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Investigation of Adsorption Behavior of Oiliness Additives on Aluminum Surface by Molecular Dynamics Simulation

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Oiliness additives which adsorbed on aluminum surface have a significant influence on the lubricating function in the rolling process. The lubricating property is closely related to the adsorption behavior of oiliness additive molecules followed by formation of oil film. In this article, oiliness additives composed of fatty acids and fatty alcohols are selected to investigate the adsorption behavior on aluminum surface by molecular dynamics simulation. Simulation results indicate that fatty acid molecule shows stronger adsorptive power than fatty alcohol, and the adsorption strength between single molecule and aluminum surface increases with the increase of carbon chain length of oiliness additive molecule. But there is no obvious difference about adsorption strength of multiple molecules of different oiliness additives. The structures of oiliness additive molecules adsorbed on aluminum surface are intertwined and keep irregular, and the peak of the number density curve appears around 2.5 Å to the surface. The electrostatic interaction mainly decided by the polar group plays a decisive role in the adsorption film strength, and the oil film strength formed by fatty acid is much bigger than that of fatty alcohol. Furthermore, the oil film strength will decrease with temperature increasing while little change occurs on the structure of oiliness additive molecules.

Keywords: Oiliness additives; Adsorption; Oil film; Molecular dynamics simulation

1. INTRODUCTION

Metalworking fluid has been widely used for metal forming and machining due to its excellent functions of lubricating [1, 2]. In most cases, it is used in the rolling process of metals such as aluminum and aluminum alloys, in order to prevent sticking and control friction forces between strip and roll [3, 4]. Lubricating oils for metal rolling which have been widely used are usually prepared by compounding base oil, oiliness additives, and other ingredients such as antioxidants, extreme pressure

agents. Oiliness additive which is one of the most important additives plays a leading role of lubrication [5, 6]. Constantly renewing surface of aluminum will be produced while rolling, and the lubricating property of oiliness additives was closely related to their adsorption behavior [1, 7, 8]. Some experimental studies have been done about lubrication and wear performance of oiliness additives. Seiya Igari and Sigeyuki Mori investigated the lubrication characteristics of aliphatic diols and polyalkylene glycol [9], it indicated that adding of alkyl group(s) to diol could decrease aluminum wear. J.G.Lenard investigated the effect of lubricant additives on the coefficient of friction in cold rolling [5]. The adsorption and corrosion inhibition abilities of anion surfactants were studied using the weight loss method, which might relate to the adsorption capacity of additives [10]. Although the lubricating property of oiliness additives has been researched by some experimental methods, there are barely thorough explanations about the adsorption behavior of oiliness additives which resulting in the lubrication behavior.

Due to the limitations of experimental conditions, it is difficult to compare the adsorption behavior of different kinds and amounts of oiliness additives on aluminum surface. In this regard, molecular dynamics (MD) method has been used to investigate the interfacial behavior at microscopic molecular level. Zhang and Zhong used MD method to investigate the adsorption of different oil components on quartz surface [11, 12]. Adsorption of sulfanilamide onto aluminum oxide was also been simulated by MD simulation [13]. Although some interfacial phenomenon has been studied by means of MD simulations [14-18], there are barely relevant literatures about the adsorption behavior of oiliness additives on aluminum surface. In this work, a series of oiliness additives were chosen to investigate their adsorption behavior on aluminum surface by MD simulations. It provides a new approach to elucidate the adsorption and lubrication mechanism of oiliness additives onto metal surface, which will be helpful in guiding the lubrication additive design.

2. METHODS

To investigate the adsorption behavior of oiliness additives of different kinds and amounts on aluminum surface, fatty acids ($CH_3(CH_2)_8COOH$, $CH_3(CH_2)_{10}COOH$, $CH_3(CH_2)_{12}COOH$, $CH_3(CH_2)_{14}COOH$, $CH_3(CH_2)_{16}COOH$) and fatty alcohols ($CH_3(CH_2)_9OH$, $CH_3(CH_2)_{11}OH$, $CH_3(CH_2)_{13}OH$, $CH_3(CH_2)_{15}OH$, $CH_3(CH_2)_{17}OH$) which are commonly used in the rolling process of aluminum were chosen as oiliness additives. The MD simulations of the adsorption behavior of oiliness additives on aluminum surface were performed with Discover and Amorphous Cell modules in Materials Studio package. And the adsorption model was constructed with oiliness additive layer and aluminum surface.

