigate the removal processes of poly-atomic molecules. Chemical reactions between chemical species in burnt gas and adhered molecules should play important roles in these flame treatment processes. However, as a first approach to such processes by the molecular dynamics method, chemical reactions between gas molecules and adherent molecules were ignored so as to investigate thermal removal mechanism in the evaporation processes of adherent molecular layers on surfaces in the present study. Macroscopic flow velocity of gas molecules was also assumed to be negligible in the present study to understand the fundamental phenomena in a simple way even though such forced convection is one of important physical factors in these processes. Adherent molecules were assumed to be methanol molecules so as to consider the simplest hydroxy polyatomic

molecules including a carbon atom instead of fatty acid used in real industrial processes. Molecular dynamics mechanisms in removal processes of such adherent molecules by gas molecular collisions were discussed by the precise observation of molecular behaviors.

2. NUMERICAL METHOD

Figure 1 shows configuration of the calculation domain used in the present study. Temperature of a gas region in the range of 40 angstrom distance from upper boundary, namely a gas temperature control region, was controlled and maintained at T_g K. Temperature of surface molecules in the range of the first layer from bottom boundary, called a surface temperature control region, was controlled and kept at T_s K. The center of mass of the bottom layer in a surface region was fixed artificially for numerical calculations. Mirror boundary condition was used as upper boundary condition at gas temperature control region. Periodic boundary conditions were employed in x and y directions of the calculation system in Figure 1. Temperatures of surface temperature control region and gas temperature control region can be considered to be T_s K and T_g K, respectively, from a macroscopic point of view. As initial conditions, the distribution of molecular kinetic energy in a gas region was controlled in a thermally equilibrium state at T_g K. Molecules in a surface region and an adherent region were settled to be in a thermally equilibrium state at T_s K, too. After relaxation calculations, the system can be considered to be a stable state with energy flow from a gas temperature control region to a surface temperature control region. Molecular dynamics calculations with these initial conditions simulated collision processes of gas molecules to adherent molecules and their evaporation processes in a nanometer scale. Two methods are well-known to realize an unsteady molecular system where a substantial energy flux exists as a calculation condition. One method is to control temperatures of two boundary regions at constant temperatures (Watanabe and Kotake, 1993; Ohara *et al.*, 1998; Ohara, 1999). The other is to control the magnitudes of heat flux at boundary conditions (Kotake and Wakuri, 1994; Maruyama and Kimura, 1999).

In the present study, temperature control method was used to investigate effects of boundary temperature (T_g, T_s) clearly on the interfacial phenomena near surface and to model burnt gas collision to a metallic surface kept at room temperature. Oxygen molecules, methanol molecules and iron atoms were employed as gas molecules, adherent molecules and surface atoms, respectively, to simulate removal processes of adherent molecules on metallic surface.

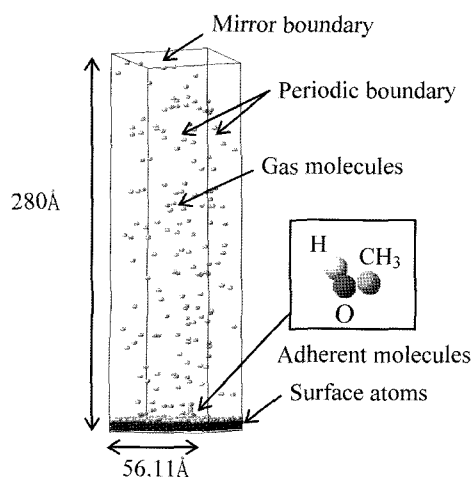Lennard-Jones (12-6) potential functions were applied

Figure 1. Configuration of the simulation domain.

Table 1. Potential parameters :
Lennard-Jones (12-6) potential functions.

	ε [$\times 10^{-21}$J]	σ [A]
Gas-gas	1.779	3.362
Adherent (O–O)	1.182	3.070
Adherent (CH$_3$–CH$_3$)	1.439	3.775
Surface-surface	40.00	2.243

Table 2. Potential parameters :
OPLS potential functions.

