

# Static SIMS studies of fatty alcohols, amines and esters on gold and aluminium–magnesium alloy surfaces

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Static secondary ion mass spectrometry was used to study the chemical reactions and lateral distributions of fatty amines, alcohols and esters spin coated onto gold surfaces and commercial aluminium–magnesium (Al–Mg) alloy surfaces, cleaned using UV–ozone. The aim of this study is to develop an understanding of the interactions of model lubricants with metal surfaces, such as gold and aluminium. This static SIMS study of organic thin films has been able to identify specific reaction products on the aluminium surface for each functional group. This work demonstrates that organic molecules with alcohol, ester and amine functional groups undergo specific chemical reactions with oxidized Al–Mg alloy surfaces. For example, films composed of the fatty alcohol dodecanol were observed to emit monomers, dimers and trimers with discrete distributions. In addition, negative secondary ion mass spectra indicate that a surface carboxylate is formed from the alcohol. The formation of carboxylate reaction products was confirmed by Fourier transform infrared spectroscopy. On Al–Mg alloy surfaces, a direct interaction with the amine and aluminium oxide surface is observed by the detection of a molecular ion that corresponds to the mass of dodecylamine and  $\text{AlO}^-$ , characteristic of aluminium oxide. Ethyl laurate was shown to eliminate the ethyl group, leaving the laurate anion. This study demonstrates the ability of time-of-flight (ToF) SIMS to discriminate and detect chemical reaction products formed between model lubricant molecules and metal surfaces. As a result of this study, the use of ToF-SIMS to identify reaction products of model lubricants can be extended to provide a better understanding of the interactions of lubricants and metal surfaces at high temperatures and pressures that more closely resemble the conditions encountered in industrial rolling processes. Copyright © 2005 John Wiley & Sons, Ltd.

**KEYWORDS:** static SIMS; FTIR; fatty alcohols; carboxylates; aluminium–magnesium alloys

## INTRODUCTION

Fatty organic molecules with head group functionalities, such as amines, esters and alcohols, are known to display varying adsorptive behaviour on metals and metal oxide surfaces. This is dependent on the chemical properties of the substrate and the type of organometallic products formed by surface reactions with each functional group. For example, recent work<sup>1</sup> has used this knowledge in the development of anodized aluminium wire as a microextraction fibre to extract alcohols and petroleum products, selectively, from gaseous samples. The extraction efficiency of anodized aluminium wire, containing an  $\text{Al}_2\text{O}_3$  oxide layer, was much greater for aliphatic alcohols compared with polished aluminum wire having only a small oxide layer present. This indicates that the porosity and thickness of  $\text{Al}_2\text{O}_3$  oxide layers play a key role in the adsorption of fatty organic molecules on the surface of such fibres.

Air-formed oxides on other metals have been employed also as 'sensor surfaces' for straight-chain alcohols and esters found in food aromas.<sup>2</sup> Changes in the relative conductance of the oxide surface, before and after exposure to a specific organic functional group, have resulted in the ability of oxides of tin, tungsten and copper to distinguish between various functional groups. This work provides further evidence for varying degrees of reactivity of long-chain organic molecules, dependent on the functional group and substrate material.

The present work uses imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the lateral distribution and reaction products formed when fatty alcohols, esters and amines are spin coated onto two different substrates. Additional studies were also carried out using Fourier transform infrared (FTIR) spectroscopy to confirm the molecular species observed in the SIMS spectra. Sputter-deposited gold films were used as substrates due to the ability of gold to readily cationize organic molecules in static SIMS, allowing long-chain molecules to be detected easily in high yield with gold atoms attached.<sup>3</sup> Aluminium–magnesium (Al–Mg) alloy substrates were

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also used due to the importance of metal oxide surface interactions with fatty organic molecules in the lubrication of rolled aluminium sheet. The aim of this study is to demonstrate the ability of ToF-SIMS to discriminate and detect specific reaction products between each organic molecule and the metal surface. The use of a rolled Al–Mg alloy substrate in this study provides an initial understanding of the interactions of model lubricants with the rolled aluminium surface. The SIMS results of this study can be extended further to study lubricant films exposed to high temperatures and pressures encountered during industrial rolling processes. This work demonstrates that ToF-SIMS is a powerful and surface-sensitive method allowing the potential to understand better the complex interactions between rolling lubricants and metal surfaces that are part of industrial processes.

## EXPERIMENTAL

Dodecanol ( $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ , 186.34 g mol<sup>-1</sup>, 98%, Sigma-Aldrich), ethyl laurate ( $\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_2\text{H}_5$ , 228.40 g mol<sup>-1</sup>, >99%, Sigma-Aldrich) and dodecylamine ( $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ , 185.36 g mol<sup>-1</sup>, 98%, Sigma-Aldrich) were spin coated from 10 mM solutions in HPLC-grade hexane (>95%, Sigma-Aldrich) onto sputter-deposited, polycrystalline gold films and industrially rolled Al–Mg alloy (~1% Mg) surfaces (Alcan International Limited). Prior to deposition, the alloy surfaces were cleaned by sonication in methylene chloride ( $\text{CH}_2\text{Cl}_2$ , HPLC grade, 99.9%, Sigma), followed by 45 min of UV–ozone treatment. This resulted in surfaces that contain a hydrated/hydroxylated oxide with carbon concentrations at the outermost surface measured to be <20% of the total near-surface composition using x-ray photoelectron spectroscopy (XPS).

Static SIMS was performed using an Ion-ToF ToF-SIMS IV instrument. High-resolution mass spectra of positive and negative secondary ions were obtained using a pulsed 25 keV gallium (<sup>69</sup>Ga) liquid-metal ion source with a beam diameter of 3 μm. The isotopically enriched gallium beam was rastered across a 250 μm<sup>2</sup> area containing the organic adsorbate for 120 s. Using beam currents near 2.5 pA, this corresponds to primary ion dose densities of <10<sup>13</sup> ions cm<sup>-2</sup>, which is effectively below the static limit.<sup>4</sup> Secondary ion images were obtained using a finely focused gallium ion beam with a diameter and spatial resolution of 250 nm. The selected area for image analysis was divided into 256 × 256 pixels, upon which a mass spectrum was recorded at each pixel. The intensity of a selected peak in the mass spectrum is related to the intensity scale on a colour map, with a range of intensities of 0–255, resulting in a secondary ion image. Samples were analysed at a temperature of –100 °C using a liquid-nitrogen-cooled sample stage. One sample was analysed at a temperature of –30 °C, due to experimental difficulties precluding use at lower temperatures.

Experiments on selected samples using FTIR spectroscopy were carried out using a Bruker IFS-55 infrared spectrometer equipped with an MCT detector. An 85° grazing angle accessory was used for the FTIR analysis.

