Application of ToF-SIMS surface analysis to tribochemistry in metal forming processes

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Abstract

Tribochemical properties are an essential component of the efficiency of metal forming lubricants. Their understanding, a basis for the selection of adequate additives, heavily relies on surface analytical techniques. In the last ten years, we have applied time-of-flight secondary ion mass spectroscopy (ToF-SIMS) to the analysis of the reactions of strip surfaces with typical additives of cold strip rolling and deep drawing lubricants. Data analysis procedures have been evolved to perform semi-quantitative comparisons. Analytical results performed on laboratory simulation tests and on real-size processes are compared. Examples of competition and synergies between different additives in a single lubricant are described.

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1. Introduction

Tribochemistry is the phenomenon which governs boundary lubrication, involving chemical reactions between the additives of the lubricant and the surfaces. It is now recognized that these reactions do not constitute a special chemistry, they are simply characteristic of the temperature and pressure conditions prevailing in the contact in the presence of the reactive metal or oxide surfaces.

The reactions are however extremely complex and difficult to predict in detail, due to the large number – and often poor purity – of the reactants. Formulation of lubricants for boundary lubrication thus remains an art as much as a science. An enormous literature has been devoted to testing of new potential additives, which is still going on under the pressure of environmental regulations. Based on more and more powerful surface analytical techniques, and more recently nano-mechanical measurements, innumerable papers study the mechanisms and the products of the reactions: ZDDP’s (Zinc di-alkyl-dithiophosphates) form thick films of complex organo-metallic polyphosphates [1–5], chlorinated additives result in iron chlorides [6], sulphur-containing additives result in iron sulphides [7,8], whereas fatty acids form soaps on metallic surfaces [9]. Studies of multi-additivated lubricants have more recently disclosed interactions and synergies [10,11]. Finally, molecular simulation begins to be used to interpret analytical results [12].

Its high sensitivity and mass and space resolution, together with its capacity to extract large fragment ions, made time-of-flight secondary ion mass spectroscopy (ToF-SIMS) a promising candidate for tribochemical studies [13,14]. In 1994, we have started to apply this then recent analytical
technique to boundary lubrication in metal forming. This required the development of specific data analysis techniques to extract useful information from the huge number of peaks present in the mass spectra [15,16]. This methodological effort is described in the following, together with some tribochemical results.

2. Experimental equipment and procedures

2.1. ToF-SIMS analysis

2.1.1. Principle
Static ToF-SIMS consists of bombarding the surface to be analyzed with a pulsed ion beam. In the centre of the beam impact, the organic matter present on the surface is sputtered and emitted as low mass ions; but in the periphery, the process is described as a “desorption” giving birth to large fragment ions, from which the species present on the surface may be rather easily reconstructed. The detection threshold is the very first molecular layer is concerned. The secondary ions are accelerated and detected. The measurement of their time of flight from the surface sample to the detector (thanks to the pulsed beam) provides very high mass resolution. It can work in a global way, averaging over a chosen area (typically 120 μm × 120 μm) – low spatial resolution but excellent m/Δm. The global analysis is systematically used in the following. However, the amount of information is still enormous and has to be lumped to be usable. To do this, the following procedure has been evolved [15,16]:

- All the potentially present species (base oil, additives) have to be analyzed separately to build a list of characteristic peaks. These analyses are performed on the substrates of interest (Al, steel strips,…) and on non-reactive, reference substrates as well (Si wafers or gold surfaces) for comparison. On occasion, model substrates are used (e.g. a high purity zinc strip for galvanized steel, alumina for aluminium strips,…).
- To obtain chemical information on reaction products of additives at the surface of the strip, it is necessary to remove oil base in excess with hexane.
- In the complex spectra, the respective reactivity of the different additives are compared by forming ratios of the sums of the number of ions characteristic of each species.

