A combinatorial approach to elucidating tribochemical mechanisms

Michael Eglin[a,*], Antonella Rossi[a,b] and Nicholas D. Spencer[a]

[a]*Laboratory for Surface Science and Technology, Department of Materials, Swiss Federal Institute of Technology, ETH Zürich, CH-8092 Zürich, Switzerland*

[b]*Department of Inorganic and Analytical Chemistry, University of Cagliari, INSTM, Cagliari, Italy*

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A new type of combinatorial tribological experiment is presented, which explores a series of tribological conditions, such as load and relative velocity, spatially separated as a "library" on one single sample. As an example, a library displaying the results of tribological testing of an additive under a series of different loads has been prepared and analyzed. The tribological information acquired during the testing has been correlated with spectroscopic information from the tribologically stressed surface. The use of imaging and small-area X-ray photoelectron spectroscopy has allowed the identification of the different tribologically stressed areas and the acquisition of detailed spectroscopic information. The composition and the thickness of the tribofilm were found to be dependent on the applied load. The use of the combinatorial approach shows the potential to greatly facilitate rapid characterization of new lubricant additives.

KEY WORDS: tribochemistry, boundary lubrication, combinatorial tribochemistry

1. Introduction

The combinatorial synthetic approach, together with high-throughput screening of compounds, has been applied in pharmaceutical chemistry since the early eighties. A large number of molecules are synthesized in parallel and subsequently probed for chemical, physical and medicinal properties. This approach was first brought into materials science in the field of high-temperature superconductors [1], where a spatially addressable library of potential candidates for high-T_c was fabricated and tested and it has been adapted to different fields in materials science, such as semiconductors [2] or metallurgy [3]. The advantage of the combinatorial synthetic approach in both chemistry and materials science is the rapid production of many substances of varying compositions which are subsequently analyzed in a massively parallel way. This methodology speeds up the search for new substances with the desired properties.

In tribology, and especially in tribochemistry, one has to deal with a large parameter space, since the friction, wear and tribochemical reactions of a given tribological system have been shown to depend strongly on the applied conditions (e.g. relative velocity, contact pressure, sliding time, temperature) [4]. To understand the reactions that can occur in this system it is necessary to explore a significant portion of the parameter space. To date, this has been a very time-consuming process, involving an enormous number of experiments, suggesting that a variant of the combinatorial analytical approach could also be useful in a tribological context.

A wide variety of surface-analytical methods has been used to investigate tribochemical reaction products. X-ray photoelectron spectroscopy (XPS), scanning Auger microscopy (SAM), time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and X-ray absorption near-edge structure (XANES) are frequently used methods for the chemical characterization of tribochemical reaction films. Most of these methods can combine imaging and spectroscopy. While scanning Auger electron microscopy (SAM) has been used to map elemental distribution of a contact area [5], the use of imaging XPS (i-XPS) has been shown recently to be of value in investigating the distribution of chemical species according to their chemical state [6,7]. So far, the imaging possibilities of these methods were used on relatively simple systems, allowing the contact and non-contact regions to be distinguished. By carrying out a combinatorial experiment, one can take further advantage of the imaging capability. In this type of experiment a parameter library is built, applying various tribological conditions (as a function of the lateral position on the disk) on a single sample, which is subsequently analyzed by an imaging surface analytical technique. The tribological information (coefficient of friction, wear) and the spectroscopic results can afterwards be mapped onto the parameter library (see figure 1). The correlation of this data should provide insight into the application range of a lubricant additive system and help uncover mechanistic reaction pathways.

Only a very little work has been done applying a combinatorial approach to tribological problems. Green

* To whom correspondence should be addressed. E-mail: michael.eglin@mat.ethz.ch

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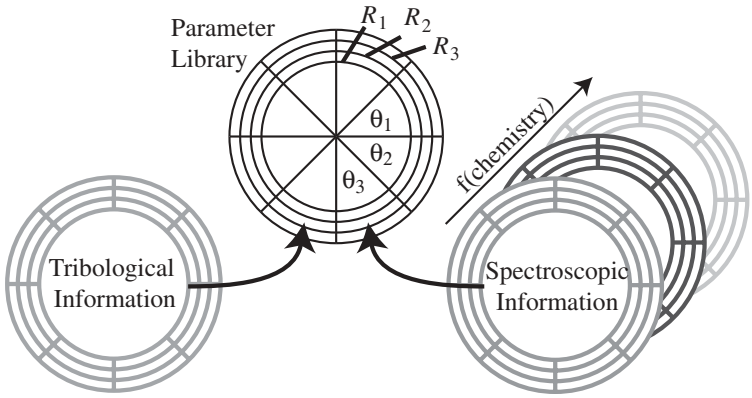

