

Global rethinking of the lubrication of ferritic stainless steel sheets – low friction and wear using strongly diluted alcohol solution of alkylphosphonic acid

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Abstract

In a recent study [1], significant improvement of the tribological behavior of bare copper was demonstrated when using alkylphosphonic acids as nano-size liquid additives in the lubricant. Indeed, these widely studied molecules graft spontaneously onto the oxidized copper surface, leading to formation of a very efficient wear protective low-friction film (tribofilm) during sliding.

The present study investigates the potential for using this more environmentally friendly and easy to clean lubrication in industrial scale forming of stainless steel, in operations such as stamping, rolling and cutting. Against this background we analyze the characteristics of the tribofilm formed on a stainless steel surface during sliding experiments performed in solutions containing alkylphosphonic acids, under various contact conditions.

It was found that an efficient tribofilm was formed, irrespective of substrate roughness, sliding speed or contact pressure, systematically leading to low wear and low friction coefficient. Specific tribological tests were designed to analyze the dynamics of the lubricating mechanism. In these tests, the active molecules were introduced either at the start or midway through the test and dynamics of the friction response was studied in detail. It was found that both the grafting of molecules and the transformation of these into an efficient tribofilm are quick processes (approximately a few seconds). Indeed, additional experiments, performed using substrates with grafted molecules immersed either in pure solvent or in solvent containing active molecules, highlight the intrinsic dynamic component of the combined phenomena. It was shown that continuous feed of active molecules onto the surface during sliding contact is needed. However, a concentration of the active molecule as low as $0.001 \text{ mol}\cdot\text{l}^{-1}$ appears to be enough to keep the friction coefficient low and stable during the tribological sliding tests.

The paper demonstrates the high potential for general applicability of this lubrication technique to reduce the friction between a ferritic stainless steel sheet and a forming tool.

Keywords: lubrication, stainless steel, low friction, alkylphosphonic acid, stamping.

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1. INTRODUCTION

There are several common materials that by experience are very difficult to form, for instance stainless steels, aluminum alloys, titanium and copper. For that reason, good lubrication is vital to avoid the well-known issues of adhesion or transfer of work material to the tool in metal forming [2, 3].

Stainless steels have very good corrosion resistance due to containing a sufficient amount of chromium, leading to their use in lots of commercial applications: kitchen sinks, cutlery, watches, washing machines, automobile components, medical and chemical apparatus, etc. According to the application, these good anti-corrosion properties have to be combined with a good formability of the grades. Unfortunately, austenitic and ferritic stainless steels are not comparable on this specific point, due to their different compositions and the resulting microstructures. Indeed, even if ferritic stainless steels can have equivalent Cr-content as

austenitic grades, the lack of Ni (whose price is both high and varying) and other γ -elements in sufficient quantities induces important differences in terms of mechanical properties, mainly characterized by a lower drawability [4]. To offset that point, it is therefore necessary to use an improved lubrication to stamp ferritic stainless steel sheets, for instance lubricants containing additives such as sulfur, chlorine and phosphorous. These compounds are designed to react chemically with the metal surfaces, forming easily sheared layers of sulfides, chlorides or phosphides [5].

However, nowadays it is essential to develop new surface functionalizations in an environmentally, socially and economically responsible way, in order to avoid the use of harmful lubricants. Indeed, the drawbacks of using extreme pressure (EP) additives are that they are either highly eco-toxic, poorly biodegradable or suspected to cause cancer. In addition, they are difficult to remove from the produced parts in the subsequent cleaning process.

One way to avoid the use of a classical lubricant is to modify metallic surfaces by using organic molecular assemblies [6, 7]. For example, Ulman [8] showed that ultrathin organic films are a remarkable and powerful way to tailor surface properties, due to their simplicity, adaptability and reproducibility. More recently, it has been proven that alkylphosphonic acids could be used to produce an easily sheared tribofilm during sliding [9, 10]. The effect of alkylphosphonic acid molecules on wear resistance was recently demonstrated in alcohol, however most of the studies have been devoted to perfect copper substrates, ultrasonically cleaned, with a pretreatment leading to well-known appropriate states of oxidized copper [1,9,11].