As to the aluminum surface, the (1 1 1) face was chosen by cleaving the aluminum crystal. And then, an aluminum supercell of 12×12×1 was rebuilt with size of 3.43 nm×3.43 nm×1.64 nm. As to the oiliness additive layer, configurations of single molecule and multiple molecules were constructed respectively in order to compare the adsorption behavior of different amounts of oiliness additives. The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field [19] was used in all the calculations. The Van der Waals and Coulomb interactions were

calculated by Atom based method and Ewald method separately, with a cutoff distance of 12 Å. The Smart Minimizer algorithm was used to perform the minimization energy procedure in the configuration optimization. To avoid the interactions between oiliness additive molecules and aluminum atoms because of the periodic boundary conditions, an 80 Å thick vacuum was added at the top of model. By using the Verlet velocity integrator, the NVT ensemble was performed at 298 K, 348 K, 398 K to investigate the influence of temperature on the adsorption behavior of oiliness additives [20]. The time step of integration was set as 1 fs. The trajectories and structures of the oiliness additive molecules during the simulation were used for analysis. In the investigation of adsorption behavior of multiple molecules, myristic acid ($CH_3(CH_2)_{12}COOH$) was selected as an example for the analysis of structure and energy.

3. RESULTS AND DISCUSSION

3.1 Adsorption behavior of single molecule

3.1.1 Adsorption structure of single molecule

In order to compare the adsorption behavior of different amounts of oiliness additive molecules on aluminum surface, single molecule placed on aluminum surface was modeled and simulated firstly. The simulation time was set as 100 ps, and the model system can be determined as equilibrium state if the fluctuations of energy and temperature are confined less than 10% [21]. On the other hand, the binding energy can be calculated and compared at different time to help us determine whether the system was thermodynamically stable. The equilibrium configurations of different oiliness additive molecules were shown in Fig.1.

No matter what initial configurations they were, attractive interaction made them move close to aluminum crystal surface and kept almost parallel with it. Then the oiliness additive molecules kept tiny vibrations near the equilibrium position. Because of the neutral surface of aluminum crystal, the main interaction force was Van der Waals' force (VDW), which was relatively weak compared with coulombic force.

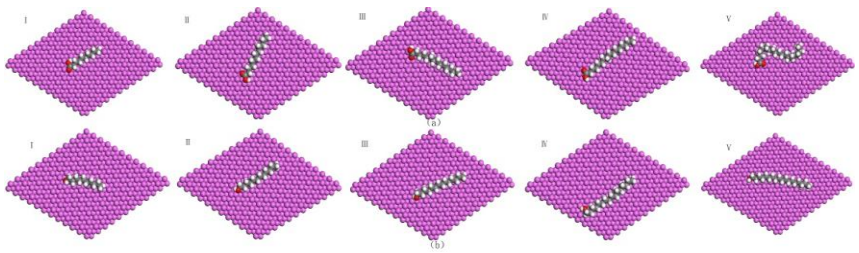

Figure 1. (a) The equilibrium configurations of (I) $CH_3(CH_2)_8COOH$ (II) $CH_3(CH_2)_{10}COOH$ (III) $CH_3(CH_2)_{12}COOH$ (IV) $CH_3(CH_2)_{14}COOH$ (V) $CH_3(CH_2)_{16}COOH$ on aluminum surface and (b) the equilibrium configurations of (I) $CH_3(CH_2)_9OH$ (II) $CH_3(CH_2)_{11}OH$ (III) $CH_3(CH_2)_{13}OH$ (IV) $CH_3(CH_2)_{15}OH$ (V) $CH_3(CH_2)_{17}OH$ on aluminum surface

3.1.2 Adsorption strength between oiliness additive and aluminum surface

To compare the adsorption behavior of different oiliness additives, the interaction energy (ΔE) between oiliness additive molecular and aluminum crystal (1 1 1) surface was calculated using the following formula [22, 23]:

$$\Delta E = \frac{E_{complex} - (E_{OA} + E_{surface})}{N} \quad (1)$$

where $E_{complex}$ is the total energy of the bound oiliness additive molecule and aluminum crystal (1 1 1) surface system after MD simulation, E_{OA} and $E_{surface}$ represent the single point energies of the free oiliness additive molecular and the aluminum crystal surface respectively. The binding energy (E_b) is defined as follows [24, 25]:

$$E_b = -\Delta E \quad (2)$$

the E_b can intuitively indicate the interaction degree of the system, and the larger E_b is, the more easily and tightly the oiliness additive molecule and aluminum crystal (1 1 1) surface combine.