## RESULTS

### Fatty alcohols on gold and Al–Mg alloy surfaces

#### Dodecanol on Al–Mg alloy surfaces

Dodecanol,  $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ , was spin coated from a 10 mM solution in hexane onto a sonicated and UV–ozone-cleaned Al–Mg alloy surface prepared using the cleaning procedure outlined above. Analysis was carried out at a temperature of –30 °C. Positive secondary ion mass spectra (Fig. 1) of the spin-coated film show three peaks attributable to the presence of dodecanol on the Al–Mg alloy surface. The dodecanol molecular ion  $\text{CH}_3(\text{CH}_2)_{11}\text{OH}^+$  is observed near mass 186. Evidence also exists for dimerization and trimerization of the alcohol, arising from peaks whose masses correspond to the ions  $[\text{CH}_3(\text{CH}_2)_{11}\text{OH}]_2\text{H}^+$  (a protonated dodecanol dimer) and  $[\text{CH}_3(\text{CH}_2)_{11}\text{OH}]_3\text{H}^+$  (a protonated dodecanol trimer).

Negative secondary ion mass spectra of the Al–Mg alloy surface coated with dodecanol (Fig. 2) contain a peak that is due to the formation of a carboxylate anion with the formula  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$ . For such a species to be formed from dodecanol, an additional oxygen atom from the aluminium oxide surface would have to be extracted by the alcohol to form the carboxylate. If the carboxylate were due to the presence of lauric acid contamination, one would expect to see characteristic positive ions indicative of lauric acid, however these were absent from the positive secondary ion mass spectrum of the surface spin coated with dodecanol. An additional molecular ion is also present in the negative secondary ion spectrum that corresponds to deprotonated dodecanol, giving rise to the ion  $\text{CH}_3(\text{CH}_2)_{11}\text{O}^-$ . The presence of a carboxylate species on the Al–Mg alloy surface was also confirmed using FTIR spectroscopy. The asymmetric and symmetric stretching vibrations of the laurate are assigned to peaks at 1600 and 1462 cm<sup>-1</sup> (Fig. 3); this is in accord with our previous analyses<sup>5</sup> and by analogy to spectra of absorbed hexadecanoic acid.<sup>6</sup>

Positive secondary ion imaging (Fig. 4) of the dodecanol dimer and trimers indicates that these molecular ions originate discretely from 'island-like' structures that exist between those regions where both the oxide substrate and a covering monolayer are seen. The islands consist of multilayer organics that prevent any secondary ion contributions from the metal substrate. The distribution of the monomer is somewhat more complex; some monomer intensity originates from most of the oxide surface, indicating a very thin layer covering the oxide. In addition, most but not all of the thicker patches of dodecanol give rise to a somewhat stronger monomer signal as well as a dimer signal that is unique to multilayer islands. Negative ion imaging of a separate area on the surface indicates the presence of aluminium oxide ( $\text{AlO}^-$ ) and the carboxylate  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$ , as shown in Fig. 5. This indicates that the formation of the carboxylate occurs on the aluminium oxide surface. The carboxylate distribution also correlates well with the lateral distribution of the deprotonated alcohol, suggesting that deprotonation occurs on the oxide surface. The same dark regions in Fig. 5 are also found in the positive ion images; these are due to multilayer islands of dodecanol.

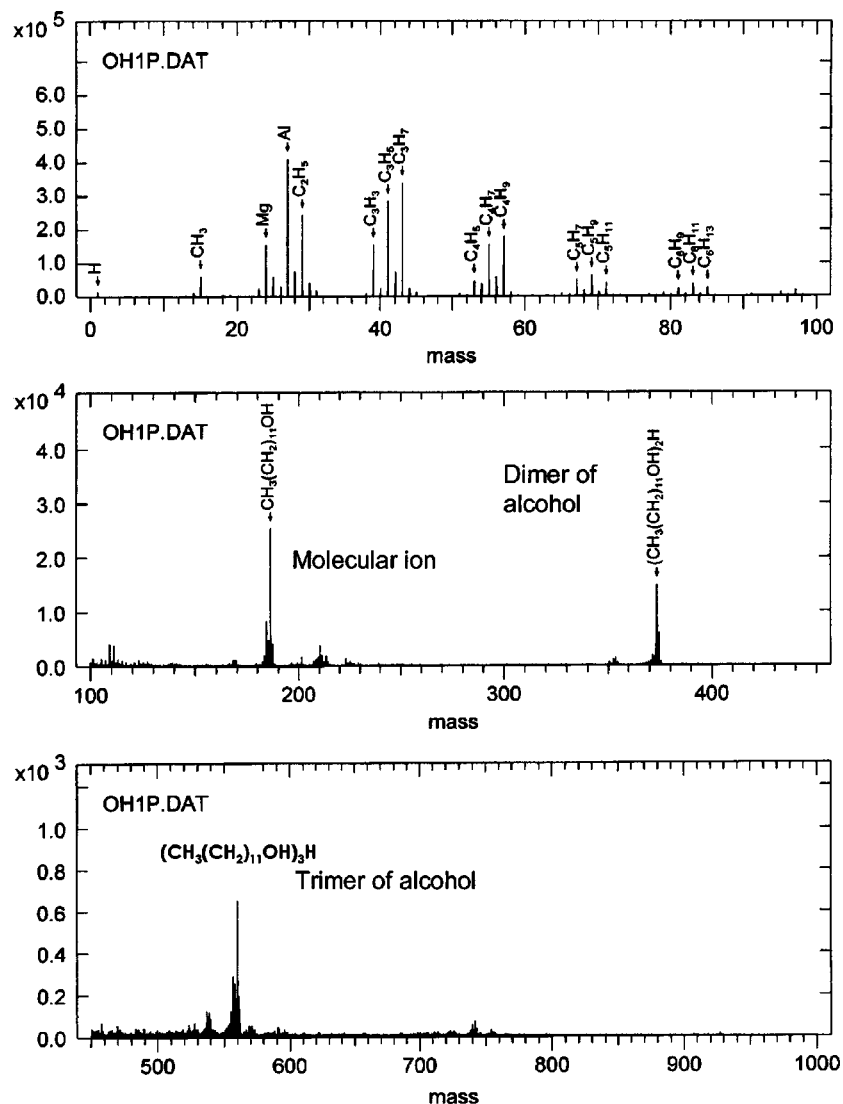


Figure 1. Positive secondary ion mass spectrum of dodecanol on an Al-Mg alloy surface.

In summary, spin coating of a 10 mM solution of dodecanol onto an Al-Mg alloy surface results in the production of multilayer islands of dodecanol that emit positively charged monomers, dimers and trimers. Emission of the monomer molecular ion is observed to occur from island structures *and* from the surrounding alloy surface. Dimer emission occurs exclusively from island shapes, revealing well-defined islands rich in the dimer that could not be seen in the monomer images. On the oxide surface surrounding the islands, deprotonated dodecanol is detected, along with the formation of a carboxylate  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$  anion due to reaction between the alcohol and oxygen atoms present in the oxide of the alloy.

