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REACTION MECHANISMS OF ALCOHOLS ON ALUMINUM SURFACES

MECHANIZMY REAKCJI ALKOHOLI NA POWIERZCHNI ALUMINIUM

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reaction mechanism, tribochemistry, chemisorption, friction reduction, fatty alcohols, oxidized aluminum surface, SIMS analysis, deuterated molecules

Słowa kluczowe:

mechanizm reakcji, tribochemia, chemisorpcja, redukcja tarcia, alkohole tłuszczowe, utleniona powierzchnia aluminium, analiza SIMS, deuterowane cząsteczki

Summary

The general aim of this work concerns the study of the lubricant/surface interaction mechanisms, such as those occurring during aluminum cold

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rolling in the presence of fatty alcohols. To improve the understanding of alcohol tribochemical reactions on an aluminum surface, friction tests followed by SIMS analyses were conducted. Deuterated alcohols were used to investigate the formation of bonds between the aluminum surface and alcohol molecules. The combination of SIMS analysis and the use of deuterated molecules have enabled us to propose a reaction mechanism between alcohols and the initial oxidized aluminum surface. This mechanism later affects the tribological behavior of the interface. In agreement with previous observations, we showed that a low steric size increases the number of acting molecules on the oxidized surface and that the alkyl chain length is of importance to protect the surface and hence reduce friction. These two key points can be easily explained by the proposed reaction pathway.

INTRODUCTION

Aluminum alloys make it possible to meet a broad range of requirements in the development of products of mass distribution, such as those used in the automotive industry. The cold rolling process provides the manufactured goods with suitable geometrical, mechanical, and metallurgical characteristics and with convenient surface properties for further treatments as well.

Friction must be sufficient to permit efficient control of the rolling mill, without being so excessive as to prevent surface degradation. Mixed lubrication is the prevalent regime, associating both hydrodynamic and boundary contributions. Compared with hydrodynamic lubrication, the understanding of boundary lubrication is less advanced. Under this regime, the presence of additives is very important, and molecules such as fatty alcohols, acids and esters are used in cold rolling.

To simulate the tool-sheet contact as found in aluminum cold rolling, many authors have studied the behavior of fatty alcohol molecules under boundary lubrication conditions. A primary linear and fatty alcohol (one hydroxyl group located at one end) with a sufficiently long chain (at least in C₁₂) seems the most suitable additive [L. 1–3].

However, if the reaction mechanisms of acids [L. 4–5] and esters [L. 6] are well described, those of alcohols remain questionable. Their interaction with the aluminum surface has not been clearly identified because the characterization of tribochemical films is a quite complicated

operation. Commonly used techniques (XPS, SIMS) do not differentiate fatty alcohols from contaminants. By carrying out both tribological tests and in situ analyses under vacuum, Boehm *et al.* [L. 7] assumed that alcoholates R-O⁻ are formed, although no formal detection was obtained.

According to Kajdas [L. 8], two simultaneous reactions occur on rubbing surfaces; the first one involves the alcoholates (R-O⁻) chemisorption and the second the formation of a durable protective film due to a recombination of radicals and bi-radicals. However, the experimental results of Dauchot [L. 9] did not fully confirm the Kajdas model. From SIMS analyses, he highlighted an oxidation reaction, but did not propose a reaction pathway. Thus, he could not confirm that the formed acids were responsible for the friction reduction.

In this work, 1-dodecanol (fatty alcohol in C₁₂) is marked using deuterium to enhance its detection. Glycerol (or propan-1,2,3-triol, alcohol in C₃) is also introduced for comparison (Table 1). Indeed, both friction coefficient and wear obtained with this alcohol are high. After tribological tests run under severe boundary conditions, the initial and worn surfaces are analyzed by two SIMS techniques: dynamic and static SIMS that give in-depth atomic information and molecular information from the top surface, respectively.