The binding energy of myristic acid system at different times was calculated separately, as shown in Table 1. It could be seen that the binding energy had no obvious change, and the average value of binding energy was calculated for analysis.

Table 1.The binding energy of myristic acid on aluminum surface at different times (kJ/mol)

E (kJ/mol)	Time				
	80 ps	85 ps	90 ps	95 ps	100 ps
ΔE	-291.7	-282.2	-282.2	-280	-285.9
E_b	291.7	282.2	282.2	280	285.9

By calculating E_b of different single oiliness additive molecule (see Table 2), it is clear that the binding energy increases with the adding of carbon chain length, which means that the carbon chain can strengthen the interaction between oiliness additive molecules and aluminum crystal surface. It also can be seen that the binding energy between fatty acid and aluminum surface is usually larger than that of fatty alcohol with the same length of carbon chain.

Table 2.The binding energy of different oiliness additives (kJ/mol)

$CH_3(CH_2)_8COOH$	212.7	$CH_3(CH_2)_9OH$	201.1
$CH_3(CH_2)_{10}COOH$	244.1	$CH_3(CH_2)_{11}OH$	243.5
$CH_3(CH_2)_{12}COOH$	284.4	$CH_3(CH_2)_{13}OH$	259.7
$CH_3(CH_2)_{14}COOH$	317.3	$CH_3(CH_2)_{15}OH$	307.1
$CH_3(CH_2)_{16}COOH$	356.6	$CH_3(CH_2)_{17}OH$	338.9

3.2 Adsorption behavior of multiple molecules

There usually more than one oiliness additive molecule adsorbed on the metal surface in most practical situations. Multiple molecules will be the existence form in most lubrication process. The lubricating property is determined primarily by the adsorption strength between multiple oiliness additive molecules and aluminum surface, and also the strength of adsorption film which formed on the metal surface. Hence, an investigation of the adsorption strength and the strength of adsorption film was conducted by the study of adsorption behavior of oiliness additives on aluminum surface.

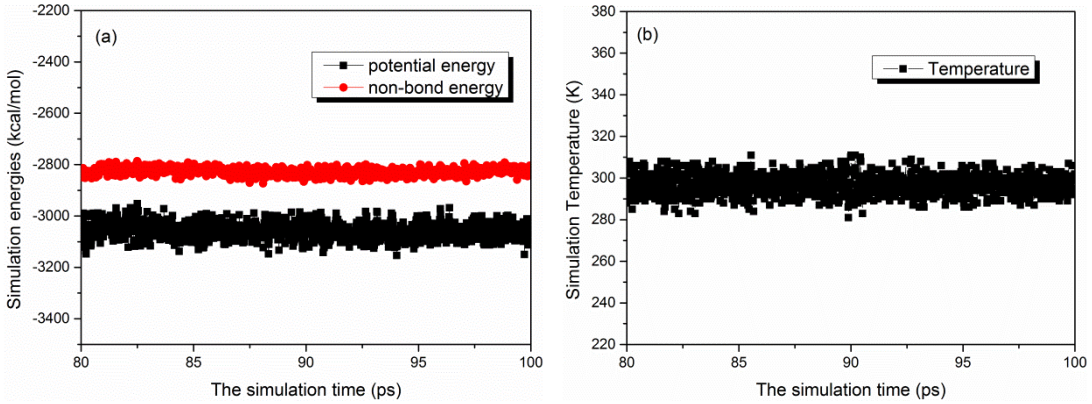

Figure 2. The energy (a) and temperature (b) profiles in the simulation process of myristic acid molecules on aluminum surface from 80 ps to 100 ps

During the simulations, the energy and temperature profiles from 80 to 100 ps were shown in Fig. 2 as an example for model system with myristic acid molecules. The mean value of energy and temperature at every 5 ps were calculated and compared. The relative deviation of temperature and energy was low enough after 80 ps MD simulation and we obtained a statistics value from the last 20 ps for calculation and analysis. The initial and equilibrium structure of myristic acid-metal were shown in Fig. 3.