Figure 1. General principle of the combinatorial approach: a parameter library is produced by varying the tribological stress on a single sample depending on the lateral e.g. radial (R) and angular (θ) position on the disk. The tribological information acquired during or after the test (coefficient of friction, wear) and the spectroscopic information (chemistry of surface film) from surface-analytical examination of the sample can then be mapped onto this parameter library and correlated.

and Lee used an AFM with chemically patterned cantilevers and tip arrays to probe adhesive forces between carboxylic acid, alcohol and methyl groups [8]. This approach reveals tribological information on the nanometer scale, whereas the tribological load scanner introduced by Hogmark uses a macroscopic, crossed-cylinder configuration [9]. In the latter setup, two elongated cylinders repeatedly slide across each other with varying load in such a manner that each point along the sliding track of both cylinders experiences a unique load. This test was used in the evaluation of hard coatings.

A model system (di-isopropyl zinc dithiophosphate (i-ZnDTP) in decane) has been chosen as a lubricant-additive system in the present study for two reasons: firstly, the tribological system was to be kept as well-defined as possible for the first experiments with this new approach, and secondly because ZnDTP is a well-studied system, which readily allows comparison of our own results with the literature. The formation of tribofilms from ZnDTP has been studied extensively and has been described by several authors [4,10–12].

2. Experimental

Steel disks (AISI 52100) were polished to a final surface roughness (R_a) below 10 nm using silicon carbide paper and diamond paste. The samples were ultrasonically cleaned in ethanol and analyzed for surface contamination by XPS immediately prior to tribotesting. Commercial 4 mm ball-bearings (AISI 52100) were used as a counter-face.

A 1 wt.% solution of di-isopropyl zinc dithiophosphate (i-ZnDTP) in decane was used as a lubricant. To dissolve the additive in the solvent, the solution was stirred at 60 °C for 30 min. The tribotests were carried out at room temperature (24 ± 0.5 °C) and the relative humidity of the air was recorded during each test and found to be always between 22 and 38%. The sample was fully immersed in the lubricant during testing. A CETR 2 tribometer (Center for Tribology, Inc., Campbell, CA, USA) was used to run the tests using a ball-on-disk geometry. This tribometer allows the independent programming of normal load, velocity, radius and duration. Prior to the actual tests, running-in of the ball was performed at 5 N load with a speed of 31.4 mm/min for 2 h, outside the region to be used for XPS analysis and in the presence of the test lubricant. The running-in was performed in order to create a flat spot on the bottom of the ball. This flat spot was then placed in contact with the surface for the subsequent runs and defined the apparent contact area.

In figure 2, a schematic of the combinatorial tribotest is presented. The experiment consisted of producing five concentric tribologically stressed annuli on a single sample; in all cases a speed of 31.4 mm/s was used. In each annulus a different load (ranging from 0.05 to 5 N) was applied. Each annulus consisted of 11 overlapping wear tracks, with radii differing from each other by 25 μm (see insert of figure 2). The width of each wear track was defined by the flat spot produced during the running-in. It was found to have a diameter of approximately 150 μm. The 11 wear tracks created together an annular test region spanning more than 250 μm. Before the XPS measurements the sample was ultrasonically cleaned in cyclohexane. On the tribologically stressed sample, an O(1s) map was collected, which evidences the different wear regions. Within each tested area a small-area XPS analysis was carried out. The analyzed area consisted of a spot of 120 μm diameter, and thus completely inside the tribologically stressed area.

The XPS analyses were performed on a PHI 5700 system with an Omni Focus IV lens system. Spectroscopic maps were acquired using the imaging capabilities of the lens system. The analyzed spot (diameter 120 μm) was electrostatically rastered over the sample (typically 64×64 pixels, 2×2 mm). For each pixel a full spectrum of the selected energy region was acquired. The typical size of an XPS map with respect to the tested