EXPERIMENTAL CONDITIONS

A modified Cameron-Plint machine was used to evaluate the frictional behavior of the model additives by simulating a sliding reciprocating motion between two specimens. The operating parameters were adjusted to simulate severe boundary lubrication conditions. The upper test specimen (steel cylinder) was held in contact with the fixed specimen (aluminum plate), by an applied load of 230 N. The upper specimen was driven with a reciprocating motion of 7.5 mm stroke amplitude at 1 Hz. The surface roughness was $R_q = 0.5 \mu\text{m}$ for the cylinder and $R_q = 0.6 \mu\text{m}$ for the plate. The lubricant was placed in a temperature-controlled container at a constant temperature of 70°C. Only five cycles were performed in ambient air. The actual friction coefficient varies during each cycle since it depends on the relative velocities of the specimens. Friction coefficients reported in this study are averaged values: they were calculated from the stable friction zones measured at each cycle and from at least two distinct experiments.

The model additives used in this study were deuterated alcohols (**Table 1**). Deuterated 1-dodecanol ($C_{12}D_{25}OH$) and glycerol ($C_3H_3O_3D_3$) were commercially available from Sigma Aldrich. The concentration of the deuterated form was 98%.

Table 1. Studied additives

Tabela 1. Badane dodatki

Deuterated molecules	
1-dodecanol	$C_{12}D_{25}OH$ $CD_3-(CD_2)_{11}-OH$
	$C_{12}H_{25}OD$ $CH_3-(CH_2)_{11}-OD$
Glycerol (or propan-1,2,3 triol)	$\begin{array}{ccc} CH_2 & -CH- & CH_2 \\ & & \\ OD & OD & OD \end{array}$
Non-deuterated molecules	
1-hexanol	$CH_3-(CH_2)_5-OH$
Glycerol mono-oleate	$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-O-\begin{array}{c} CH_2-CH-CH_2 \\ \quad \quad \\ C \quad OH \quad OH \\ \\ O \end{array}$

Hydroxyl deuterated 1-dodecanol ($C_{12}H_{25}OD$, **Table 1**) was obtained in an equilibrium chemical reaction between pure 1-dodecanol ($C_{12}H_{25}OH$) and heavy water (D_2O). The result was a blend of original alcohol (43.3% mol.), deuterated alcohol (39.0% mol.) and DOH (17.7% mol.). Deuteration of either the hydroxyl group or the main alkyl chain allowed the identification of hydrogen atoms stemming from the carbon chain from those coming from the alcohol group and/or from environmental contamination.

We ensured that deuterium did not influence the tribological behavior of the model additives by comparing the friction coefficients obtained with deuterated alcohols and their non-deuterated compounds.

Dynamic SIMS spectra were obtained using a SIMSLAB Instrument with a Ga^+ source. According to the analysis conditions, the abrasion speed was between 0.2 and 0.5 Å/sec.