2.1.2. Apparatus

The analyses described below have been performed on a Charles-Evans TRIFT I Apparatus (now Physical Electronix). The beam has the following characteristics: Ga⁺ ions, energy 15 keV, DC intensity 0.5 nA, bunched pulse width 1 ns, 12 kHz. Spectra acquired on our rough industrial samples have a typical mass resolution m/Δm = 4000 and a mass range of [1, 1000] amu.

2.1.3. Analytical procedure
Results are obtained as complex spectra (e.g. see Fig. 2). The technique can be used in the imaging mode, with a maximal lateral resolution of 0.2 μm; then each pixel contains such a spectrum, but with poor mass resolution. Or it can work in a global way, averaging over a chosen area (typically 120 μm × 120 μm) – low spatial resolution but excellent m/Δm. The global analysis is systematically used in the following. However, the amount of information is still enormous and has to be lumped to be usable. To do this, the following procedure has been evolved [15,16]:

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2.2. Materials

Experiments have been performed on the following alloys (strips):
- IF-Ti ultra-low carbon steel: 20 mm wide, 0.6 mm thick; Ra = 1.0 μm
- AAS182 (4.5% Mg): 30 mm wide, 0.65 mm thick; Ra = 0.5 μm
- Zinc: 98.8% purity, 10 mm wide, 1 mm thick, Ra = 1.0 μm
- Galvanized steel: 30 mm wide, 0.66 mm thick, 13 μm thick Zn coating, Ra = 1.3 μm

The lubricants used in the present studies are models of typical carbon steel or aluminium strip rolling or deep drawing oils. In these industries, the nature and percentage of the additives used strongly depends on the metal to be formed. Major constraints include moderate friction (but not too low, otherwise rolling becomes unstable); strip cleanliness, i.e. ease of degreasing and/or absence of carbon residues after annealing at high temperature; and of course, low toxicity, and low cost – because of high consumption.

Thus, carbon steels are deformed with mineral oils blended with generally heavy esters, fatty acids and extreme-pressure additives (mostly S-containing ones). Synthetic esters are replacing natural fats mainly in view of strip cleanliness; here, glycerol tri-oleate (GTO in the following)
2.3. Mechanical processing of strips

Analyses are performed after different treatments:

- purely chemical reaction, dipping a strip into a temperature-controlled lubricant bath for a given duration
- mechanical activation (manual scratching of the strip in the bath with a sharp tool, Fig. 1).
- plastic deformation, either in a laboratory simulation test, or by strip rolling (Fig. 1).

2.3.1. Plane strip drawing test

The strip (30 mm wide) is pressed by an hydraulic press between two flat WC-Co tools (10 mm in the drawing direction; \( R_a = 0.7 \mu m \)). The normal force \( F_n \) is measured by a 4-strain-gauge transducer; it is ramped to induce an increasing nominal pressure, from 0 MPa at the beginning of the strip to 60 MPa at its end. The rig is equipped with an alignment system to ensure homogeneous pressure, checked before the test using pressure paper (Fuji Prescale Film HS). The drawing force \( F_t \) is also continuously recorded; the drawing velocity is \( 1.7 \times 10^{-3} \) m/s. The applied pressure is designed not to produce any bulk plastic deformation; only superficial microplasticity occurs, so that the friction coefficient is obtained by:

\[
\mu = \frac{F_t}{2F_p}
\]  

2.3.2. Plane strain compression test (PSCT)

The strip thickness is reduced between two flat anvils by an hydraulic press. The force is imposed and the resulting thickness reduction is measured afterwards using a caliper (±1 μm). The friction factor \( \bar{m} \) is deduced using [17]:

\[
F = aL\frac{2\sigma_0}{\sqrt{3}} \left( 1 + \frac{\bar{m} a}{h} \right) \frac{\sigma_0 (\bar{\varepsilon})}{h} \]  