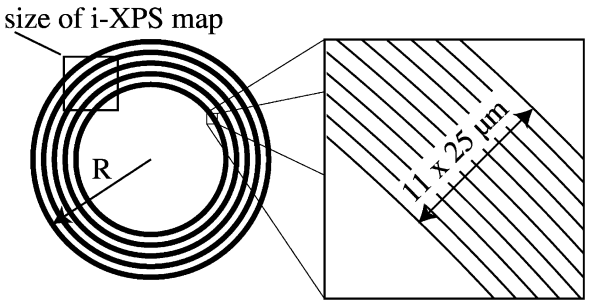

Figure 2. Schematic of the tribotest: the tests were performed in 5 concentric annuli consisting of 11 single tracks, each with a radius differing by 25 μm. The wear tracks are partially overlapping due to the width of the apparent contact area, which is defined by the flat spot ($\oslash$150 μm) produced on the ball during the running-in of the tribotest. For each annulus, a different load (L) was applied ($R = 3.5$ mm, $L = 0.05$ N; $R = 4$ mm, $L = 0.1$ N; $R = 4.5$ mm, $L = 0.5$ N; $R = 5$ mm, $L = 1$ N; $R = 5.5$ mm, $L = 5$ N). The square in the top left corner represents the area analyzed by i-XPS.

areas is displayed in figure 2. The acquired spectroscopic maps were processed with PHI Multipak (V6.0) software.

3. Results

In figure 3, the coefficient of friction (COF) acquired during a test is displayed versus the number of turns for loads from 5 to 0.1 N. The COF is averaged over one full turn of the disk and displayed versus the turn number. The error bars represent the standard deviation during one full turn. It can be noticed that at 0.5 and 1 N the COF decreases after the beginning of the test and shows a sudden increase after each fifth turn. This increase coincides with the 25 μm steps that occur after every five turns. After the increase, the COF decreases again and at the end of a five-turn cycle the COF has reached a steady state. This steady state is assumed to indicate that a tribofilm has been formed that is representative of the applied conditions. Thus the average of the COF during the last full turn of the test is given in table 1 as a representation of the tribological properties of the tribofilm. The COF shows a small decrease with increasing load.

The morphology of the wear tracks and the ball used for the tribotest were examined with an optical microscope. The ball shows a circular flat spot with a diameter of 150 μm, which was worn off mainly during the running-in period of the tribotest. It defines the apparent contact area during subsequent tests. On the tribologically stressed disk, the areas tested with 5 and 1 N are clearly visible by optical microscopy, but for lower loads no differences can be recognized between the contact and the non-contact area. Without additional information from imaging XPS it would be difficult to locate the areas tested at lower loads.

The total O(1s) intensity map of the tribologically stressed sample is presented in figure 4(a). Arcs of higher

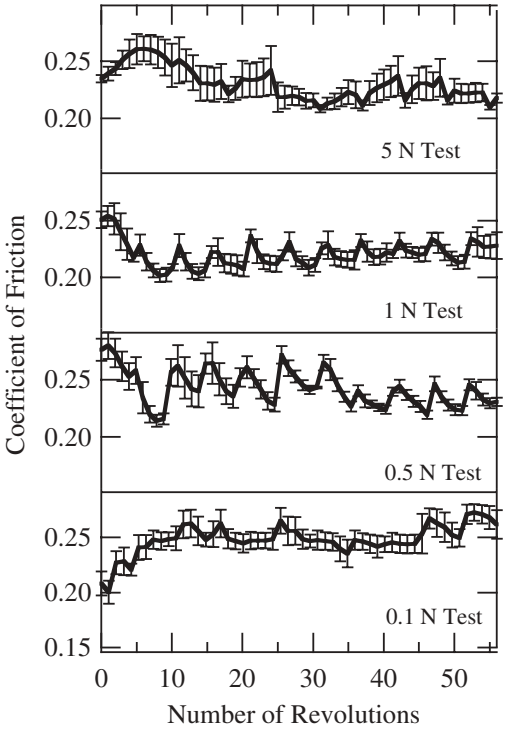

Figure 3. Coefficient of friction (COF) of a tribotest for the loads from 5 to 0.1 N. The COF is averaged over 1 full turn of the disk; the error bars represent the standard deviation during one turn. The increase of the COF after the 25 μm steps after each fifth turn can be seen (see text).

intensity can be seen running from the bottom left to top right, indicating the location of the tribologically stressed annuli. Each pixel of the O(1s) map contains the entire spectroscopic information for the O(1s) region. The spectra of the most intense and the least intense areas are extracted and displayed in figure 4(b). The dark areas (which correspond to a lower oxygen signal intensity) reveal a spectrum that is characteristic for the surface of an oxidized steel, showing a peak at 530 eV and a shoulder at a binding energy that is approximately 1.5 eV higher than the main peak. The bright areas show a different peak shape in the O(1s) region. The main peak is found at 531.7 eV plus a shoulder at 530 eV. The peak at 531.7 eV is characteristic for oxygen bound in a phosphate group, while the shoulder is due to contributing oxide. In the following, this shape of the O(1s) spectrum is referred to as being of the phosphate type.