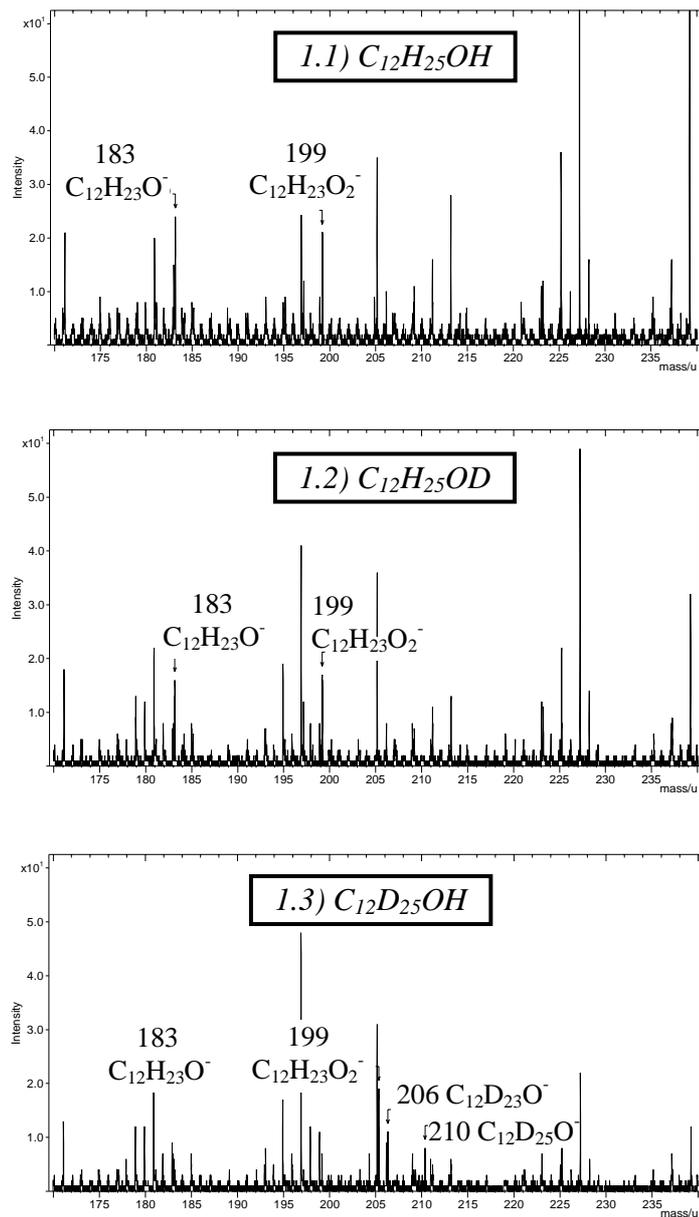


Fig. 1. 1-dodecanol and deuterated 1-dodecanol static SIMS spectra obtained on silicon wafers

Rys. 1. Widma SIMS 1-dodekanolu i deuterowanego 1-dodekanolu zarejestrowane techniką statyczną na płytkach silikonowych

Static SIMS measurements were carried out using a TOF-SIMS IV (ION-TOF). High mass resolution spectra of $M/\Delta M > 7500$ at $m/z = 28$ were recorded using beams of Au^+ (for the aluminum surface) or Bi^+ (for the silicon wafer) ion pulses with an impact energy of 25 keV. The measured mass range was $m/z = 1\text{--}1500$. The total ion doses used in these measurements were approximately less than or equal to $5 \cdot 10^8$ ions/cm².

Before each analysis, the aluminum surface was rinsed with heptane, without ultrasonic assistance [L. 10]. This cleaning permits removal of excessive fluids and analysis of the top surface of aluminum specimens.

Three types of surface were analyzed: silicon wafers, non-rubbed surfaces consisting of initially oxidized aluminum just outside the wear track, and rubbed surfaces.

RESULTS AND DISCUSSION

In this study, we concentrated only on the emission of negative ions. Deuterated alcohols references were obtained by static SIMS on silicon wafers to identify their characteristic ions. Reference spectra obtained from different types of 1-dodecanol deposited on silicon wafers are reported in **Figure 1**. Authors such as Murase et al. [L. 10] did not detect the molecular ion $\text{C}_{12}\text{H}_{25}\text{O}^-$, supposed to be a characteristic ion of 1-dodecanol. Because of the carbon chain deuteration, the equivalent ion ($\text{C}_{12}\text{D}_{25}\text{O}^-$, 210 amu in **Figure 1.3**) was detected with a low intensity using silicon substrate. Moreover, we highlighted a particular ionization of fatty alcohols from static SIMS analysis. Thus, other molecular ions such as $\text{C}_{12}\text{D}_{23}\text{O}^-$ in **Figure 1.3** (206 amu) were found with 1-dodecanol and in the same way $\text{C}_3\text{H}_3\text{D}_2\text{O}_3^-$ has been identified with glycerol.