In the present study, the frictional properties of non-pretreated ferritic stainless steels, with different surface states, were tested in lubricated sliding conditions against ball bearing steel balls, either in rotational ball-on-disc setup or in a linear unidirectional scratch tester. During testing, both substrates and balls were immersed in an alcoholic solution containing a given concentration of alkylphosphonic acid.

Friction measurements, surface analyses after tests and also experiments with special operating modes proved alkylphosphonic acids to be highly efficient as an additive, quickly forming an easily sheared tribofilm from grafted molecules after their transformation during sliding.

2. EXPERIMENTAL

2.1 Chemicals

De-ionized water (Milli-Q, resistivity 18M Ω cm) was distilled twice before use. 1-bromoalkanes (ALFA AESAR, > 98 %), hydrochloric acid (SIGMA ALDRICH, 37%, 7647-01-0), triethylphosphite (ALFA AESAR, 98 %, 122-52-1), absolute ethanol (ACROS, pure, 64-17-5), sodium hydroxide (ACROS, 97 +%, 1310-73-2), potassium hexacyanoferrate(II) trihydrate (SIGMA ALDRICH, 98.5+%, 14459-95-1) and sodium sulfate (SIGMA ALDRICH, 99+%, 7727-73-3) were used as received.

2.2 Synthesis of alkylphosphonic acid compounds (we will use the abbreviation CP)

The Arbuzov reaction was performed in a distillation apparatus fitted with a 5-10 cm Vigreux column. Triethylphosphite (35 mL, 0.2 mol) was added dropwise during 2 hours at 190-200 °C to the appropriate 1-bromoalkane (0.2 mol) while stirring. Distillate temperature was kept below 45 °C. After further reaction (30 min), the mixture was cooled and the crude phosphonate used without purification for the subsequent hydrolysis in alkylphosphonic acid.

Alkane-1-phosphonic acid (other than butane-1-phosphonic acid) was obtained by boiling crude diethyl alkylphosphonate (0.1 mol) in 12 M aqueous HCl (200 mL) for 18-24 h. After slow cooling to room temperature, the crude phosphonic acid was filtered and washed with water to pH > 3.

Recrystallization from cyclohexane afforded pure product in 60-70 % yield.

2.3 Material

Ferritic stainless steel substrates (X2CrTiNb18 – 1.4509,) were used as received, without additional polishing steps. The trade name K41 will be used thereafter. To investigate the effect from surface roughness

on the tribological response in specifically designed tests, two surface finishes were used: an industrial finish "2B" and a manually polished substrate, with surface roughness Ra equal to 0.35 μm and below 0.1 μm , respectively. Concerning the 2B roughness, this one was imprinted during the last rolling-step (skin-pass operation), leading to oriented roughness. The roughness measurements were carried out perpendicular to the rolling direction. The Fig.1 illustrates the "2B" industrial finish state obtained after a final skin-pass operation.

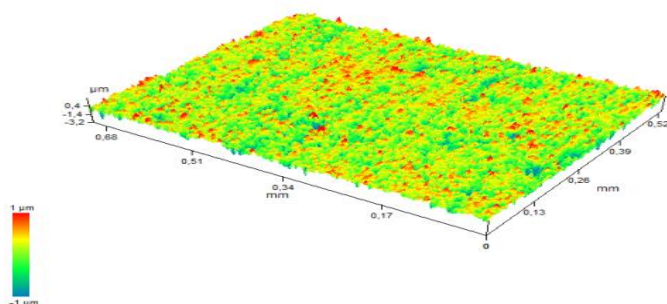


Figure 1: Topographic optical image of the K41 2B

2.4 Tribological measurements

To explore the friction behavior, tests were performed on different tribometers: a rotational pin-on-disk tribometer (with a circular track of 3 mm radius) and a scratch tester (with a linear track of 10 mm). Since tribofilms are formed through agglomeration and compaction of wear fragments, wear particles generated in a rotating test have a smaller likelihood of existing in the wear track, and fragments pushed in front of the ball will instead be integrated into the tribofilm. We have almost the same phenomena in using scratch tester but some of wear particles can be observed outside the end-point of the wear track, after having been pushed in front of the ball. But the crucial difference is that, in the case of scratch tester, there is a constant sliding direction with the rolling direction.