*Dodecanol on gold surfaces*

Dodecanol was also studied as spin-coated films on sputter-deposited gold substrates. Positive secondary ion mass spectra obtained from this surface indicated the presence of secondary ions that were also observed in experiments with the Al-Mg alloy. The dodecanol molecular ion  $\text{CH}_3(\text{CH}_2)_{11}\text{OH}^+$ , along with a protonated dodecanol dimer of formula  $(\text{CH}_3(\text{CH}_2)_{11}\text{OH})_2\text{H}^+$ , were found to be present

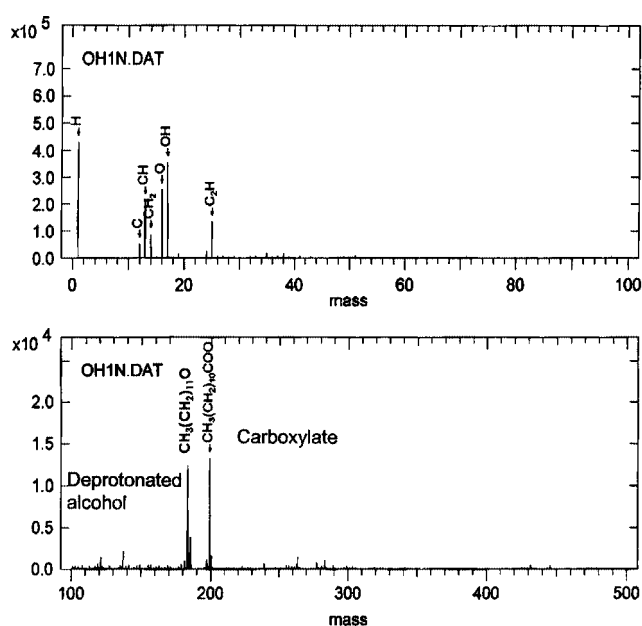
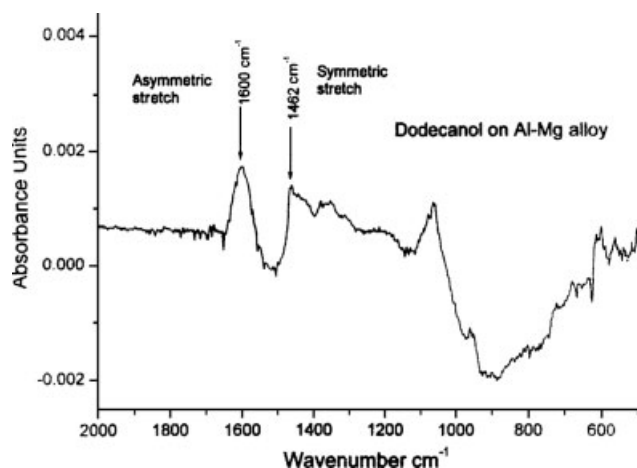
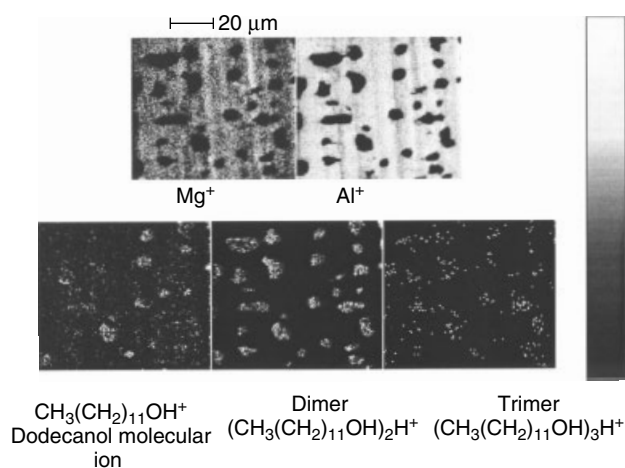


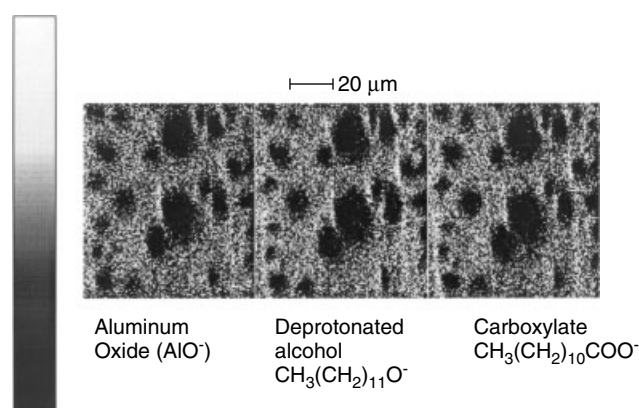
Figure 2. Negative secondary ion mass spectrum of dodecanol spin coated onto an Al-Mg alloy substrate.



**Figure 3.** The FTIR spectrum of dodecanol spin cast onto an Al-Mg alloy substrate.



**Figure 4.** Positive secondary ion images of dodecanol, a fatty alcohol, spin coated onto an Al-Mg alloy substrate.



**Figure 5.** Negative secondary ion images of deprotonated dodecanol and carboxylate formed on Al-Mg alloy substrates. The dark areas are due to multilayer islands of dodecanol.

in positive secondary ion mass spectra (data not shown). New peaks were also observed that involve an interaction of the alcohol with the gold substrate. For example, a peak is observed with a mass that corresponds to the dodecanol molecule with a single gold atom attached ( $C_{12}H_{26}O\text{Au}^+$ ). A

peak also can be found that corresponds to the cationization of dodecanol with two gold atoms; the peak is labelled  $C_{12}H_{26}O\text{Au}_2\text{H}^+$ . A dodecanol dimer cationized by a gold atom is also present, with the formula  $(C_{12}H_{26}O)_2\text{Au}^+$ . An additional peak, labelled  $C_{12}H_{24}O^+$ , is observed two mass units below the dodecanol molecular ion. This is likely to be due to the formation of a carbocation by dehydrogenation.<sup>7</sup>

Negative secondary ion mass spectra (not shown) of the dodecanol film on gold contain a high-intensity peak that corresponds to the formation of a carboxylate species with the formula  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$ . Similarly, a carboxylate dimer with a single gold atom attached,  $(C_{12}H_{23}O_2)_2\text{Au}^-$ , was also present near mass 600. The formation of a carboxylate from dodecanol on gold was initially somewhat surprising. Secondary ion imaging (not shown) of the peak corresponding to the carboxylate  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$  anion indicated that the carboxylate distribution matched the distribution of oxygen ( $\text{O}^-$ ), indicating that the formation of the carboxylate anion from dodecanol occurs on regions that are rich in oxygen and from other oxygen-containing contaminants introduced during the sputter deposition process used to prepare the gold substrates. The formation of the carboxylate on oxygen-rich areas present on the gold surface is consistent with previous observations of the carboxylate, formed by reaction of dodecanol and oxygen incorporated from the oxide on the Al-Mg alloy surface.