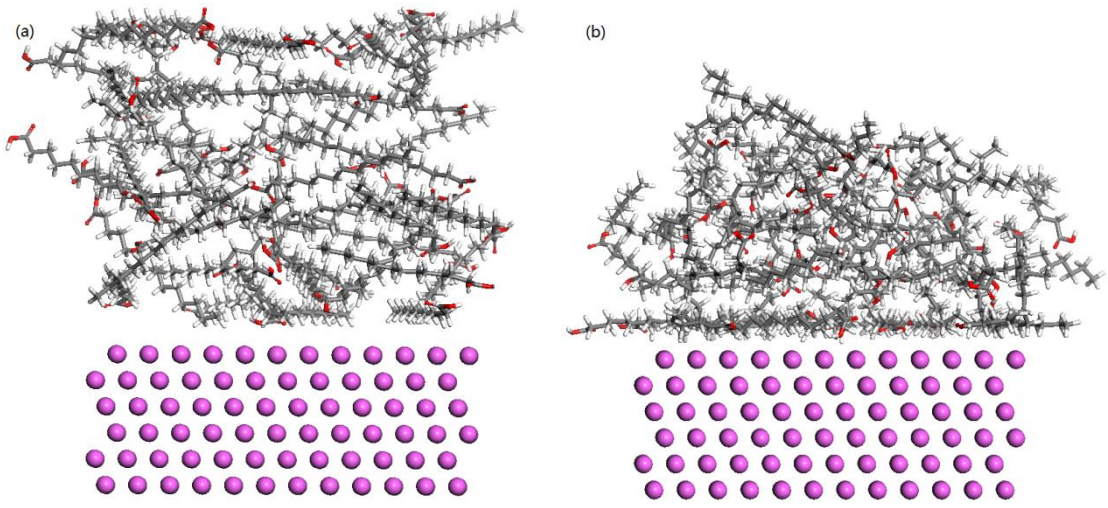

Figure 3. The (a) initial structure and (b) equilibrium structure of myristic acid on aluminum surface

3.2.1 Adsorption structure of multiple molecules

The research of adsorption film is always a hot topic in the fields of tribology and interfacial heat transfer [1, 6, 26-29]. Further, the adsorption structure of the adsorbents will have a significant influence on the lubrication action. As shown in Fig.4, the equilibrium structures of molecules next to the aluminum surface are not perpendicular to the surface of aluminum crystal, but intertwined and irregular structures instead. The individual molecule penetrates bulk phase to connect the layer adsorption film next to the surface with other molecules in the bulk phase, which was like the adsorption structures in [16-18, 30-32]. This phenomenon was different from equilibrium adsorption configuration of acetic acids [12], might because of a huge difference of the carbon chain length between them.