In both tests, the counter surface was a steel ball (100Cr6) with a diameter of 10 mm applying a normal load of 10 N (leading to a Hertzian mean contact pressure of 680 MPa). However, to investigate the effect of roughness tests were also performed using a Si_3N_4 ball (very smooth in comparison to the steel ball) and different normal loads, up to 50 N, which corresponds to a Hertzian mean contact pressure of 1.28 GPa.

The sliding speed was $0.01 \text{ m}\cdot\text{s}^{-1}$ for rotational pin-on-disk experiments and $0.01 \text{ m}\cdot\text{min}^{-1}$ for the scratch tests. These two sliding velocities are too low to allow hydrodynamic effect. For each lubrication condition (dry sliding and lubricated sliding in pure solvent or containing 0.001M CP dissolved in solvent), three repeated tests were performed, at room temperature. Prior to testing, substrates and balls were ultrasonically cleaned in ethanol. After the sliding tests all balls were analyzed by optical microscopy. The stainless steel sample surfaces were investigated using Scanning Electron Microscopy (SEM). The SEM analysis was performed using a low acceleration voltage of 2 kV to achieve surface sensitive imaging in order to have a better visibility of tribo-layers. Elemental composition was analyzed using Energy Dispersive X-Ray Spectroscopy (EDX).

3. RESULTS AND DISCUSSION

3.1 Friction behavior

Although galling occurred between the stainless steel disc and the steel ball already before 100 cycles in dry conditions (without any lubricant) the sliding behavior was relatively stable in the pure solvent (see Fig. 2), with μ slowly increasing up to a stable value close to 0.4. The very initial friction was high in both cases, followed by a linear increase with the number of sliding cycles.

Contrastingly, the addition of alkylphosphonic acids in alcoholic solution strongly reduced the friction, as shown in Fig. 2 (green line). With the selected contact conditions (pin on disk, $V=0.01 \text{ ms}^{-1}$, $P=10 \text{ N}$), the friction coefficient stayed invariably stable below 0.1. This value is similar to previous results obtained on copper substrates, under the same testing conditions but using different solutions containing molecules of several alkyl chain lengths [1]. Moreover, the friction was strongly reduced from the initial sliding up to the

tenth cycle (Fig. 2b) due to the formation of a low-friction tribofilm. After this transition period, the tribofilm stabilized friction coefficient, close to 0.08.