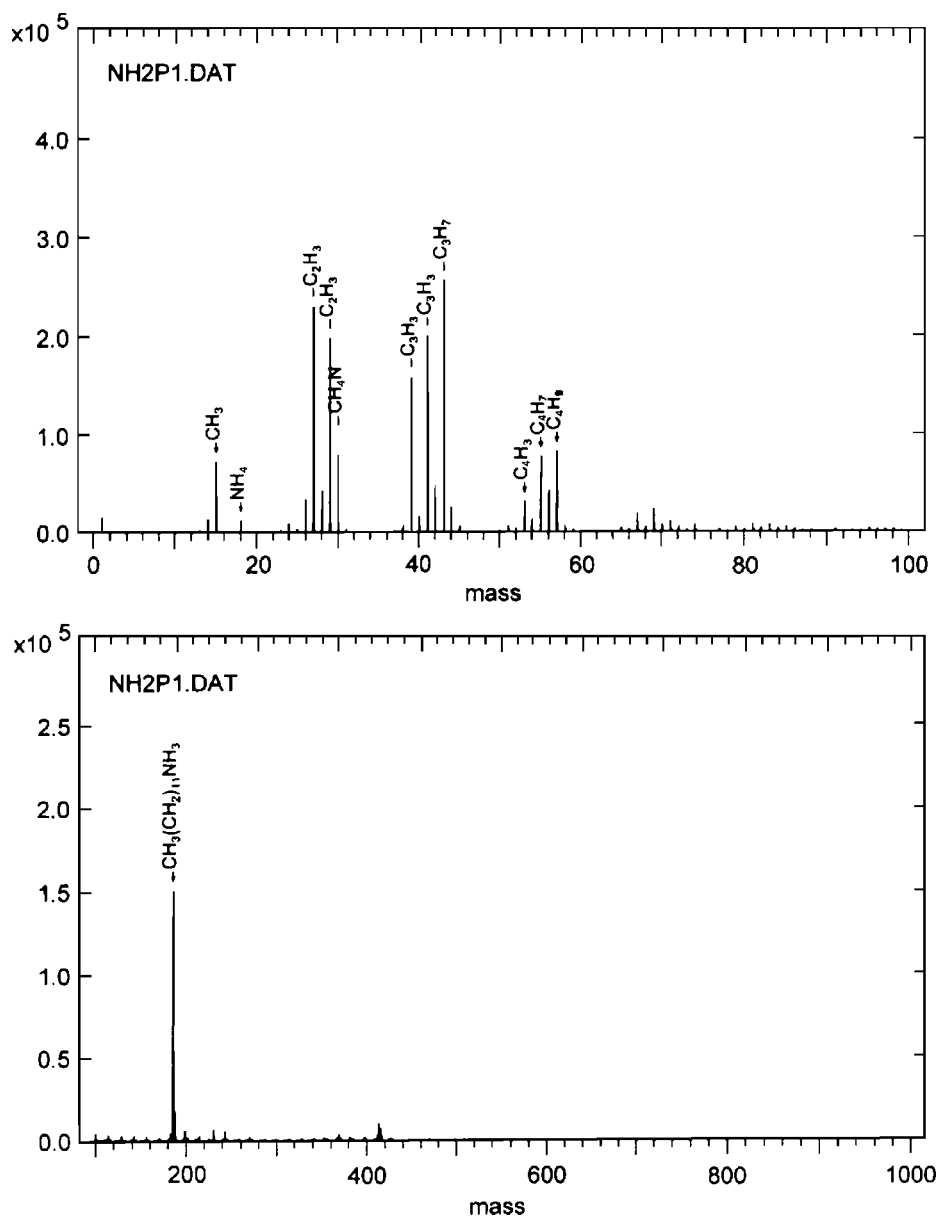
#### Fatty amines: dodecylamine on gold and Al-Mg alloy substrates

Dodecylamine,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ , was spin coated onto gold and cleaned Al-Mg alloy substrates, prepared using the sonication and UV-ozone procedure outlined earlier. Analysis using ToF-SIMS was carried out at a temperature of  $-100^\circ\text{C}$ .

##### *Dodecylamine on Al-Mg alloy substrates*

Positive secondary ion mass spectra of dodecylamine deposited onto the Al-Mg alloy surface (Fig. 6) contain a high-intensity peak with a mass that corresponds to protonated dodecylamine, with the formula  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+$ . Low-molecular-weight fragments, which would indicate the presence of an amine on the surface, can be observed; these fragments are  $\text{NH}_4^+$  and  $\text{CH}_4\text{N}^+$ . Negative secondary ion mass spectra (Fig. 7) taken of the same surface, held at a temperature of  $-100^\circ\text{C}$ , show a negatively charged species with a mass corresponding to the molecular weight of dodecylamine, in addition to  $\text{AlO}^-$ , an aluminium oxide fragment. The formula of this ion is  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{AlO}^-$ . This peak suggests that a bond has formed between the amine and aluminium of the oxide. A second peak of higher mass, attributable to an amine dimer bound to the aluminium oxide, with the formula  $[\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2]_2\text{AlO}^-$ , is also observed.

Secondary ion imaging of the positive ions (data not shown) emitted from the dodecylamine film indicates that protonated dodecylamine  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+$  and the low-molecular-weight fragments  $\text{CH}_4\text{N}^+$  and  $\text{NH}_4^+$  are evenly distributed on the surface, with slight variations appearing due to topographic features of the surface. However, negative molecular ion imaging (Fig. 8) of the above amine bonded to



**Figure 6.** Positive secondary ion mass spectrum of dodecylamine on Al–Mg alloy surfaces.

the aluminium oxide  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{AlO}^-$  shows a patchy distribution on the oxide surface. This ion is emitted from regions where a strong chemical interaction has occurred between the amine and aluminium oxide substrate. A comparison of the ion image with a secondary electron image of the topography of the sample shows that the reaction has occurred preferentially on metallic areas that stand proud of the grooves.