	CH$_3$	O	H
q	0.265	−0.700	0.435

to the potential functions between gas molecules, surface atoms and other molecules. Potential parameters in the study of Reid *et al.* (1977) were used for the determination of 12-6 Lennard-Jones potential parameters.

$$\phi(r)=4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right\} \tag{1}$$

Length parameter σ is kept constant between different molecules A and B as $\sigma_{AB} = (\sigma_A + \sigma_B)/2.0$ based on the simple combination rule. Energy parameter e is also kept constant as $\varepsilon_{AB} = \sqrt{\varepsilon_A \times \varepsilon_B}$. These combination rules are called as Lorentz-Berthelot combination rule. OPLS potential functions were employed between methanol molecules and can be expressed as summation of Coulomb potential function and 12-6 Lennard-Jones potential function (William *et al.*, 1984; William *et al.*, 1986). Potential parameters in 12-6 Lennard-Jones potential functions and OPLS potential function are written in Tables 1 and 2.

$$\phi_{ab}=\sum_{i}^{a}\sum_{j}^{b}\left[\frac{q_iq_je^2}{r}+4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right\}\right] \tag{2}$$

Newton's equations and Euler's equations were solved numerically to calculate translation motions of atoms and molecules, and rotational motions of methanol molecules. The Verlet integration and the Leap-frog method were used for the numerical calculation of Newton's equations and Euler's equations with the time step of 2 fs. Ewald summation method was used for the calculation of Coulomb potentials (Ueda, 1990).

3. RESULTS AND DISCUSSION

3.1. Effects of Adherent Quantity on Molecular State and Behavior in the Vicinity of Surface

● Gas molecule   ● CH$_3$ ● O   ● H

(a) L$_1$: Adherent quantity = 3.308*10^{-4} kg/m^2

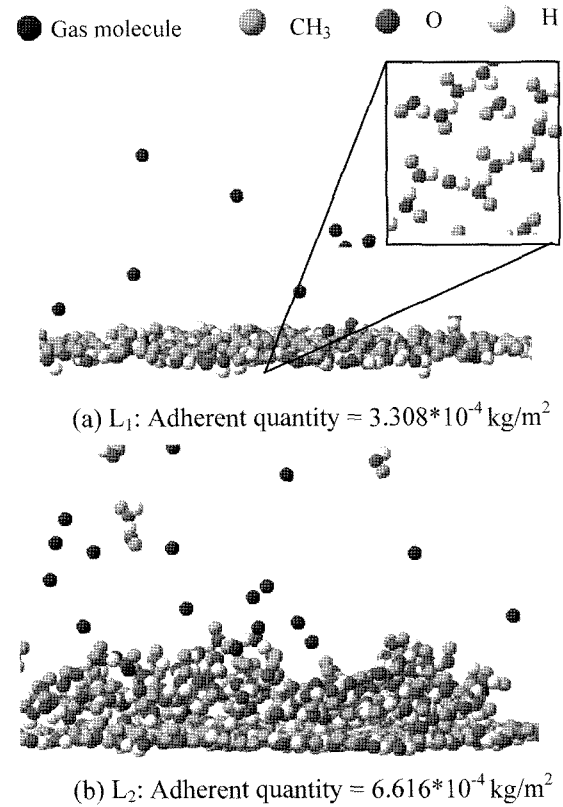(b) L$_2$: Adherent quantity = 6.616*10^{-4} kg/m^2

Figure 2. Snapshots of adherent molecules in the vicinity of the surface with different adherent quantity of L$_1$ and L$_2$.

In order to investigate effects of adherent quantity on molecular state and behavior in the vicinity of surface, the quantity of adherent molecules were changed from 3.308×10^{-4} kg/m^2 (L$_1$) to 6.616×10^{-4} kg/m^2 (L$_2$) and the molecular dynamics simulation was conducted under various thermal conditions. The adherent quantity corresponds to adherent thickness from one molecular layer to two molecular layers of methanol molecules when the adherent molecules are averaged over the surface area. Figures 2(a) and 2(b) show the snapshots of adherent molecules in the vicinity of the surface with different adherent quantity of L$_1$ and L$_2$, respectively. In Figure 2(a), methanol molecules are attached to surface in the first molecular layer. The methanol molecules are also hydrogen-bonded and attached to surface in line. In Figure 2(b), methanol molecules formed molecular clusters on the first methanol layer attached to surface in line.