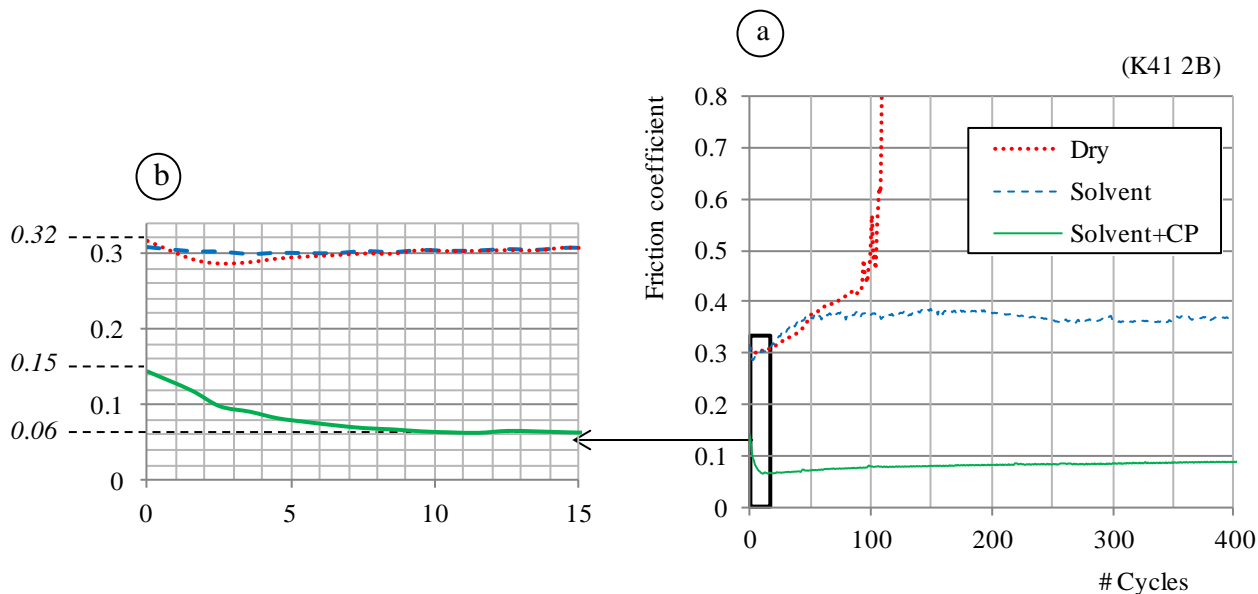


Figure 2: Evolution of mean friction coefficient (pin on disk circular track of 3 mm radius, $V= 0.01 \text{ ms}^{-1}$, $P=10 \text{ N}$ leading to a Hertzian mean contact pressure of 680 MPa) versus number of cycles. Red curve corresponds to dry sliding conditions, blue curve corresponds to lubricated sliding conditions in pure solvent and green curve corresponds to lubricated sliding conditions in alkylphosphonic molecules dissolved in solvent (b). Zoomed in view of the first ten cycles in (a).

It may be noticed that the initial friction was almost halved, due to the presence of alkylphosphonic molecules grafted on the surface: 0.15 instead of 0.32 (Fig. 2b). So, it may be reasonable to suppose that the molecules immediately separate the two metallic surfaces, even before their subsequent modifications, as highlighted by previous studies [12, 13]. During the first ten passes, the grafted molecules become transformed into a tribofilm, again almost halving the friction: 0.06 instead of 0.15.

Surprisingly, even if the test starts in pure solvent, characterized by a friction coefficient close to 0.3, the addition of active molecules leads to a significant and immediate friction fall (Fig. 3a). Again, a few cycles (after injection of the molecules) were sufficient to reduce the friction coefficient, now by a factor of four (Fig. 3b).

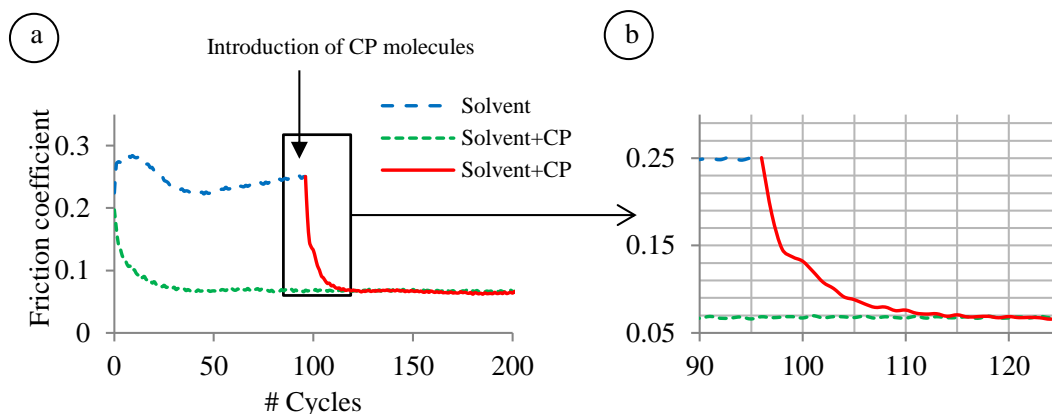


Figure 3: Evolution of mean friction coefficient versus number of cycles. (Pin on disk, circular track of 3 mm radius, $V= 0.01 \text{ ms}^{-1}$, $P=10 \text{ N}$ leading to a Hertzian mean contact pressure of 680 MPa). Blue curves correspond to lubricated sliding conditions in pure solvent during 95 cycles, red curves correspond to lubricated sliding conditions after introducing molecules, and green curves correspond to lubricated sliding conditions in alkylphosphonic molecules dissolved in the solvent (a). Zoomed in view of the first cycles after introducing the molecules (b).