#### *Dodecylamine on gold substrates*

Positive secondary ion mass spectra of dodecylamine spin coated onto gold (data not shown) contain a high-intensity peak due to the protonated dodecylamine molecule  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+$ . This peak was observed also in positive secondary ion mass spectra obtained using the Al–Mg alloy substrate. A peak corresponding to an amine dimer cationized with a single gold atom,  $(\text{C}_{12}\text{H}_{27}\text{N})_2\text{Au}^+$ , is present. Negative secondary ion mass spectra of dodecylamine on gold surfaces contained a prominent peak for dodecylamine

attached to the fragment CNO. This is likely the result of a reaction between the amine and surface impurity species.

In summary, deposition of dodecylamine films on Al–Mg alloy and gold surfaces both resulted in the detection of a protonated amine molecule with the formula  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+$ . Negative secondary ion mass spectra of the amine film contain a peak corresponding to the molecular weight of dodecylamine with an additional fragment attached. In the case of samples prepared on Al–Mg alloy surfaces, peaks were found with masses that corresponded to one and two dodecylamine molecules with an aluminium oxide ( $\text{AlO}^-$ ) fragment attached. This suggests that an interaction occurs between the amine and the metal oxide surface. An adduct of a different nature was observed in spectra on gold surfaces where a single high-mass peak was found corresponding to the mass of dodecylamine with a CNO<sup>-</sup> fragment attached. This suggests an interaction with one or more adsorbed molecules containing this group, as opposed to interaction directly with the gold surface.

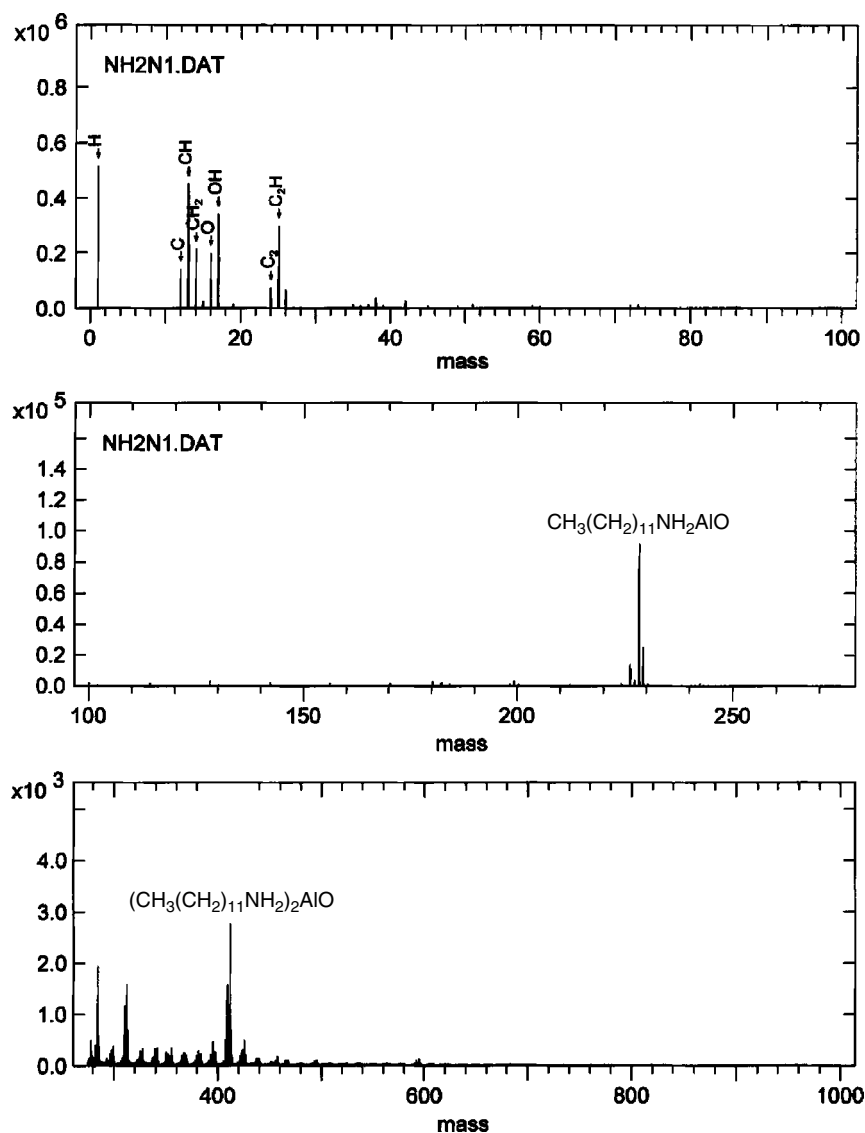


Figure 7. Negative secondary ion mass spectrum of dodecylamine on Al–Mg alloy substrates.

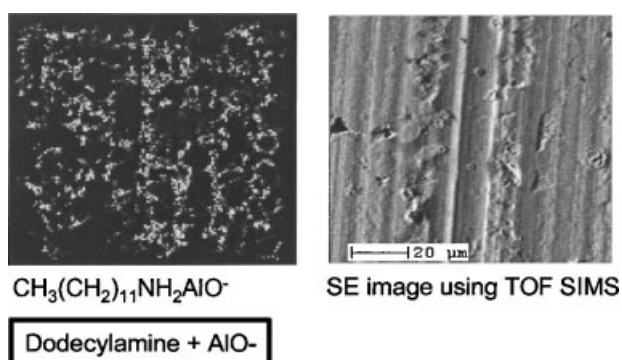


Figure 8. Secondary ion and secondary electron (SE) images depicting the lateral distribution of the dodecylamine–aluminium oxide complex.

### Fatty esters: ethyl laurate on gold and Al–Mg alloy substrates

#### Ethyl laurate on Al–Mg alloy surfaces

Ethyl laurate,  $\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_2\text{H}_5$ , the ethyl ester of lauric acid, was spin coated onto sonicated and UV–ozone-cleaned

Al–Mg alloy surfaces from 10 mm hexane solutions. Owing to its volatility, the sample was cooled to a temperature of  $-100^\circ\text{C}$  before analysis using ToF-SIMS.

Negative secondary ion mass spectra (Fig. 9) indicate that the ethyl group is lost from the ester and the laurate remains. This is indicated by the presence of a peak with a mass corresponding to the formula  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$ . The formation of a carboxylate species ( $\text{COO}^-$ ) on this surface has been confirmed by FTIR spectroscopy (Fig. 10). Peaks due to asymmetric and symmetric stretching<sup>5</sup> of the surface-bonded laurate are present at  $1601\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$ . A peak at  $1711\text{ cm}^{-1}$  indicates the presence of lauric acid.<sup>5</sup>

Positive secondary ion mass spectra (Fig. 11) indicate that a peak with a mass corresponding to the molecular weight of protonated ethyl laurate,  $[\text{M} + \text{H}]^+$ , is present. The mass peak labelled with the formula  $\text{C}_{12}\text{H}_{23}\text{O}^+$  is attributable to the loss of the ethoxy group ( $\text{OC}_2\text{H}_5$ ) from the ester. In addition, a higher mass peak is present that corresponds to the detection of a protonated dimer  $[2\text{M} + \text{H}]^+$  of ethyl laurate. Loss of the ethoxy group was also observed in positive secondary ion mass spectra of ethyl laurate spin coated onto gold substrates.