The difference between Figures 2(a) and 2(b) comes from the quantity of adherent methanol. In the case of L$_1$ the quantity of adherent molecules corresponds to almost one layer thickness of adherent methanol. When the adherent quantity becomes more than one molecular
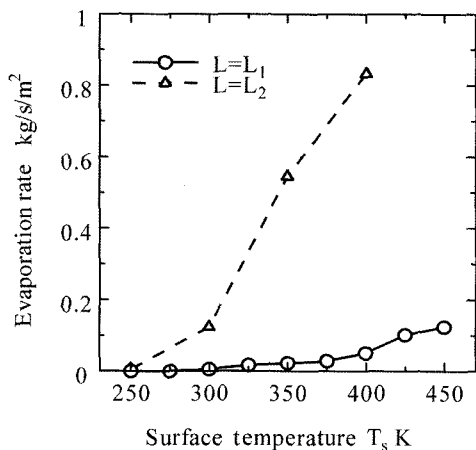
Figure 3. Effects of surface temperature and adherent quantity on evaporation rate of adherent molecules.

layer thickness of methanol, the adherent molecules form molecular cluster on the first adherent layer.

Evaporation rate of adherent molecules from surface ($kg/s/m^2$) was investigated by the molecular dynamics simulation when surface temperature was changed from 250 K to 450 K so as to investigate effects of surface temperature and adherent thickness on evaporation rate of adherent molecules. Figure 3 shows the relationship between surface temperature and evaporation rate when the adherent quantity are 3.308×10^{-4} kg/m^2 (L_1) and 6.616×10^{-4} kg/m^2 (L_2). Boundary temperature of gas molecular region was kept at 500 K as shown in Figure 3. Evaporation rate increases with the rise of surface temperature. Evaporation rate in the case of L_1 is larger than that in the case of L_2 when surface temperature is the same. When adherent quantity is about one molecular layer, in the case of L_1, evaporation of adherent molecules was not observed at less than 325 K. When adherent quantity is about two molecular layers, in the case of L_2, evaporation of adherent molecules was observed at more than 250 K although the boiling point of methanol is

337.71 K. These differences come from adherent state of methanol molecules to the surface and dynamics molecular behaviors.

In order to know the adherent molecular state in the case of $6.616 \times 10^{-4} kg/m^2$ (L_2) in Figure 3, the snapshots of adherent molecules in the vicinity of the surface were shown in Figures 4(a) and 4(b). Surface temperature T_s in Figures 4(a) and 4(b) are 250 K and 400 K, respectively. These results show the evaporation of adherent molecules was occurred mainly in the second molecular layers from the surface when surface temperature was increased to 400 K.

The average root mean square of molecular trajectories of adherent methanol (R^2) is calculated numerically as follows so as to investigate the characteristic difference of molecular motion of adherent molecules depending on adherent quantity.

$$R^2 = \langle \{ r(t) - r(0) \}^2 \rangle \tag{3}$$
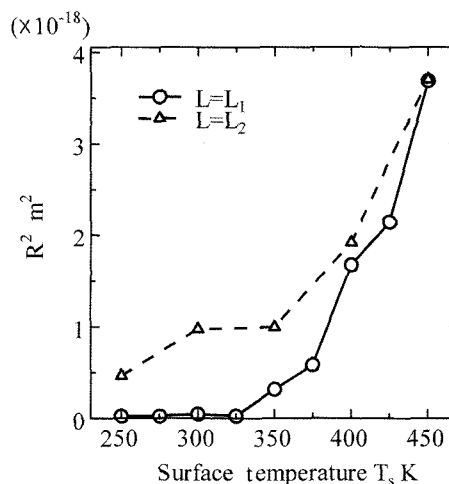

Figure 5. Effects of surface temperature and adherent quantity on RMS of molecular trajectories of adherent molecules on surface.
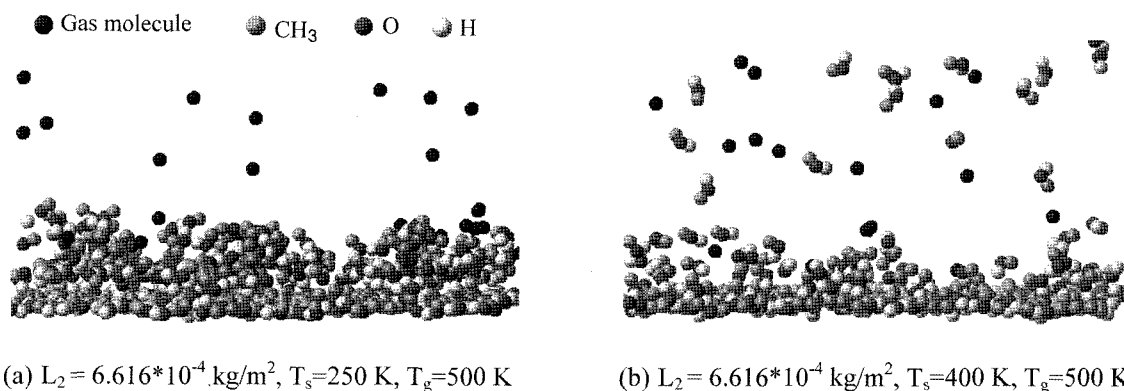