Actually, running the test in pure solvent before introducing the CP molecules resulted in the same friction response (Fig. 3 red curve) as when performing the entire test in the active solution (Fig.3 green curve). Indeed, even if both surface states evolve during the first part of the test, with a potential transfer of the work material to the ball in pure solvent, probably also associated with high local contact pressures, no effect on the friction behavior are observed. From a friction point of view, this effect is so pronounced that we can talk of a real healing effect. Regardless of prior sliding in pure alcohol, the friction dropped to a very similar level around 0.07, once the active molecules are introduced.

In order to discriminate the effect from grafting molecules onto the surface from the effect of mechanically transforming these molecules into a tribofilm, a series of analogue tests were performed. In these tests, only the holding time after introducing the active molecules into the pure solvent was varied: 1 min, 30 min and 2 h (Fig. 4).

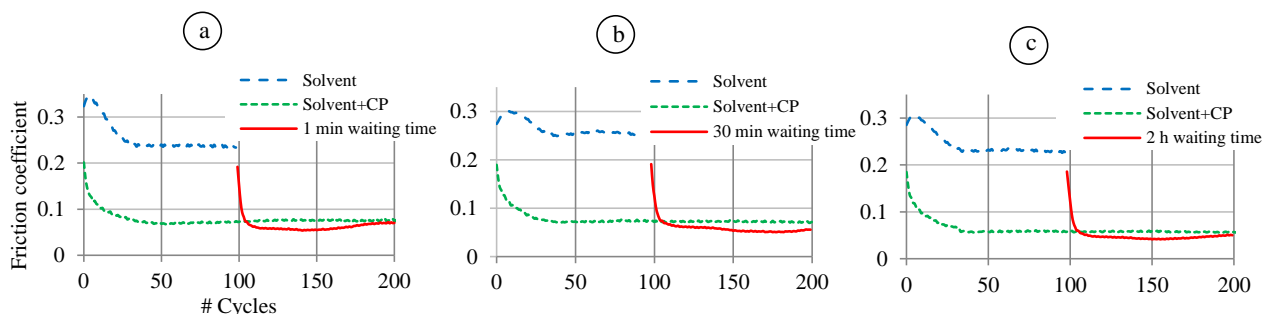


Fig. 4 Evolution of mean friction coefficient versus number of cycles (Pin on disk test, circular track of 3 mm radius, $V=0.01\text{ ms}^{-1}$, $P=10\text{ N}$, leading to a Hertzian mean contact pressure of 680 MPa). Blue curves correspond to lubricated sliding conditions in pure solvent during 100 cycles, red curves correspond to lubricated sliding conditions after 1 min, 30 min or 2 h holding time after introducing the molecules, green curves correspond to lubricated sliding conditions in alkylphosphonic molecules dissolved in solvent, (CP at [0.001M]).

As clearly illustrated by Fig. 4, the friction coefficient is always lower when restarting after the waiting period, irrespective of waiting time. This effect highlights the direct contribution from the grafted molecules on the friction reduction.

In the present case as shown in Fig. 5, the friction coefficient dropped a distinct level (a) during the waiting time. The drop is practically independent of the length of the waiting time. Once the sliding has restarted, the friction again gradually decreases, following practically the same curve regardless of waiting time. This gradual decrease corresponds to a large extent on the formation of a functioning tribofilm in the contact, caused by the repeated friction contact with the sliding ball. This two-step mechanism was already mentioned during the analysis of the Fig. 2.