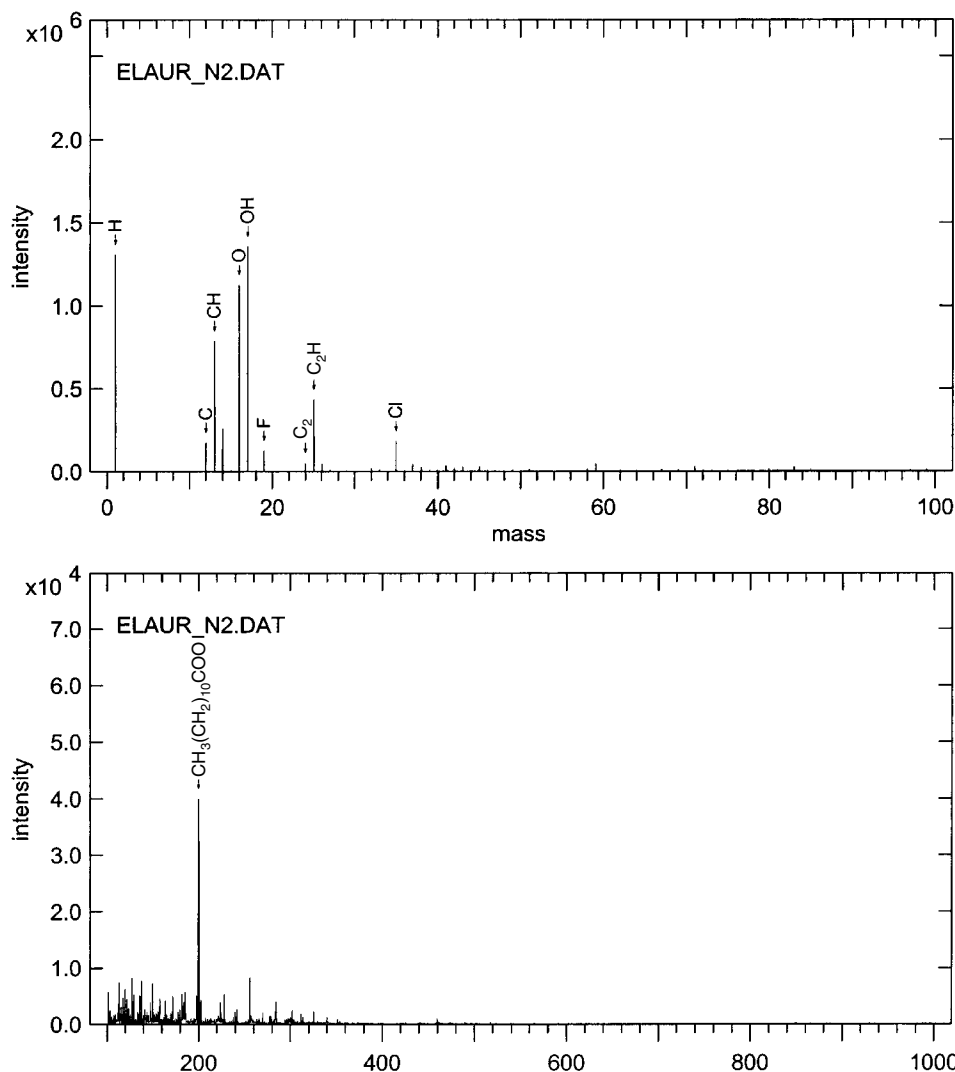


Figure 9. Negative secondary ion mass spectrum of ethyl laurate deposited onto an Al–Mg alloy substrate.

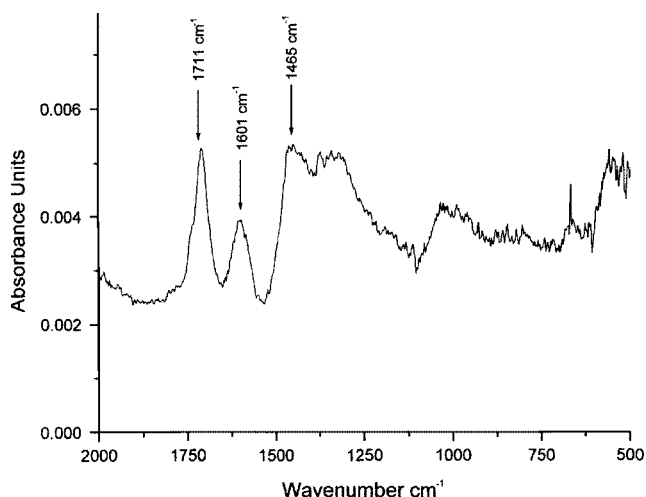


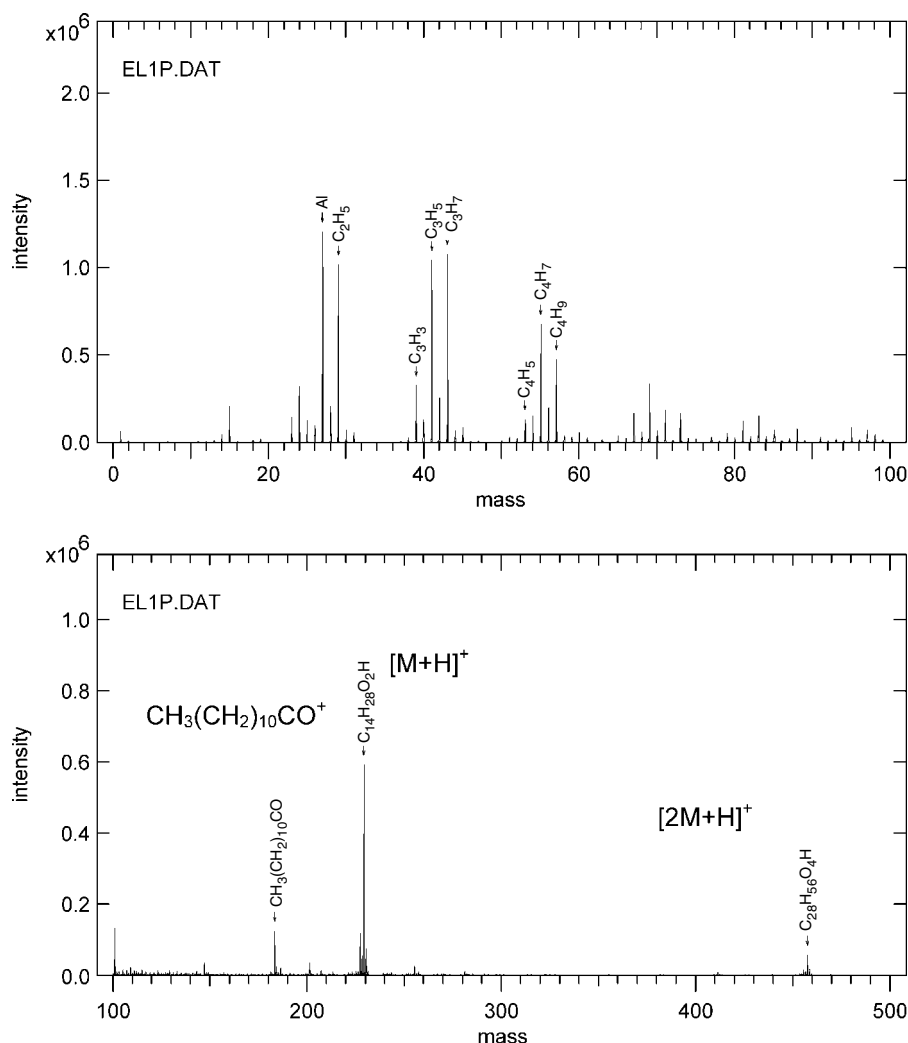
Figure 10. The FTIR spectrum of ethyl laurate spin coated onto an Al–Mg alloy substrate.