\( \sigma_0 (\bar{\varepsilon}) \) is the strain-hardening curve, the plastic strain is given by \( \bar{\varepsilon} = \frac{2}{\sqrt{3}} \ln \left( \frac{h_{\text{ini}}}{h} \right) \). \( L = 20 \) mm \( \gg a = 5 \) mm \( \gg h = 0.6 \) mm ensures quasi-plane strain deformation. The tests can be performed above room temperature, in which case the heat is provided by resistances inserted in the punch-holders. The strip is heated by contact with the punch under a small contact force for a few minutes before each test; the contact temperature is checked with a portable thermocouple.
2.3.3. Rolling

The strip has been rolled on our experimental, high-speed (20 m s⁻¹), non-reversing rolling mill equipped with front and back tension systems [18]. IF-Ti strips 20 mm wide, 0.6 mm thick have been used, initial $Ra = 1.0 \mu m$. Rolls are 95 mm in diameter, 100 mm in barrel length. Front and back tensions were respectively set to 55 and 85 MPa. The reduction was 40%; the rolling velocity has been varied between 1 m s⁻¹ and the maximum allowed by the mill power (120 N m per roll); the velocity reached is thus all the higher as friction is low.

3. Fatty acid reactivity on metals and on oxides

3.1. Comparison of Fe and Al

Metals such as Fe and Al have different reactivity towards additives [19]. This is exemplified here using stearic acid (a 1% solution in a paraffinic oil). After dipping the strip in the lubricant bath and scratching, ToF-SIMS analysis displays mono-, di- and tri-stearates everywhere on the iron strip (Fig. 2): no significant difference in reactivity is observed between the naked metal (in the scratch) and the undeformed oxide (outside the scratch).

On the contrary, Al and Mg stearates are detected only in the scratch (naked metal) of the AA 5182 strip (Fig. 3): alumina is not reactive towards stearic acid. This difference is essential to the boundary lubrication phenomena.

3.2. Reaction products concentration profiles

Contact conditions are not necessarily homogeneous in a large contact area, especially for a forging-like deformation process as PSCT. It is well known that an oil pocket is trapped in the centre of the contact, leaving the periphery in boundary contact [20]. Chemical consequences may be expected and have indeed been detected [21]. ToF-SIMS analyses of a PSCT indentation are detailed here, Fig. 4 on the punch and Fig. 5 on the strip. The spatial evolution of normalized intensities shows a lot of Al on the punch at the periphery of the contact (transfer film testifying for boundary lubrication [17]), whereas the centre shows almost pure iron (protected by the trapped oil film). On the strip surface, aluminium stearates are found at the periphery, which shows that the oxide layer has been broken there, giving way to reactive, naked metal. In the centre, the oil film has protected the oxide and reaction with stearic acid remained at a minimum.

![Fig. 2. ToF-SIMS mass spectra (negative ions) from steel strip surfaces scratched in a bath of paraffinic oil + 1% stearic acid. Fe stearates are detected on both scratched and non-scratched areas. Horizontal axis: ion mass (amu). Vertical axis: number of ions counted.](image)

![Fig. 3. ToF-SIMS spectra (negative ions) from 5182 Al-Mg alloy strip surfaces scratched in a bath of paraffinic oil + 1% stearic acid at 20 °C. Al and Mg stearates are detected only on scratched (naked Al) areas.](image)
of aluminium (in Al$_2$O$_3$ form) at the extreme outer surface of the Zn layer (a few nm thick). Al is added in the galvanization bath to form Fe–Al interlayers, preventing the formation of brittle Fe–Zn intermetallics. Variable Al$_2$O$_3$ coverage can be found [22,23].

We have shown [24] that Zn presents the same kind of reactivity towards fatty acids (here oleic acid) as Fe: both oxide and naked metal react significantly (Fig. 6), in particular by the formation of tri-oleates which we believe witness for rather thick soap layers. On the contrary, for Al again, the reactivity on naked metal is found much larger than on oxide; the behaviours of Al and Zn are even more contrasted at higher temperatures (Fig. 6).