(a) $L_2 = 6.616 \times 10^{-4} kg/m^2$, $T_s = 250$ K, $T_g = 500$ K

(b) $L_2 = 6.616 \times 10^{-4} kg/m^2$, $T_s = 400$ K, $T_g = 500$ K

Figure 4. Snapshots of adherent molecules in the vicinity of the surface with different surface temperatures.

239.40 ps   239.60 ps

373.60 ps   373.80 ps

239.80 ps   240.00 ps

374.00 ps   374.20 ps

240.20 ps   240.40 ps

374.40 ps   374.60 ps

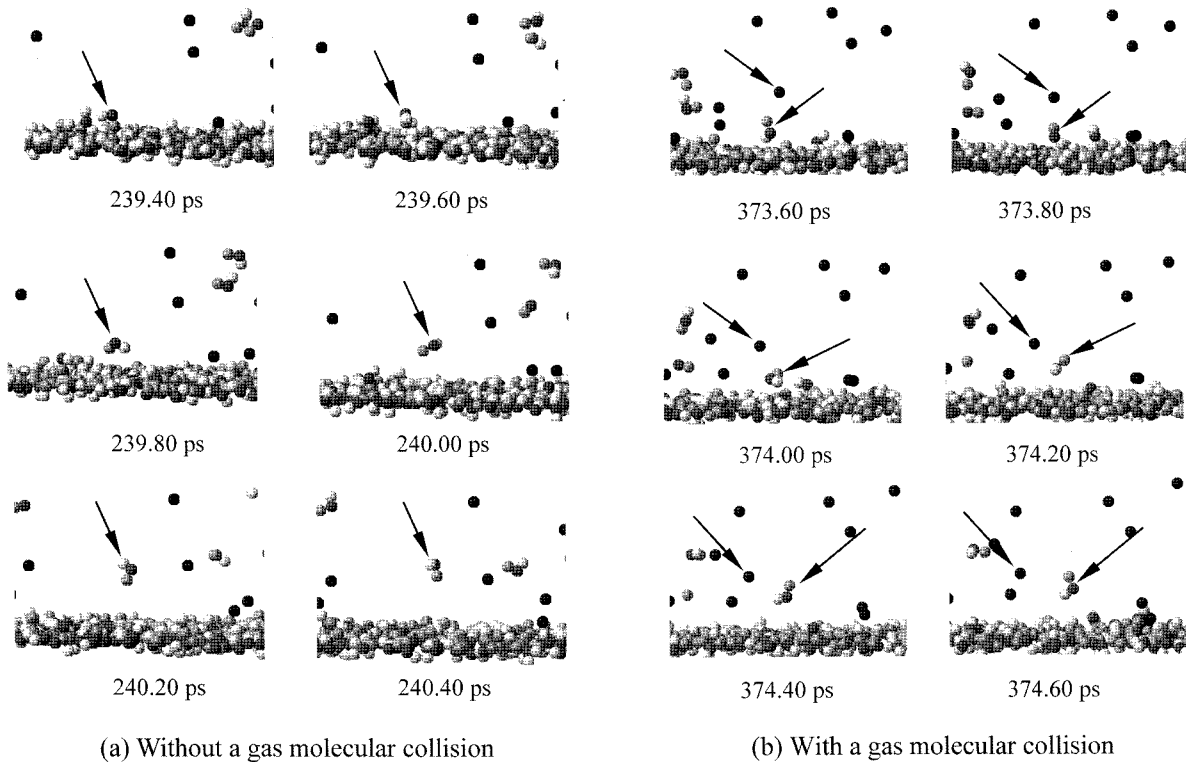(a) Without a gas molecular collision   (b) With a gas molecular collision

Figure 6. Snapshots of an evaporation process of an adherent molecule.

Where $r(0)$ and $r(t)$ are molecular positions at initial state and at time t, the bracket means the value averaged over all adherent molecules. Figure 5 shows the average root mean square of molecular trajectories of adherent molecules depends on the surface temperature T_s and the quantity of adherent molecules.