Positive secondary ion imaging (Fig. 12) indicates that the distribution of the ethyl laurate molecular ion  $[M + H]^+$  and ester fragment  $C_{12}H_{23}O^+$  correlates with the aluminium image, indicating that the film distribution is uniform across

the imaged area. Negative ion imaging (Fig. 13) of the laurate anion  $CH_3(CH_2)_{10}COO^-$  shows that their distributions correlate well with the aluminium oxide distribution, as indicated by imaging the mass corresponding to  $AlO^-$ . No patchy areas are observed compared with other additives. In summary, deposition of solutions of the ethyl laurate ester onto Al–Mg alloy surfaces and gold substrates indicates that the ester eliminates the ethyl group, leaving the laurate anion  $CH_3(CH_2)_{10}COO^-$ .

## DISCUSSION

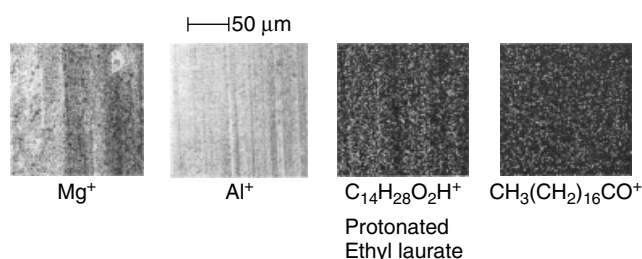
The results of this study demonstrate the ability of ToF-SIMS to detect reaction products formed when long-chain organic molecules interact with gold and Al–Mg alloy surfaces. Reaction products such as carboxylates, complexes with aluminium oxide and the detection of polymeric species such as dimers and trimers were observed in secondary ion mass spectra of these surfaces. The presence of carboxylate species found in negative secondary ion mass spectra was confirmed using FTIR spectroscopy. This indicates that the species detected in the secondary ion mass spectra are due to specific chemical reaction products that are formed on the surface



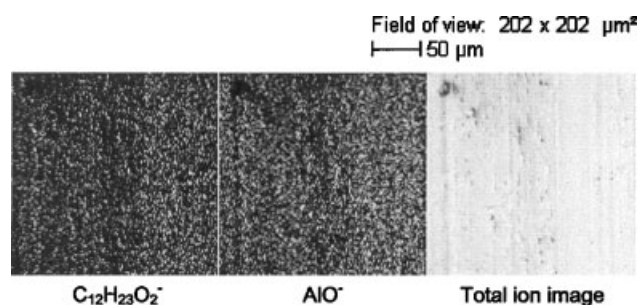
**Figure 11.** Positive secondary ion mass spectrum of ethyl laurate on Al–Mg alloy surfaces.

and are not the result of a general ionization mechanism. If this were the case, similar secondary ions would be detected for each long-chain molecule. The secondary ions detected in mass spectra that are part of this study were unique to the organic molecule studied and the interaction with the substrate material.

Based on the static SIMS studies outlined in this work, deprotonated alcohol is detected on both the Al–Mg alloy and gold surfaces. It is known that the O–H bond of alcohols breaks upon adsorption of the alcohol on metal surfaces, producing an adsorbed alkoxide and surface hydrogen.<sup>8</sup> Following deprotonation, the carbon–oxygen bond of the



**Figure 12.** Positive secondary ion images of ions emitted from an Al–Mg alloy substrate spin coated with ethyl laurate.



**Figure 13.** Negative secondary ion images from Al–Mg alloy surfaces coated with ethyl laurate.

alcohol is retained on metals such as silver, gold and copper.<sup>9</sup>

Noble metals such as gold and silver have been shown to be unreactive towards alcohols unless coadsorbed atomic oxygen is present on the surface. Atomic oxygen acts as a Brønsted base, facilitating O–H bond scission.<sup>10,11</sup> Based on the results in the present work, deprotonation of dodecanol on an Al–Mg alloy surface must occur at metal–oxygen surface sites on the oxide surface. Studies of dodecanol on gold using imaging ToF-SIMS have indicated that secondary ion images of deprotonated dodecanol correlate with areas



known to contain adsorbed oxygen, suggesting that the location of adsorbed oxygen provides an active site for deprotonation of the alcohol.

The reactivity of surface oxygen atoms also has been demonstrated in the present work by the detection of a carboxylate species formed by surface reactions with dodecanol. It is known that lattice oxygens of a metal oxide can be involved in interactions with chemisorbed molecules. Many oxides, such as those of copper and zirconium,<sup>12</sup> are known for their ability to perform selective oxidation reactions. The formation of a carboxylate species ( $\text{RCOO}^-$ ) from an alcohol ( $\text{R-OH}$ ) occurs by oxygen addition to adsorbed dodecanol, not as the oxide  $\text{O}^{2-}$  but in the form of a neutral oxygen atom.<sup>7</sup> Oxidation of an adsorbate such as dodecanol in this manner must be accompanied by reduction of the substrate. This leads to a localized decrease in the oxidation state of metal atoms at the surface; however, these reactions have been proposed to occur on non-reducible substrates.<sup>12</sup> This is likely because the formation of a carboxylate species was observed to occur on localized areas of adsorbed oxygen present on gold substrates used in this work. Secondary ion images of oxygen ( $\text{O}^-$ ) and the carboxylate species correlate with each other, indicating that the carboxylate is formed on these areas.