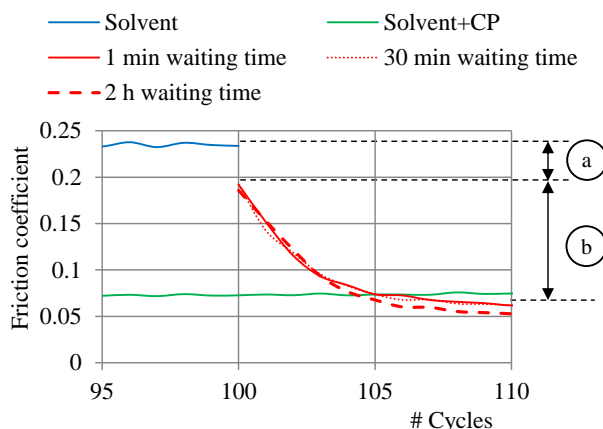


Figure 5: Zoom of Fig. 4: a) first drop in friction due to the grafting effect, b) second drop in friction due to the tribofilm formation.

Analogously, the healing process shown in Fig. 3 was due to rapid formation of efficient tribofilms, requiring both grafted molecules on the stainless steel surface and their gradual transformation during sliding.

In order to improve the understanding of the dynamics of the tribofilm formation, further tests were carried out. Compared to the above tests, which were performed on perfectly cleaned substrates immersed either in pure solvent or in solvent with low concentration of active molecules, the new tests were conducted with pre-grafted substrates (Fig. 6). These were grafted by 8 h immersion into a solution containing active molecules; a duration well-known for achieving an optimal state in terms of electrochemical surface blocking by active molecules (92%, [12]). This means that here a well-organized phosphonic acid monolayer, with a good surface coverage (up of 95%), was grafted onto the stainless steel surface.

The red curves in Fig. 6 represent the evolution of the friction coefficient in pure solvent for pre-grafted surfaces. Three tests were performed and stopped at 5, 12 and 30 cycles, respectively. Regardless of their tribological response, the good reproducibility and accuracy of the measurements is remarkable. Moreover, it may be noted that the initial friction coefficient is the same between tests performed in alcohol + CP with a virgin substrate (green curve) and in alcohol with the pre-grafted substrates (red curves). The equivalent friction coefficient, equal to 0.15 at the beginning of the test, can be assigned to the grafted molecules on the stainless steel surface and must be compared to the value obtained in pure solvent without any grafted molecules (blue curve): 0.3. Consequently, as previously illustrated, the active molecules have a distinct and immediate effect on the friction response before any transformation due to sliding.