In the case of L_1, the average RMS is larger than that in the case of L_2. In the case of L_1, the average RMS is very small when the surface temperature is less than 350 K. These results show that surface temperature and quantity of adherent molecules affect the average dynamic behavior of adherent molecules on the surface and the average molecular behaviors have close relationships with the average evaporation rate of adherent molecules.

3.2. Effects of Surface Temperature and Gas Temperature on Evaporation and Removal Mechanism of Adherent Molecules

Figures 6(a) and 6(b) show two typical cases of evaporation processes of adherent methanol molecules. Figure 6(a) shows typical snapshots of an evaporation process of an adherent molecule without a gas molecular collision. In Figure 6(a) an adherent molecule stayed at the top of the first layer and migrated on the surface. The adherent molecule collided with another adherent molecule in the first layer of adherent molecules. The adherent molecule has been separated from surface without any direct interaction of gas molecular collision. On the other hand, Figure 6(b) shows typical snapshots of an evaporation process of an adherent molecule assisted by a gas molecular collision. First, an adherent molecule stayed at the top of the first layer of adherent molecules. A gas molecule that had large amount of kinetic energy collided with the adherent molecule. After molecular collision between an adherent molecule and a gas molecule, the adherent molecule collided with surface again and the adherent molecule has finally separated from the surface and the evaporation of the adherent molecule has completed. Thus the evaporation can be classified into the two cases, that is, without and with a gas molecular collision. Therefore the evaporation procedures can be classified into two cases numerically by investigating trajectories of all atoms and molecules in adherent and gas regions.

Figure 7 shows effects of surface temperature and adherent quantity on the rate of removed molecules from surface by gas molecular collisions. The removal rate by gas molecular collisions was calculated by dividing the number of adherent removal cases by gas molecular collisions to the number of total removal cases. Surface boundary temperature was changed from 300 K to 500 K in Figure 7. Adherent quantity are 3.308×10^{-4} kg/m^2 (L_1)

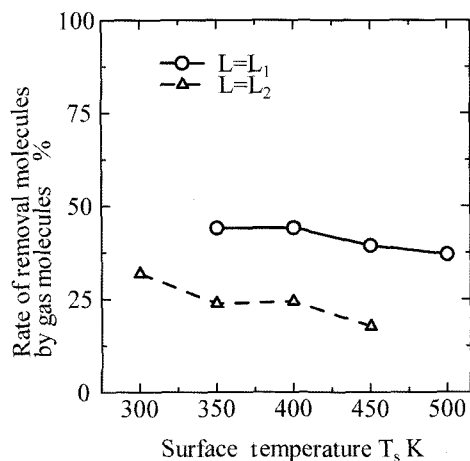Figure 7. Effects of surface temperature and adherent quantity on rate of removal molecules by gas molecular collisions.

Figure 8. Effects of gas temperature and surface temperature on the rate of removal molecules by gas molecular collisions.

and 6.616×10^{-4} kg/m^2 (L$_2$), respectively. Rate of removed molecules by gas molecular collision decreases with the increase of surface temperature (T$_s$) in both cases of 3.308×10^{-4} kg/m^2 (L$_1$) and 3.308×10^{-4} kg/m^2 (L$_1$). This is because the removed adherent molecules need assists of gas molecule to evaporate from statistical point of view when surface temperature is relatively low. In other words, the removal of adherent molecules can be enhanced by collisions of gas molecules that have larger kinetic energy. The magnitude of removal rate by gas molecular collision in the case of 3.308×10^{-4} kg/m^2 (L$_1$) is larger than that in the case of 6.616×10^{-4} kg/m^2 (L$_2$) at all surface temperature. The difference of removal ratio relates to differences of adherent state and dynamic behavior in two cases shown in Figures 2 and 5. When the adherent quantity is 3.308×10^{-4} kg/m^2 (L$_1$), the adherent molecules are attached to the surface in line shown in Figure 2(a) and RMS of molecular motion is smaller than that in the case of 6.616×10^{-4} kg/m^2 (L$_2$) shown in Figure 5. Larger amount of energy for removal and evaporation in the case of 3.308×10^{-4} kg/m^2 (L$_1$) is necessary than that in the case of 6.616×10^{-4} kg/m^2 (L$_2$). Therefore the removal rate of gas molecular collisions in the case of 3.308×10^{-4} kg/m^2 (L$_1$) is larger than that in the case of 6.616×10^{-4} kg/m^2 (L$_2$). When the adherent quantity is 6.616×10^{-4} kg/m^2 (L$_2$), the adherent molecules form molecular clusters on the first adherent layer as shown in Figure 2(b). The effective cross section for gas molecular collision in the case of 3.308×10^{-4} kg/m^2 (L$_1$) becomes smaller than that in the case of 6.616×10^{-4} kg/m^2 (L$_2$). However, the total evaporation rate of removed molecules by gas molecular collisions is much larger in the case of 3.308×10^{-4} kg/m^2 (L$_1$) than that in 6.616×10^{-4} kg/m^2 (L$_2$). In the case of 3.308×10^{-4} kg/m^2 (L$_1$), the contribution of gas molecular