For 1-dodecanol deuterated on the hydroxyl group, detection problems of the characteristic ions were encountered. Only the D^- and OD^- ions will be studied to follow the hydroxyl group.

In-depth localization

After tribological tests, the non-rubbed and the rubbed surfaces were analyzed by the dynamic SIMS technique. **Figure 2** represents the spectra obtained with $\text{C}_{12}\text{D}_{25}\text{OH}$ on the top surface of the non-rubbed and rubbed zones. After friction, the characteristic peaks of D^- and OD^- ions strongly increase. The comparison of the peaks corresponding to mass 2 (D^-) and 18 (OD^-) allows following the evolution of the alkyl chain. The OD^- ions

result from a recombination between deuterium coming from the alkyl chain and O^- ions coming from the oxide layers or from contamination. This phenomenon is actually specific to the dynamic mode and explains the OD^- detection.

Whatever the type of the analyzed surface, the in-depth profiles of D^- and OD^- ions were similar: the concentration on the top surface drops suddenly.

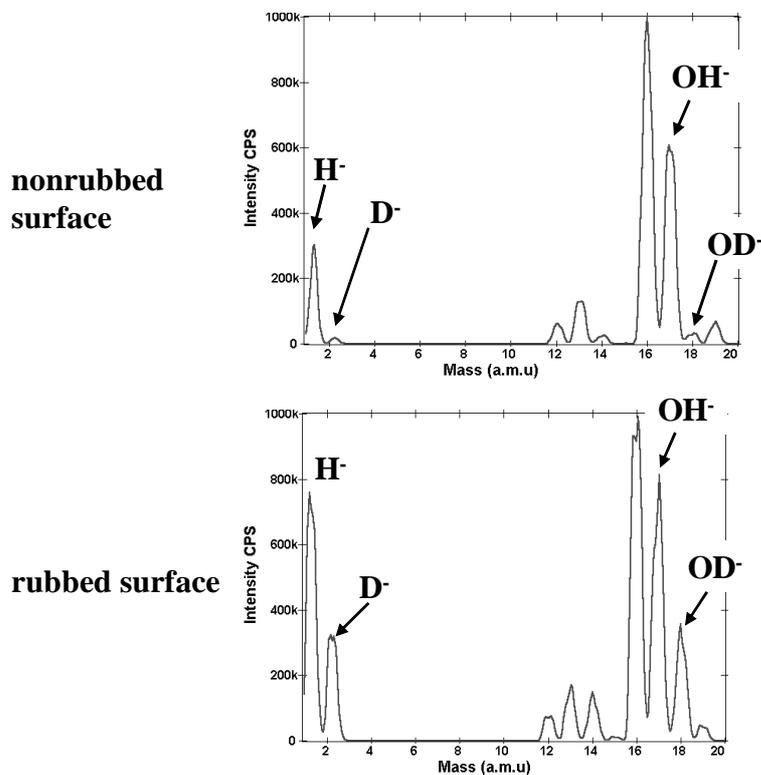


Fig. 2. Dynamic SIMS spectra of 1-dodecanol $C_{12}D_{25}OH$ on aluminum top surfaces

Rys. 2. Widma SIMS 1-dodekanolu $C_{12}D_{25}OH$ zarejestrowane techniką dynamiczną z powierzchni aluminium

Thus, friction only increases the number of adsorption sites occupied by 1-dodecanol because the density of D^- and OD^- increases, but not their thickness, as can be deduced from in-depth profile analysis (species only present on top surface, whatever the surface). Essential information being present only on the top surface, the static SIMS technique is sufficient.