On galvanized strips (Fig. 7), a similar phenomenon is found [24]: those strips having more Al$_2$O$_3$ at their surface (strip A) form less Zn soaps after the plane strip drawing test, due to their high coverage by the non-reacting alumina, as compared to less “polluted” Zn layers. The main difference is the absence of the 908-amu peak of zinc tri-oleate.

4. Competition and synergy

In the following section, the case of multi-additive lubricants is addressed and interaction between two additives are examined. The context is steel strip rolling. The full lubricant is composed of a paraffinic oil (HB, viscosity $20 \times 10^{-3}$ Pa s at 40°C), stearic acid (AS, 1%), another oiliness additive, glycerol tri-oleate (GTO, 10%), a sulphur-containing additive, di-terti-1-dodecyl-penta-sulphide (DTDP, 3%, i.e. 1 wt.% S), and a phosphate additive, tri-cresyl-phosphate (TCP, 3%); the latter is not detailed here. Tests have been performed with partially formulated versions of this lubricant; analyses have been made after strip dipping, PSCT and rolling. Some of the results are described hereafter [16,25,26].

4.1. Competition between stearic acid and glycerol tri-oleate (GTO) on Fe/FeO$_x$

The competition between stearic acid and GTO is studied first, by dipping in an oil bath. At 50°C, stearic acid
ToF-SIMS peaks are found to dominate (see the relative intensities in Fig. 8, left); it is impossible to conclude on coverage rates, since the emission yields may be different. What is conclusive however is the evolution when the oil bath temperature is 150 °C: the GTO peaks are now dominating (left-centre). Several other tests have been included, where dipping started at 50 °C, then temperature was raised to 150 °C. The two cases on the right show how GTO replaces stearic acid on the surface when the time at 150 °C increases. Note that quite a long time is necessary for the substitution.

To what extent may strip dipping be considered representative of metal forming? Rolling experiments have been performed with the dual lubricant (this time, GTO concentration is 10%, as in the fully formulated lubricant). As rolling speed increases, so does the strip surface temperature; and ToF-SIMS shows that at higher speeds, the peaks characteristic of stearic acid (e.g. C\textsubscript{18}H\textsubscript{35}OFe) are replaced by those of GTO (C\textsubscript{18}H\textsubscript{33}O, C\textsubscript{39}H\textsubscript{71}O\textsubscript{4}) (Fig. 9), an effect qualitatively similar to the purely chemical reaction described above.

Fig. 7. ToF-SIMS spectra from galvanized steel strips after plane strip drawing with an oil containing 1% oleic acid. The strip possessing less Al\textsubscript{2}O\textsubscript{3} on its surface (B) shows greater reactivity with oleic acid (in particular proved by the presence of trioleates).

Fig. 8. Relative ion intensities from steel strips after dipping in a warm bath of hexadecane + 1% AS + 1% GTO. At higher temperatures, ions characteristic of GTO (namely, oleyl ion and Fe oleates) replace those characteristic of AS (stearyl ion and Fe stearates). The two cases on the right represent initial adsorption at 50 °C followed by heating to 150 °C before analysis: if a stearic acid layer has been formed (at 50 °C), it takes quite some time at 150 °C for the replacement by oleic acid to occur.

Fig. 9. ToF-SIMS spectra from steel strips after rolling at different rolling speeds with a paraffinic oil + 1% stearic acid + 10% GTO. On the right, close-up on the 300–380 amu range, for the lowest and highest speeds. GTO characteristic ions (lettered in black) replace stearic ions (in grey) at higher rolling speeds, i.e. higher surface temperatures.
4.2. Synergy between sulphur additives and oiliness additives on Fe/FeOx

The question of the necessity of S- or P-containing extreme-pressure additives is often raised in metal forming. Here, the association of a S-additive and a fatty acid is tested. First, strip-dipping is used at various temperatures. Fig. 10 compares ToF-SIMS relative intensities; at all temperatures, the stearic acid molecular ion is more abundant in the presence of the sulphur additive. In particular, its desorption at \( T > 150 \, ^{\circ}C \) is cancelled. This has been attributed to the higher adsorption enthalpy of stearic acid on FeS than on Fe2O3 [27].