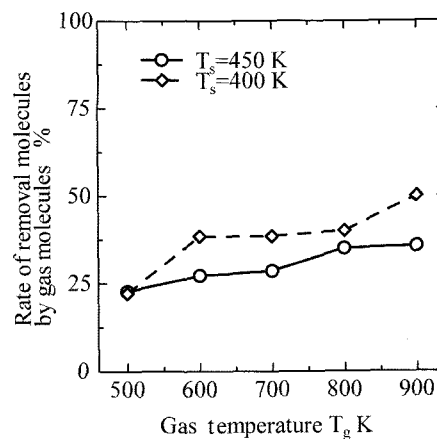collision is especially large compared with more adherent layer cases.

Figure 8 shows effects of gas boundary temperature and surface temperature on the rate of removed molecules by gas molecular collisions to the total removed molecules. Gas boundary temperature T$_g$ was changed from 500 K to 900 K. Surface boundary temperature T$_s$ was changed from 300 K to 500 K, and results of 400 K and 450 K are shown in Figure 8. Adherent molecular quantity is 3.308×10^{-4} kg/m^2 (L$_1$) for all cases in Figure 8. Rate of removed molecules by gas molecular collision increases with the increase of gas temperature (T$_g$) when surface temperature is 400 K and 450 K. Rate of removed molecules by gas molecular collision in the case of 400 K is larger than that in the case of 450 K. When surface temperature is constant, the removal rate by gas molecular collision becomes larger with the increase of gas boundary temperature. By controlling temperature of gas flow, the removal rate of adherent molecules by gas molecular collision can be enhanced.

3.3. Effects of Adhesion Strength between Surface Molecules and Adherent Molecules

In order to investigate the effects of adhesion strength between surface molecules and adherent molecules, molecular dynamic simulation was conducted with changing ε_{as}, which is an energy parameter between adherent molecules and surface molecules and corresponds to the molecular adhesion strength to the surface. Effects of adhesion strength on the surface temperature and the evaporation rate in the case of 3.308×10^{-4} kg/m^2 (L$_1$) are shown in Figure 9.

From this result, effects of adhesion strength between surface molecules and adherent molecules were observed largely in the case of high surface temperature compared
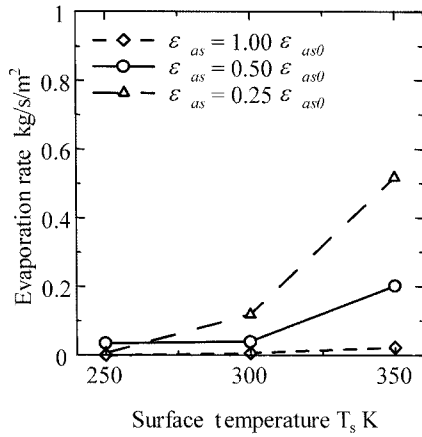
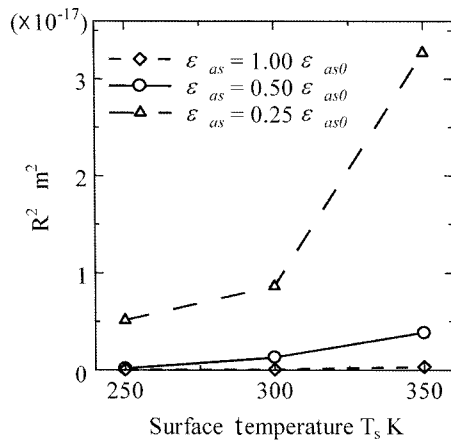Figure 9. Effects of adhesion strength on surface temperature and evaporation rate of adherent molecules.