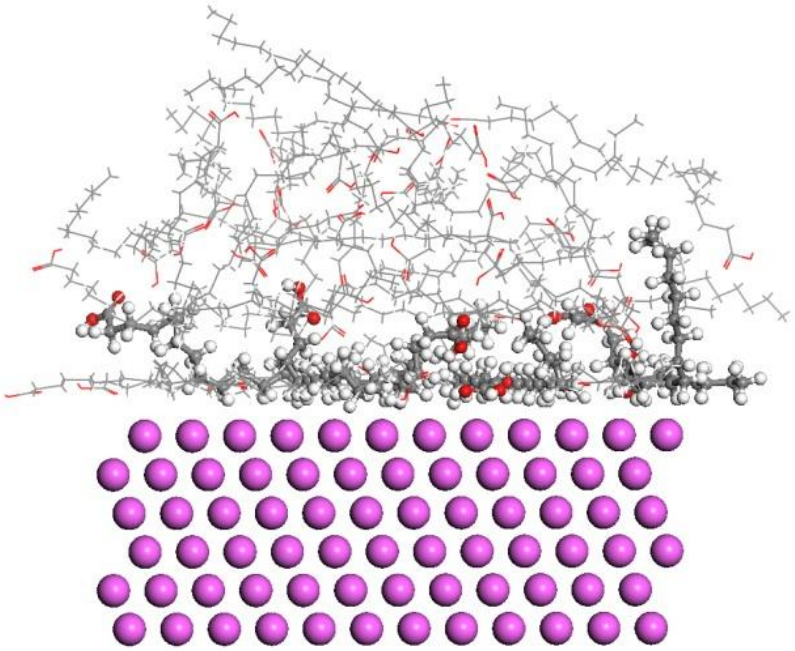

Figure 4. The structures of oiliness additive molecules next to aluminum surface

Thickness of adsorption film can be predicted through the graph of relative concentration distribution along z axis. In order to express the compactness of layer films, the number density of atoms was calculated according to formula (3), and Fig. 5 showed the details.

$$n = N/V \quad (3)$$

where n is the number density, V represents the volume and N represents the number of atoms in V.

It can be seen that the thickness of the layer next to the surface are almost the same among different oiliness additives, about 3 Å to 5 Å. The peak of the number density curve appears around 2.5 Å in the simulated system, and their atom numbers has no obviously difference because of the existence of saturated extent of adsorption.

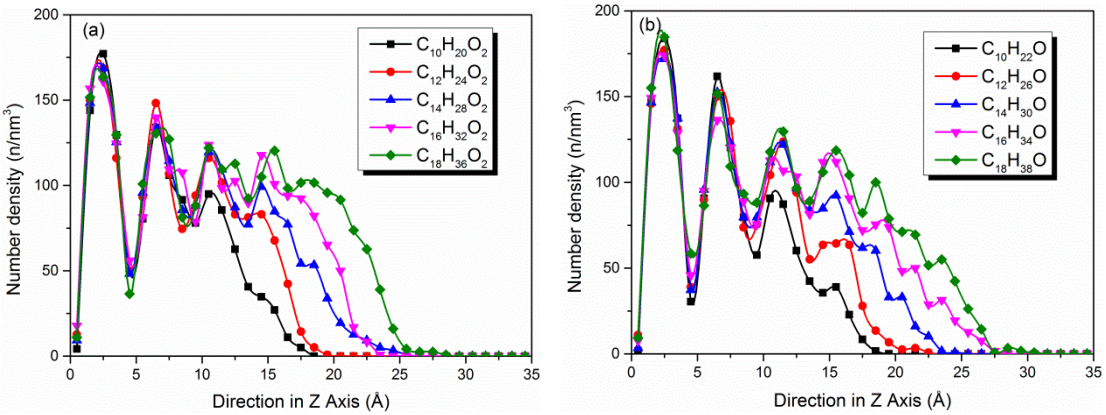

Figure 5. The atomic number density of oiliness additives along z axis

3.2.2 Adsorption strength and oil film strength

In the machining process, chemical adsorption is the mechanism that results in the formation of boundary films. The adsorption strength to the metal and the oil film strength have a significant influence on the lubricating property [5]. In the shear simulation of lubricant additive, the thickness of adsorbed layers and distribution of density is also the focus [30, 31, 33-35], while little-studied aspect of interaction energy in the model system. The adsorption strength is decided by the binding energy between adsorbents and metal surface and the interaction of adsorbent molecules themselves decides the strength of the adsorption film, as shown in Fig. 6.

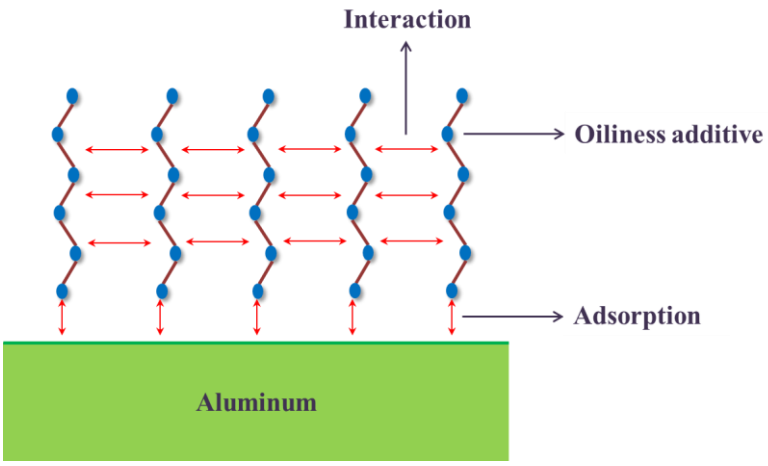

Figure 6. The schematic diagram of interaction force for adsorption of oiliness additive