The tribological consequences have been examined by PSCT. Fig. 11 compares friction factors measured with the base oil alone (HB), HB + stearic acid (AS), HB + DTDP, HB + AS + DTDP, at diverse temperatures. At room temperature, stearic acid is found to be a much better friction-limiter than DTDP, as expected. However, alone, it cannot withstand temperatures of 100 °C or above. Associated with the S-containing additive, it is able indeed to maintain moderate friction up to 150 °C, similar to the conclusions from the strip dipping test.

4.3. Correlation with strip rolling tests

Finally, PSCT itself is only an approximation of rolling, so that the work has to be completed with rolling experiments (Fig. 12). Here, tests are performed at increasing speed under a constant reduction (40%). Displayed are [16,25]:

- friction coefficients \( \mu \), deduced by inverting a 2D, FEM/slab method coupled strip rolling model.
- strip exit temperatures estimated with a thermocouple on the coiled strip at the end of the test.
- relative intensities in ToF-SIMS, measured on coupons of steel carefully taken from the rolled strips.

With only stearic acid, friction increases above 5 m s\(^{-1}\); then at 10 m s\(^{-1}\), it reaches so high values that the rolling mill power is insufficient, and the test stops. DTDP alone gives a slightly higher friction at low speeds (i.e. moderate strip surface temperature), but rolling remains possible up to 12 m s\(^{-1}\). The lubricant with both stearic acid and DTDP shows constantly decreasing friction and the highest rolling...
speeds can be reached. Note that the measured strip temperatures increase in the order DTDP + stearic acid, DTDP, stearic acid. Finally, in ToF-SIMS spectra, the ion intensity of stearic acid is highest in the presence of DTDP, which connects these results with the above-mentioned ones. It is concluded that the same chemical effects are present in rolling, by which the reaction of DTDP with the strip surface gives a FeS layer (detected also) on which adsorption of stearic acid is more durable at high temperature. This prevents galling observed in the absence of the sulphur additive (see the micrographs at the bottom of Fig. 12).

Note that part of the effects observed (in particular the decrease of friction when speed increases) is certainly connected with hydrodynamic effects; it is well known that rolling is best performed under a mixed lubrication regime. However, it seems clear here that in the absence of an efficient additive package, friction is high, implying increased temperature, decreased oil viscosity, film failure and seizure, starting at velocities too low to promote sufficient hydrodynamic effects. The presence of a sulphur-containing additive makes polar additives more temperature-resistant, allowing the boundary films to be preserved at higher speeds where hydrodynamic effects take over and in turn protect the boundary films. It can thus be concluded that the synergy between extreme-pressure and polar additives exists and promotes a kind of synergy between boundary and HD films.

5. Conclusion and perspectives

The sensitivity and resolution of ToF-SIMS have proved invaluable to detect and analyse the very thin tribochemical films found in metal forming. Its imaging capacity has not been exploited yet, mainly because emissivity artefacts induced by roughness, to be expected on engineering surfaces, would make dubious the distinction between plateaus and valleys, e.g. The main difficulty lies in the non-quantitative nature of the analysis, which leaves us with relative, comparative elements for discussion, with rarely clear-cut conclusions. Probably, for cleaner surfaces, calibration with well-controlled sub-monolayer films (Self-Assembled Monolayers, Langmuir-Blodgett) could help; but nothing suggests that calibration curves obtained on such ideal systems could be easily transposed to our real surfaces. This difficulty also makes coupling with other techniques necessary; in this respect, XPS is ideal since it combines precise quantification with more-than-elemental analytical capability; such coupling has been widely applied in our
laboratory to adhesive bonding [28] as well as to tribochemistry. But theoretical approaches such as molecular dynamics [12,29] would also certainly show high complementarity to ToF-SIMS.

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