Static SIMS analyses

For the three deuterated alcohols, the deuterium percentages $P(D)$ and $P(OD)$ of the D^- and OD^- ions were normalized according to the intensities of H^- and OH^- , respectively. **Figure 3** shows that the relative percentage of $P(D)/P(OD)$ obtained with $C_{12}D_{25}OH$ is almost the same as the reference on the non-rubbed and rubbed zones. Thus, the alkyl chain does not undergo any modification. On the other hand, for the two alcohols deuterated on their hydroxyl group, the relative percentage $P(D)/P(OD)$ increases on the non-rubbed zone and friction enhances this increase in the case of 1-dodecanol. However, for glycerol the high wear observed by optical microscopy (ploughing, see **Figure 4**) must eliminate the species formed by tribochemical effects.

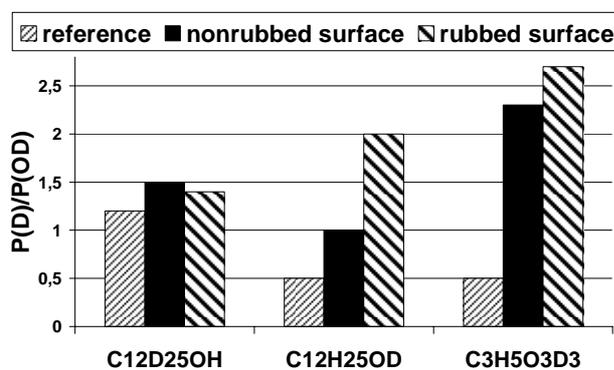


Fig. 3. Deuterium relative percentage obtained on three different surfaces

Rys. 3. Względna zawartość procentowa deuteru na trzech różnych powierzchniach

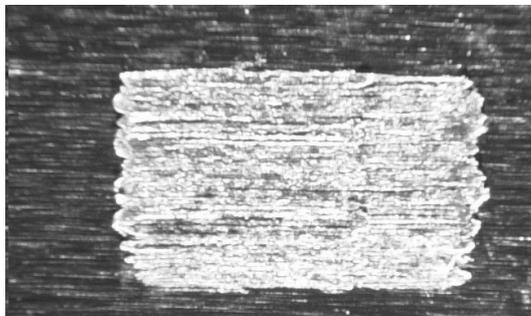


Fig. 4. Worn surface obtained after friction with glycerol (wear track length = 7.5 mm)

Rys. 4. Powierzchnia zużycia po tarcia w obecności gliceryny (długość śladu zużycia 7,5 mm)