Both the deprotonated alcohol, or alkoxide ( $\text{R-O}^-$ ), and carboxylate species were readily detected as negative secondary ions. A negative ion lubrication mechanism has been proposed for alcohols to explain the formation of aluminium alkoxides in a lubrication process.<sup>13</sup> The present work has shown that alkoxides are readily formed in the absence of high stresses and temperatures encountered in a lubrication system, and are detected without any metal cations associated with the alkoxide anion. The negative ion lubrication mechanism is based on the emission of low-energy (2–4 keV) electrons from aluminium surfaces that occurs in rolling or cutting processes where the metal is deformed.<sup>14</sup> This further demonstrates that SIMS is a very useful technique to study the surface chemistry of lubricant molecules and metal surfaces.

The action of emitted electrons on adsorbed alcohol molecules has been known to produce negatively charged alkoxide ions ( $\text{R-O}^-$ ) that are proposed to react with positively charged sites on the deformed aluminium surface. The detection of alkoxide in negative secondary ion mass spectra, in the absence of any metal deformation processes, suggests that static SIMS has the potential to examine the lubrication mechanisms of alcohols subjected to the stresses and temperatures encountered during industrial rolling of aluminium sheet.<sup>15</sup>

The interaction of molecules containing amine functional groups with metal oxide surfaces is important in metal manufacturing processes. Amines are used in the metal working industry where such molecules are used in metal surface pretreatment preparations or as lubricants in the rolling of sheet metal.<sup>16</sup> In addition, the adsorption of amine functional groups on metal surfaces has been used as a model system, in particular to study aluminium–organic adhesion in epoxies containing amines that are commonly used in the

fabrication of aluminium components for the aerospace and automotive industry.<sup>17,18</sup>

Frictional studies of amines on aluminium alloys suggest that the lubrication properties are determined by the probable formation of an aluminium–amine complex.<sup>16</sup> Model studies that involve amine-containing epoxy resins in the adhesion of manufactured aluminium alloy components in the aerospace industry indicate that the interaction of the amine with the aluminium oxide surface occurs via the lone pair of the nitrogen atom with the oxide surface.<sup>17,18</sup>

Based on the experimental results in the present work, two distinct molecular ions were detected for dodecylamine spin coated onto Al–Mg alloy substrates. These include the detection of a protonated dodecylamine molecule, with the formula  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+$ , and a negative ion with a mass corresponding to the amine molecule with an aluminium oxide fragment attached,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{AlO}^-$ . The detection of a protonated amine molecule has been observed previously in static SIMS studies of octadecylamine monolayers on silver substrates.<sup>19</sup> The formation of a protonated amine species would indicate that the amine molecule interacts with protons present at surface hydroxyl groups on the oxide. This mechanism has been proposed for earlier studies of ammonia ( $\text{NH}_3$ ) on iron oxides, where surface hydroxyls were determined to be of importance in the reaction mechanism to produce ammonium ( $\text{NH}_4^+$ ) ions on the surface.<sup>20</sup> Protonated dodecylamine was also present on gold surfaces, suggesting that this ion could be formed by proton exchange with gas-phase species inside the spectrometer.

Other detailed studies<sup>21–25</sup> of the adsorption of amines on metal oxides have concluded that bonding of the amine with the metal oxide occurs through the lone-pair electrons of the nitrogen atom with aluminium or magnesium cations present at the oxide surface. In this manner, the lone pair of electrons of the nitrogen atom act as a Lewis base (electron donor) to cations of aluminium or magnesium, which can be considered as Lewis acids (electron acceptors).<sup>21</sup>

It was mentioned previously that a protonated amine molecule was detected. This can be explained using the Brønsted acid/base theory by considering the amine to be classified as a Brønsted base (proton acceptor) that has interacted with Brønsted acid sites on the oxide surface, consisting of hydroxide. Based on these results, two surface sites are used in the reaction of amines with the oxide surface. Protonated amines are reactive with hydroxy- or oxygen-containing sites of the oxide. In addition, the metal cations of the oxide, such as aluminium and magnesium, are known to bond with the amine.<sup>21</sup> Temperature-programmed static SIMS measurements may be useful in distinguishing between these two surface sites, because they are believed to occur by different bonding interactions. In addition, the interaction of amines with aluminium surfaces is important in the determination of acid/base properties of a surface, believed to control adhesion between metal and organic molecules.<sup>26</sup>

In contrast to fatty alcohols and amines, few studies have been published on the interaction of fatty esters with metal and metal oxide surfaces. Recent studies have focused

on the interaction between the ester functional group and sputter-deposited metal atoms, such as aluminium and chromium.<sup>27,28</sup> Both of these studies provided evidence for the formation of complexes between metal atoms and the ester functional group. In both cases, it has been suggested that the ester molecule remains intact with the attachment of metal atoms to the carbonyl group. Lubrication mechanisms of fatty ester molecules have indicated that esters can react chemically with oxide surfaces to form a metal carboxylate, under the stresses and temperatures encountered in an industrial rolling mill.<sup>29</sup> In the present work, decomposition of the ester has been observed due to the detection of the laurate anion  $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$  on both gold and Al–Mg alloy surfaces, in the absence of high temperatures and pressures that would occur in a lubrication system. Analysis of these layers using static SIMS did not result in the emission of any aluminium or magnesium soaps from the film of the ester.

## CONCLUSIONS

This work has demonstrated the ability of ToF-SIMS to detect reaction products between organic molecules and metal substrates. More importantly, this study outlines the reaction products formed in the interaction of model lubricant molecules that contain alcohol, amine and ester functional groups with rolled Al–Mg alloy surfaces. This work can be extended to study additional systems where thin films of lubricant molecules are exposed to high temperatures and pressures that more closely resemble those encountered in industrial rolling processes. The reaction products for each molecule are outlined below:

- (1) Dodecanol (a fatty alcohol) when spin coated onto Al–Mg alloy substrates results in the formation of regions that emit positively charged dimers, trimers and often monomers, with discrete distributions. A carboxylate species is also formed due to a reaction between the alcohol and oxygen atoms present in the oxide of the alloy. Regions on gold substrates that contain oxygen are observed. This results in the emission of carboxylate anions from these areas due to reaction of dodecanol with adsorbed oxygen on the gold surface.
- (2) On both gold and Al–Mg alloy surfaces, protonation of dodecylamine occurs. In addition, negative secondary ion mass spectra of the amine on both substrates display a peak with a mass that corresponds to the molecular

weight of dodecylamine with an additional fragment attached. On Al–Mg alloy surfaces, dodecylamine interacts with aluminium on the metal oxide surface. Amines interact with adsorbed species on the gold surface.

- (3) Surface reactions of ethyl laurate, a fatty ester, indicate that the ester decomposes on both gold and Al–Mg alloy surfaces to form the carboxylate species.

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