In order to reflect the adsorption strength and oil film strength, the binding energy between oiliness additive molecules and aluminum surface and the non-bond energy among oiliness additive molecules themselves were calculated respectively, as showed in Table 3. The non-bond energy is composed of Van der Waals energy and electrostatic energy, and the relationship was given as follows:

$$E_{\text{non-bond}} = E_{\text{vdw}} + E_{\text{electrostatic}} \quad (4)$$

Because of the electric neutrality of aluminum surface, the binding energy is produced by the van der Waals interactions between oiliness additive molecules and aluminum surface. From Table 3, it can be seen that the binding energy of all kinds of oiliness additives is about 57~63 kJ/mol, there are no significant difference between them. On the contrary, the non-bond energy of fatty acid molecules is much larger than that of fatty alcohol molecules, because the electrostatic interaction mainly decided by the polar group plays a decisive role in the adsorption film strength. It means that the interaction force of fatty acid molecules will be more powerful, and the strength of adsorption film formed by fatty acid molecules will be harder to destroy. Additionally, the strength of adsorption film will also increase with the increase of carbon chain length, but the impact is relatively smaller than that of the types of oiliness additives. The results may give explanation to the experimental results in [9] in some ways.

As a consequence, although the adsorption strength of compound with solid surface has been studied thoroughly [12, 13, 21-23], the oil film strength has been little investigated. It is meaningful to pay attention to the study of the strength of oil film which adsorbed on the metal surface.

Table 3. The Non-bond energy and binding energy of oiliness additives (kJ/mol)

	vdw	electric	Non-bond	Bind
$CH_3(CH_2)_8COOH$	-24.5	-138.7	-163.2	62.8
$CH_3(CH_2)_{10}COOH$	-32.1	-137.2	-169.3	59.7
$CH_3(CH_2)_{12}COOH$	-40.9	-136.7	-177.6	60.9
$CH_3(CH_2)_{14}COOH$	-49.5	-134.2	-183.7	62.5
$CH_3(CH_2)_{16}COOH$	-57.2	-134.0	-191.2	59.4
$CH_3(CH_2)_9OH$	-23.6	-13.5	-37.1	61.3
$CH_3(CH_2)_{11}OH$	-31.7	-12.8	-44.5	57.2
$CH_3(CH_2)_{13}OH$	-38.2	-12.1	-50.3	58.6
$CH_3(CH_2)_{15}OH$	-43.8	-11.4	-55.2	57.5
$CH_3(CH_2)_{17}OH$	-51.4	-13.6	-65.0	57.1

3.3 Influence of temperature on adsorption behavior

The heat by friction and metal deformation is constantly produced in the process of machine works. The adsorption behavior of oiliness additives will also be influenced by temperature. To investigate the influence of temperature on their adsorption behavior, the adsorption of different oiliness additives at different temperatures (298 K, 348 K, 398 K) were considered and compared in the simulation. The number density of myristic acid and tetradecyl alcohol along z axis were calculated as samples (Fig. 7). It can be seen that there is no significant difference on the adsorption structure and number density of oiliness additives at different temperatures. Although the temperature rise results in the violent vibration of oiliness additive molecules, they still keep the adsorption configurations due to the adsorption force of aluminum surface.