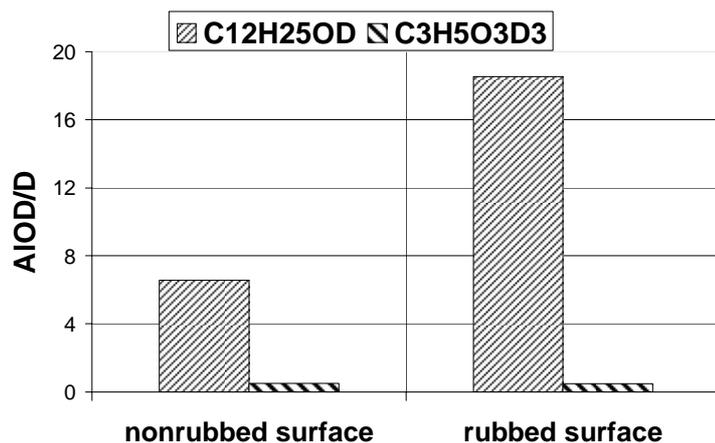


Fig. 5. Comparison between deuterated alcohols on nonrubbed and rubbed surfaces

Rys. 5. Porównanie alkoholi deuterowanych na powierzchni przed i po tarcia

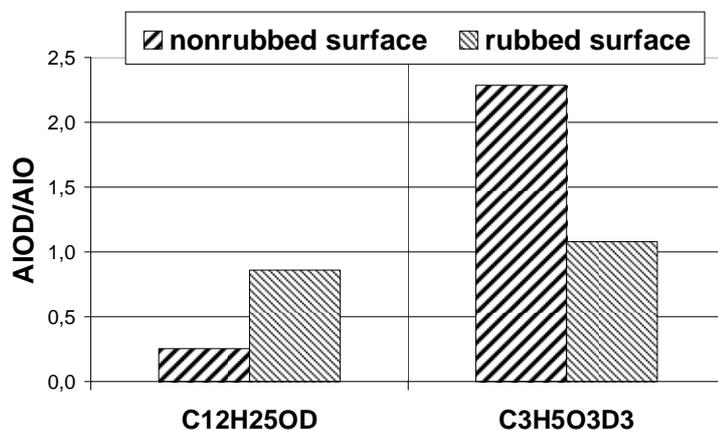


Fig. 6. AIOD⁻ evolution with friction for alcohols deuterated on their hydroxyl group

Rys. 6. Powstawanie AIOD⁻ podczas tarcia dla alkoholi z deuterowanymi grupami hydroksylowymi

At this stage, we can suppose that a surface reaction takes place between the proton of the hydroxyl group and the oxidized initial surface. Thus, with deuterated alcohols R-OD, we clearly detect the AIOD⁻ ions on the non-rubbed zone, chemical structure similar to AIOH⁻. According to Pearson [L. 11], the reaction between AIO and R-OH is an acido-basic

reaction involving a strong acid and a strong base that favor an easy and quick reaction process. On the other hand, this process can also be described as the first step in the NIRAM-HSAB model proposed by Kajdas [L. 12]. Whatever the surface was, the AlOD^- intensities normalized with regard to the D^- ions intensity (Figure 5) showed that the reaction was much more advanced for 1-dodecanol.

To compare rubbed and non-rubbed surfaces for each deuterated alcohol R-OD, the intensities are normalized with regard to the surface, i.e. the AlO^- ion (Figure 6). After friction, the relative intensities increase with 1-dodecanol and decrease with glycerol because this later generates surface ploughing.

In view of these surface analyses, a first sequence of the reaction mechanism taking place between an alcohol and an oxidized aluminum surface is deduced:



The second stage of the reaction mechanism could be the immediate oxidation of the formed alcoholate:



On the initial oxidized surfaces, the „acid” ions are detected with glycerol and 1-dodecanol (Figure 7). But after friction, as for the AlOD^- ions, the relative intensities of the „acid” ions increase considerably with 1-dodecanol and remain almost constant with glycerol (Figure 7). In this figure, the intensity of the „acid” ions is normalized by the intensity of their associated alcohol ions, indicating the degree of conversion in the oxidation process. However a more detailed analysis can be realized using static SIMS results. Figure 8 reports a comparison between spectra obtained with $\text{C}_{12}\text{D}_{25}\text{OH}$ on initial and rubbed aluminum surfaces. A first comparison between spectra reported in Figures 1.3 and 8.1 (plotted using different intensity scales) shows a significant increase of $\text{C}_{12}\text{D}_{23}\text{O}_2^-$ ion on the initial oxidized aluminum surface. Another change is found by comparing Figures 8.1 and 8.2: a further increase of $\text{C}_{12}\text{D}_{23}\text{O}_2^-$ ion is observed and confirms the acid ions presence enhanced by friction. These results definitely confirm the second stage of the reaction pathway between alcohols and aluminum surfaces shown above, Reaction (2).

The most likely final step would be the acid chemisorption onto the protonated surface. However, the analyses performed in this work do not permit formal validation of the occurrence of this reaction.