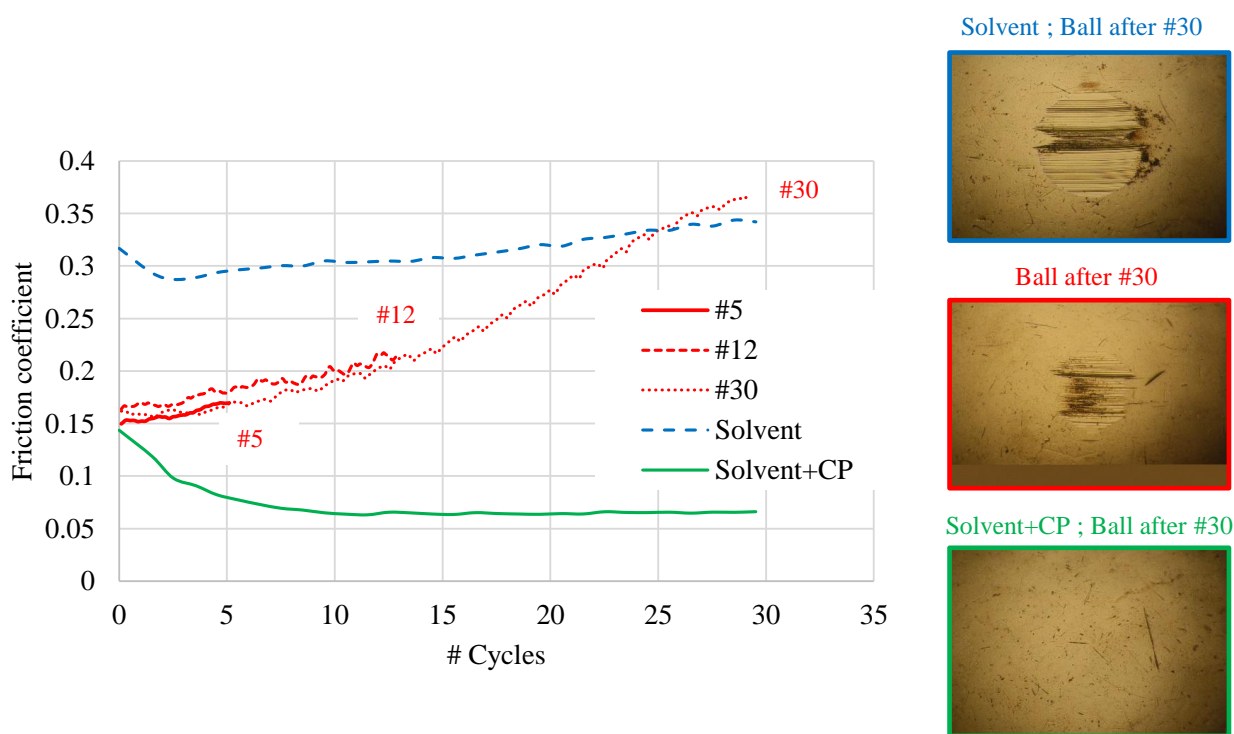


Figure 6: Evolution of mean friction coefficient versus number of cycles. (Pin on disk tests, circular track of 3 mm radius, $V= 0.01ms^{-1}$, $P=10N$ leading to a Hertzian mean contact pressure of 680 MPa). Blue curve corresponds to lubricated sliding conditions in pure solvent and green curve corresponds to lubricated sliding conditions in alkylphosphonic molecules dissolved in solvent, (CP at [0.001M]). Red curves correspond to lubricated sliding conditions in pure solvent for a pretreated substrate (dipped into in a bath containing CP at [0.001M] during 24 h).

On the contrary to the previous tests carried out immersed in the active solution, the friction coefficient continuously increases with the number of cycles and appears so to be sensitive to the fact that the liquid surrounding the contact is pure solvent, with no possibility for new active molecules to regenerate the tribofilm. This underscores the importance to continuously feed new molecules into the contact to obtain a low and stable friction behavior. Moreover, optical images show that friction may be directly correlated to the amount of transfer to the sliding ball. While no transfer area was visible in optical microscopy after solvent + CP test, adhesive wear occurred both with functionalized substrates and not functionalized

substrates during test performed in pure solvent (red and blue curves respectively) as illustrated in the pictures of Fig. 6.

3.2 Tribofilm formation

With alkylphosphonic acids in alcoholic solution, an excellent tribological behavior has been observed until now for stainless steel substrates. The tribological performance has been shown as depending on the feeding of new molecules into the contact and their dynamic transformation due to the sliding.

In order to evaluate and analyze more accurately the formation of such dynamic transferred tribofilm on the surface, scratch tests using constant normal load with same contact conditions as previously studied in the pin on disk test, were conducted. With only 5 successive passes in the same 9 mm length track, the aim is here to focus on the tribofilm formation (Fig. 7).