The O(1s) map was further processed with the linear-least-squares (LLS) algorithm of the PHI Multipak (V6.0) software. This algorithm fits the spectra of the selected areas (shown in figure 4(b)) with the spectra in each pixel of the map. The correlation is shown in the chemical-state maps (figure 4(c) and (d)). Bright areas in figure 4(c) show areas with high correlation with the oxide-type spectra, while bright areas in figure 4(d) show high correlation with the phosphate-type spectra. The phosphate-type spectrum is most prominently repre-

Table 1
COF and elemental ratio for the various loads of two independent samples. The detailed analysis of the XP spectra is presented elsewhere [13].

Load	COF		P/S		$O_{phosphate}/P$	
0.05 N	0.25	0.31	0.66	0.68	5.1	7.0
0.1 N	0.26	0.31	0.71	1.13	5.0	4.7
0.5 N	0.23	0.21	0.94	1.30	4.1	4.5
1 N	0.22	0.20	0.95	1.42	4.0	4.5
5 N	0.20	0.19	0.91	1.45	3.6	4.2

sented in the outermost test area (5 N load) and decreases with decreasing load. The O(1s) peak shape characteristic of oxide (''oxide type'') is almost absent in the area tested with 5 N but seems to be increasingly present at lower load and it is predominant in the non-contact area.

From the chemical-state map it is possible to select ''areas of interest'' for more detailed (small-area) XPS analysis. The results are summarized in table 1 and a more detailed spectral analysis can be found elsewhere [13]. No differences in the binding energies of the spectra taken in the various tested areas could be found, although changes in intensity ratios were observed. With increasing applied load, the phosphorus-to-sulfur ratio in the tribofilm was observed to increase. The ratio of the oxygen bound in a phosphate group (component at 531.7 eV, see figure 4(c)) to phosphorus was found be close to 4 : 1 for high loads, indicative of PO_4^{3-}. The binding-energy value of the P(2p) peak (133.6 eV) is also in agreement with phosphorus being bound within a phosphate group [14].

4. Discussion

The combinatorial approach to tribological testing presented here involves the creation of a set of spatially separated areas on a single sample that have undergone tribological tests under a variety of loads. The frictional information gathered during tribological tests as a function of test conditions can then be mapped onto subsequent, spatially resolved surface-analytical data. This methodology can be considered as the generation of a parameter library on the sample, which then serves as a means to relate tribological conditions with both friction and subsequent tribochemical reactions.

As described above, the COF increases after every fifth turn of the disk due to the 25 μm step that is performed to ensure a contact area wide enough for XPS analysis (see figure 2). At the end of a five-turn cycle, the COF reaches a steady-state value, indicating that a tribofilm characteristic of the applied load is formed and thus a representative surface analytical analysis can be carried out within these contact areas. This behavior of the COF is most evident in the 1 N and 0.5 N tests. It can be assumed that due to the high load, a surface film is formed more rapidly than at lower load.

The resolution of the load cell measuring both frictional force and normal load is $\pm$5 mN. The friction force for the low-load experiments is on the order of 20