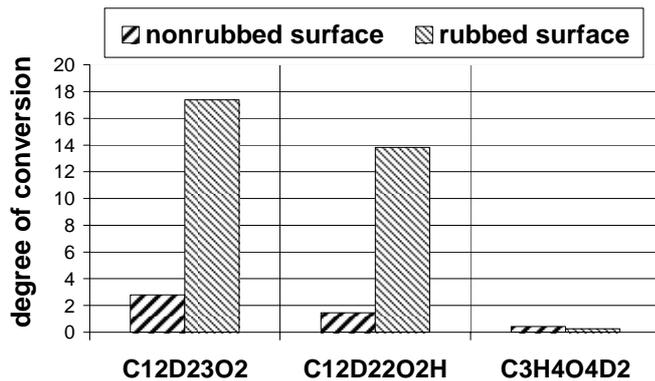


Fig. 7. Acid evolution with friction

Rys. 7. Powstawanie jonów „kwasu” podczas tarcia

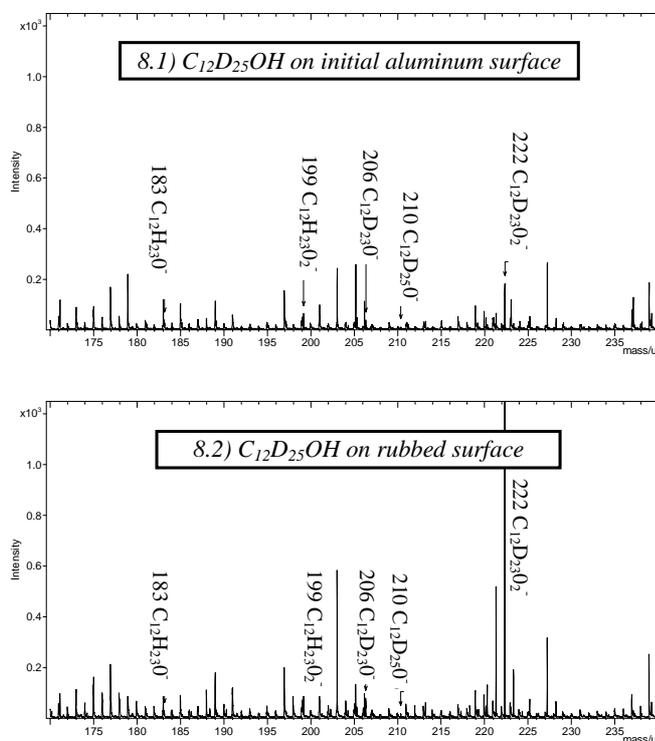


Fig. 8. Deuterated 1-dodecanol static SIMS spectra before 8.1) and after 8.2) rubbing on aluminum substrate

Rys. 8. Widma deuterowanego 1-dodecanolu uzyskane techniką statyczną: 8.1) przed, 8.2) po tarcii po podłożu aluminiowym

Proposed chemical pathway and consequences on friction

The alcohol reaction mechanism occurring on an oxidized aluminum surface can be summarized as follows:

- 1) Acido-basic reaction between R-OH and AlO that leads to alcoholates (R-O⁻) and protonated aluminum surface (AlOH) formation.
- 2) Immediate oxidation of alcoholates R-O⁻ by environmental oxygen.
- 3) Acid chemisorption onto the protonated aluminum surface.

Then, under boundary conditions, the amounts of acid compounds and AlOH increase with friction for 1-dodecanol. On the other hand, since the glycerol chain length is insufficient to protect the surfaces, the species formed during friction are eliminated by ploughing. Nevertheless, we observe (**Figure 6**) that an acido-basic reaction occurs again on the wear track, because AlOD⁻ ions are still detected after friction.

Validation and conclusions

The proposed reaction mechanism could be similar for all types of alcohol, but friction and wear vary according to the chemical structure of the alcohols considered. These different behaviors can be explained by an interaction between the initial surface and the alcohol, and by the acid chemisorption, both reactions being dependent on two parameters: the steric size and the chain length. Thus, an efficient alcohol must be rather primary (without any secondary function) and linear, allowing a larger percentage of chemisorbed acid to react on the initial oxidized aluminum surface. Furthermore, a carbon chain of a sufficient length permits a more efficient surface protection during friction.