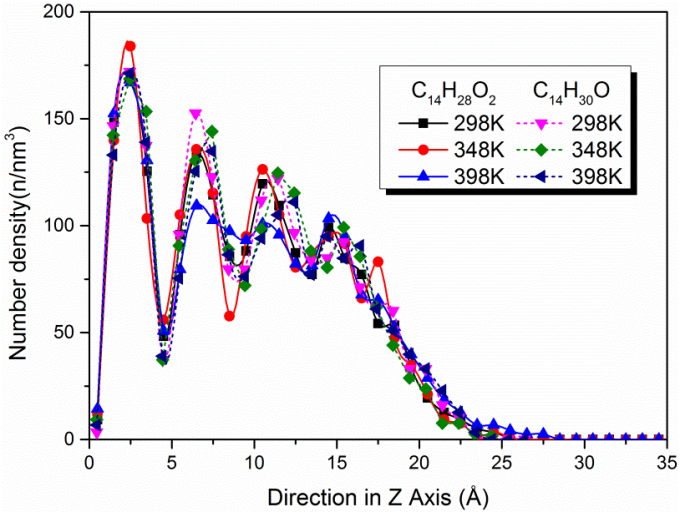

Figure 7. The atomic number density of myristic acid and tetradecyl alcohol at different temperatures

The non-bond energy of different oiliness additives at 298 K, 348 K, 398 K were also calculated and compared, and Fig. 8 showed the details. With the increase of temperature, the non-bond energy of oiliness additives decreases. It means that the strength of adsorption film will decrease when temperature rises. The increased carbon chain length helps to increase the strength of oil film. And the oil film strength developed by fatty acids is generally greater than that of fatty alcohols.

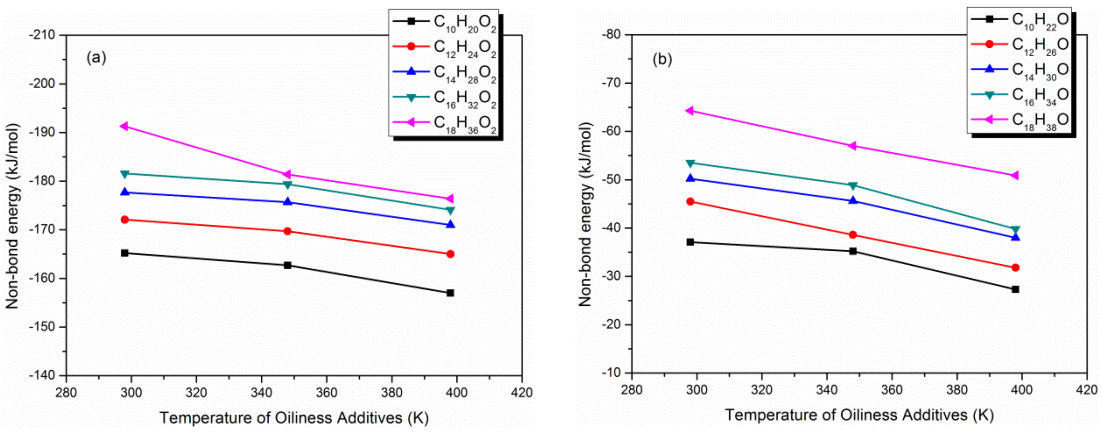

Figure 8. The non-bond energy of oiliness additives at different temperatures

4. CONCLUSION

In this article, fatty acids and fatty alcohols were selected as oiliness additives to investigate their adsorption behavior on aluminum surface by means of molecular dynamics simulations. The adsorption behavior of single molecule and multiple molecules were investigated respectively, and the adsorption strength and oil film strength of oiliness additives were also analyzed and discussed. The findings were summarized as follows:

1. The adsorption behavior of single oiliness additive molecule on aluminum surface was studied firstly. The equilibrium shape of single molecule is to keep parallel with the metal surface. The fatty acid shows stronger adsorptive power to aluminum surface than that of fatty alcohol, and the adsorption energy increases with the increase of carbon chain length of oiliness additive molecule.

2. When the number of oiliness additive molecules is enough to cover the aluminum surface, the equilibrium structure of adsorbed molecules is intertwined and irregular. The thicknesses of the absorbed layer nearby aluminum surface formed by different oiliness additives are almost the same, and the peak of the number density curve appears around 2.5 Å.

3. The type of oiliness additives contributes more to oil film strength rather than adsorption strength. The oil film strength will increase when the carbon chain length of oiliness additive molecule increases, while there is no obvious difference about adsorption strength of different oiliness additives because of the existence of saturated concentration of absorption on the aluminum surface.

4. When temperature rises, the strength of the oil film formed by the adsorption of oiliness additive molecules will decrease because of decline of the interaction energy among these molecules. But the equilibrium structure of the adsorption of oiliness additive molecules changes very little.

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