Figure 10. Effects of adhesion strength on surface temperature and RMS of molecular trajectories of adherent molecules on the surface.

(a) $\varepsilon_{as} = 1.00\varepsilon_{as0}$

(b) $\varepsilon_{as} = 0.50\varepsilon_{as0}$

(c) $\varepsilon_{as} = 0.25\varepsilon_{as0}$

Figure 11. Effects of adhesion strength on snapshots of adherent molecules in the vicinity of the surface ($T_s = 350$ K).

with those in the case of low surface temperature. In the case of low surface temperature, small effects of adhesion strength on the evaporation rate were observed in Figure 9.

Figure 10 shows the average root mean square of molecular trajectories of adherent molecules dependent on surface temperature and energy parameter ε_{as}. The average root mean square in the case of $\varepsilon_{as} = 0.25\varepsilon_{as0}$ is larger especially in the case of $T_s = 350$ K than those in the case of low temperature. The examples of snapshots of adherent molecules in the vicinity of surface in the case of $T_s = 350$ K are shown in Figure 11.

As the adhesion strength becomes weaker, the adherent molecules can easily move on the surface molecules relatively. Therefore, adhesion strength between surface molecules and adherent molecules is influenced largely by the increase of surface temperature.
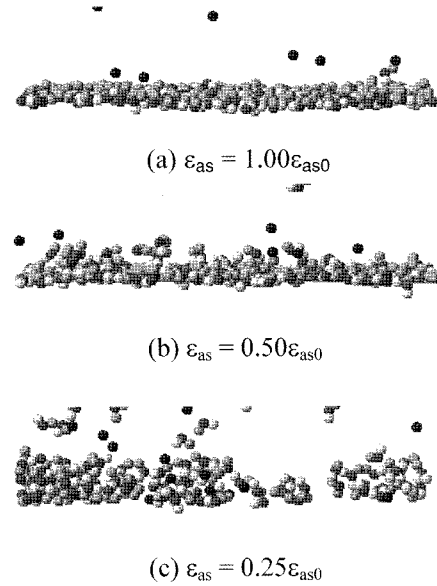
An experimental study on a dry-type degreasing method using flames was conducted and the degreased quantity of fatty oil on the surface was investigated by changing adherent quantity and reference temperature of specimen. The relationship between the degreased quantity and the surface temperature are similar to the calculation results by the molecular dynamics simulation shown in Figure 3 even though the adherent molecules in experiments are different from those in the molecular dynamics simulation. Chemical reactions between gas molecules and adherent molecules were ignored in the simulations. In the results of the molecular dynamics simulations in the present study, the removal of adherent molecules was observed when the surface temperature was lower than the boiling temperature of adherent molecules. These results show that the evaporation or removal of adherent molecules from the surface is important rather than the dissociation of adherent molecules when we consider effect of surface temperature on evaporation rate in the degreasing procedures. To discuss relationships between the removal rate and burnt gas in detail more complex function of potential energy is necessary for adherent polyatomic molecules and their dissociation processes should be considered in the molecular dynamics simulations.

4. CONCLUSIONS

The interaction between adherent molecules and gas molecules was modeled in molecular scale and simulated

by the molecular dynamics method to understand evaporation and removal processes of adherent molecules on metallic surface by using high temperature gas flow.

(1) The methanol molecules sticking to the surface are hydrogen-bonded in the first layer from the surface when the adhesion quantity on the surface corresponds to one layer of methanol molecules. The methanol molecules form molecular clusters on the first adherent layer when the adhesion quantity on the surface corresponds to more than two layers of methanol molecules. The state of adhesion in molecular scale was changed largely depending on the quantity of adherent molecules.

(2) As for the evaporation and removal processes of adherent molecules on surface, the evaporation and removal rate consists of the cases without and with gas molecular interactions, respectively.

(3) With the increase of gas boundary temperature and the decrease of adhesion quantity, the ratio of evaporation with gas molecular interactions to that without gas molecular interactions has been enhanced. With the decrease of surface temperature, the ratio of evaporation by gas molecular collisions has increased relatively.

(4) Adhesion strength between surface molecules and adherent molecules is influenced largely by the increase of the surface temperature.

(5) Evaporation and removal rates of adherent molecules from the metallic surface calculated by the molecular dynamics method showed the similar dependence on surface temperature in experimental results.

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