These results are confirmed by tribological tests performed with 1-hexanol and glycerol mono-oleate (**Figure 9**). For instance, in spite of its linear chain with one end composed of a single hydroxyl group, 1-hexanol gives high friction coefficients because of its too-short alkyl chain. Besides, glycerol mono-oleate molecules present a quite long chain length: this alcohol shows higher friction coefficients than those measured with 1-dodecanol because of its larger steric size, which limits the density of adsorption sites. These results confirm that friction will reach a minimum when the steric size is low and the alkyl chain sufficiently long (approximately 12 carbon atoms).

As a consequence of the proposed reaction mechanism, the presence of oxygen is necessary for the formation of the acid responsible for the

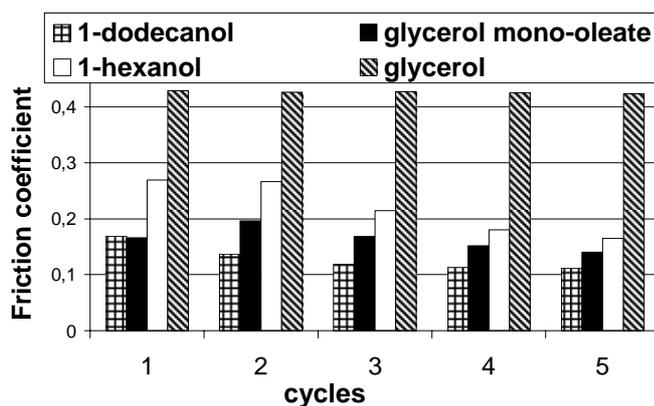


Fig. 9. Friction coefficients measured with 4 standard alcohols

Rys. 9. Współczynniki tarcia zmierzone dla 4 alkoholi wzorcowych

decrease in friction. The mechanism reported by Boehm [L. 7], following tests conducted under vacuum, cannot be representative of the real conditions, except if he simultaneously introduced oxygen and alcohol. Moreover, one might think that a basic substitution of alcohol by the corresponding acid would decrease the friction coefficient. However, we have shown that protonation also plays an important role in the bonding between molecules and the initial surface. According to Lenard [L. 13], friction is increased when fatty acids are used as unique additives in steel/aluminum contacts. 1-dodecanol remaining the most appropriate molecule; the introduction of an equivalent acid would accelerate the reaction kinetics and could be the solution for use in aluminum cold rolling. But at this time the friction values reported in the literature [L. 14–15] do not allow us to validate this suggestion.

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Recenzent:

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Streszczenie

Celem niniejszej pracy było zbadanie mechanizmów oddziaływań układu środek smarowy/powierzchnia, które między innymi mają miejsce podczas walcowania na zimno aluminium w obecności alkoholi tłuszczowych. Produkty tribochemicznych reakcji alkoholi, zachodzące na powierzchni aluminium, badano za pomocą spektrometrii masowej jonów wtórnych (SIMS). Aby zbadać tworzenie się wiązań pomiędzy powierzchnią aluminiową a cząsteczkami alkoholu, zastosowano deuterowane alkohole. Połączenie techniki SIMS oraz deuterowanych cząsteczek pozwoliło zaproponować mechanizm reakcji alkoholi i utlenionej powierzchni aluminium. Mechanizm ten wyjaśnia wpływ alkoholi na tribologiczne zachowanie się warstw wierzchnich współpracujących elementów. Zgodnie z poczynionymi wcześniej obserwacjami wykazano, że mniejszy rozmiar przeszkody sterycznej zwiększa liczbę oddziałujących cząsteczek z utlenioną powierzchnią, a także, że długość łańcucha alkilowego pełni istotną rolę w ochronie powierzchni i tym samym redukcji tarcia. Te dwa kluczowe aspekty można łatwo wytłumaczyć za pomocą zaproponowanych procesów tribochemicznych.