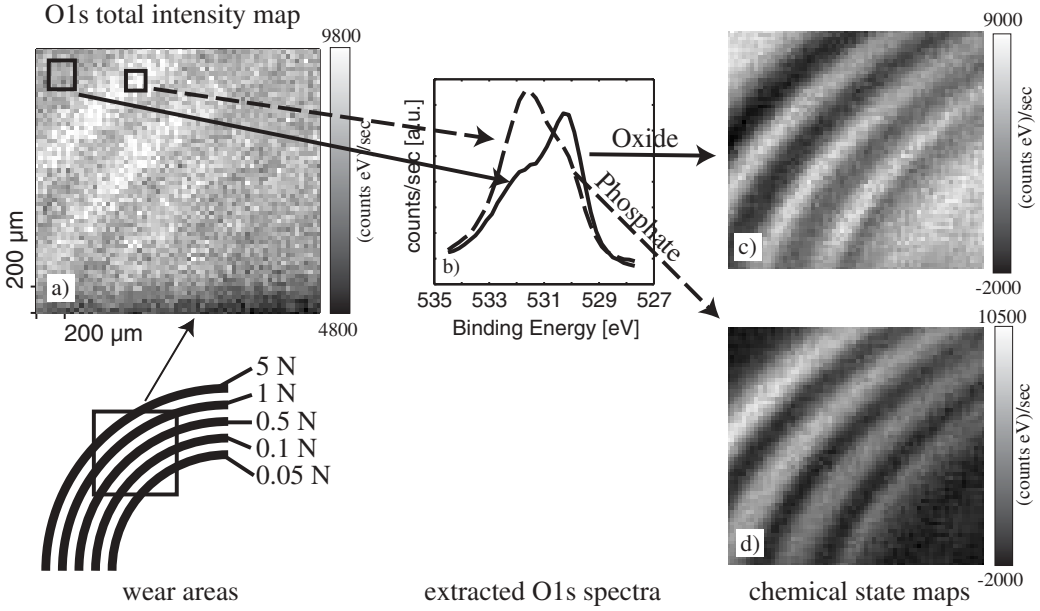

Figure 4. In the total-intensity map (left), a variation in the total intensity of the O(1s) signal can be clearly observed to coincide with the tribotested regions. The O(1s) spectra shown in the graph in the middle represent the spectra extracted in the regions marked in the map. Two different signals can be observed, a ''phosphate'' signal and an ''oxide'' signal. The linear-least-squares routine is used to correlate these two signals with O(1s) signal in each pixel of the map, producing chemical-state maps. Bright colors represent high correlation with the respective signal and thus indicate the distribution of the oxide or the phosphate.

and 10 mN for the 100 and 50 mN tests, respectively, and thus the experimental error for the friction force is on the order of 25–50% for these loads. Despite the high experimental error at low loads, a slight reduction of the COF at higher loads compared to the lower loads can be seen for both experiments reported in table 1.

A possible shortcoming of the described combinatorial test method, which involves using the same pin and disk for both running-in and load tests, can arise from the fact that the tribological conditions at the contact between the pin and disk result from the nature of the surface films present on both the pin and the disk and not just from the disk. Indeed, any change in the surface film composition of the pin might also affect the subsequent results. This needs to be determined in a controlled experiment for each system investigated. To ascertain whether any such interference was significant in the present study, oscillating load tests have been performed, during which the load is cycled from the minimum value to the maximum value, in synchrony with the angular position on the disk. These tests have shown that the coefficient of friction changes as a function of the applied load in a similar way during each cycle, as well as showing symmetric behavior during increasing- and decreasing-load phases [15]. In the presence of ZnDTP, the COF showed higher values at the smaller loads and decreased with increasing load. Results obtained performing traditional single-wear-track tests were in good agreement with those obtained during combinatorial tests for the same applied loads, confirming that the history of the pin did not influence subsequent tribological measurements in the system under investigation [15].

The decreasing oxygen-to-phosphorus ratio and the increasing phosphorus-to-sulfur ratio (see table 1) indicate that with increasing load an increasing amount of phosphate is formed in the contact area. Detailed analysis of the S(2p) spectra indicate that some of the sulfur is present in the sulfide state and some is present as organosulfur species [13]. Spectroscopic analysis of the Fe(2p) signals also indicates the presence of iron phosphate. Tribological films from ZnDTP have been reported to be polyphosphate films [4,10]. They are formed under pure thermal or combined thermal and tribological stress [11]. At temperatures above 100 °C, tribofilms with a thickness of a few tens of nanometers are found, while at lower temperatures thinner films are reported [16]. The absence of thermal activation in our experiments explains the lack of a thick polyphosphate film. Only the presence of a thin orthophosphate film is indicated.

5. Conclusion

A combinatorial experiment has been successfully applied to the investigation of a tribological system. The advantage of the combinatorial approach is that multiple experiments can be efficiently combined on a single sample and readily compared. Tribological and spectroscopic results could be acquired in one experiment for a number of conditions and mapped onto the parameter library.

Useful information concerning the reactions occurring in the tribological contact could be derived from the experiment: the i-ZnDTP molecule reacts under tribological stress with the steel surface and forms an iron phosphate-containing film. The amount of phosphate film formed and the composition is dependent on the applied load. Sulfides and organosulfur species are formed, but the amount of these species present is not as strongly load dependent as the amount of phosphate on the surface.

In future, the information density obtained in such experiments will need to be increased in order to realize the full potential of this type of experiment. The range of experimental parameters should also be enlarged in order to cover as many tribologically relevant regions of the parameter space as possible. Ideally, with one experiment the tribological conditions under which a given lubricant additive formulation shows desirable properties could be determined. This approach could therefore speed up the search for new lubricant-additive systems. The approach can also be extended to other (surface) analytical methods. Auger electron spectroscopy or time-of-flight secondary ion mass spectroscopy would have the advantage that the analysis could be performed with a higher lateral resolution and therefore allow a higher information density.

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