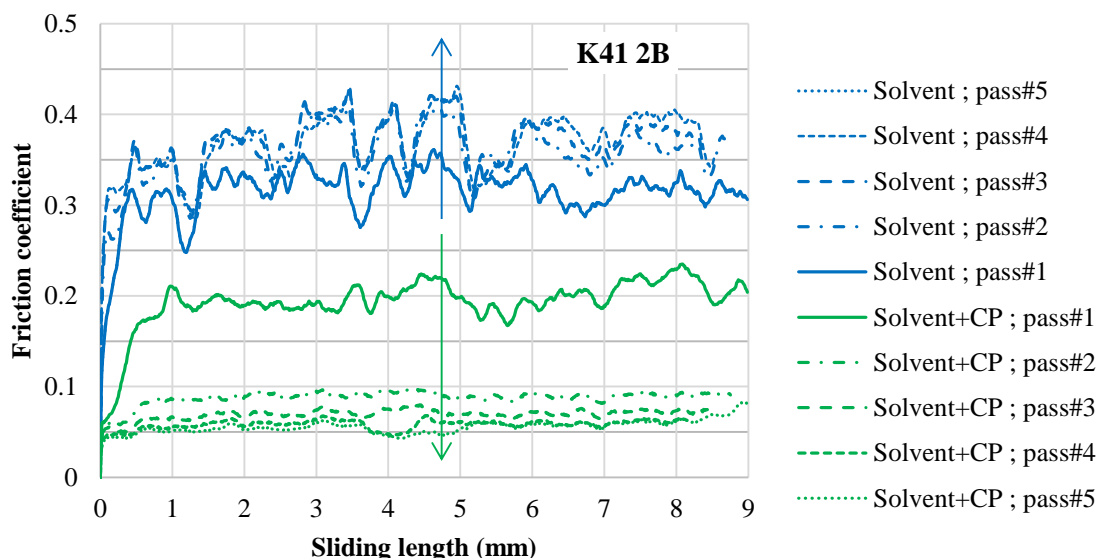


Figure 7: Evolution of mean friction coefficient versus sliding length. (Linear sliding track of 9 mm length, $V=0.01\text{ m}\cdot\text{min}^{-1}$, $P=10\text{ N}$, leading to a Hertzian mean contact pressure of 680 MPa). Blue curves correspond to unidirectional lubricated sliding conditions in pure solvent and green curves correspond to unidirectional lubricated sliding conditions in alkylphosphonic molecules dissolved in solvent, (CP at $[0.001\text{M}]$). In both cases, five passes were performed in the same track.

By comparing the two first passes with or without molecules in solvent (the two solid lines in Fig. 7, green and blue respectively), the immediate effect of molecules is clearly visible and characterized by a friction coefficient always around 0.2 instead of 0.32.

As a complementary proof of the impact of the CP molecules, scratch tests carried out in solvent with active molecules highlight a huge decrease of the friction coefficient while increasing pass number (Fig. 7), especially between the first two passes. Indeed, after the second pass, the friction coefficient became low and almost constant, witnessing of a permanent low friction regime. It may therefore be assumed that a highly efficient tribofilm has formed during the first pass. Such phenomena cannot be observed during the tests performed in pure solvent. Once again, the presence of grafted molecules and their transformation during contact strongly decreases the friction response of the system. After 5 passes conducted in solvent + CP, the friction coefficient is equal to 0.05 instead of 0.35 without the molecules.

In Fig. 8, SEM was used to study the surface morphology as well as the roughness modifications induced by the sliding tests. Moreover, EDX maps were recorded to provide information about the elemental distribution; P and C signals corresponding to the alkylphosphonic acid molecules and thus the potential tribofilm.

Elemental maps of P, C and Fe, in the wear track of the test corresponding to Fig. 7, are shown in Fig. 8. Increased signal from P and C are clearly visible in the bottom of valley and can be correlated to the tribofilm, which appears to be mechanically anchored. On the basis of the images presented in Fig. 8, it can therefore be inferred that dark areas correspond to a thicker tribo-layer, visible when low voltage is used (2

kV). Indeed, lower voltage enables extreme surface analysis while higher voltage gives deeper information of the material's composition.

Fig. 9 compares SEM images of wear tracks representative of the first and the fifth passes of the test, illustrated by the Fig. 7, with active molecules in the solution. The gradual formation of a tribofilm preferably entrenching in the roughness valleys due to an anchoring effect is thus highlighted. Moreover, no detrimental degradation of the surface roughness has been reported.

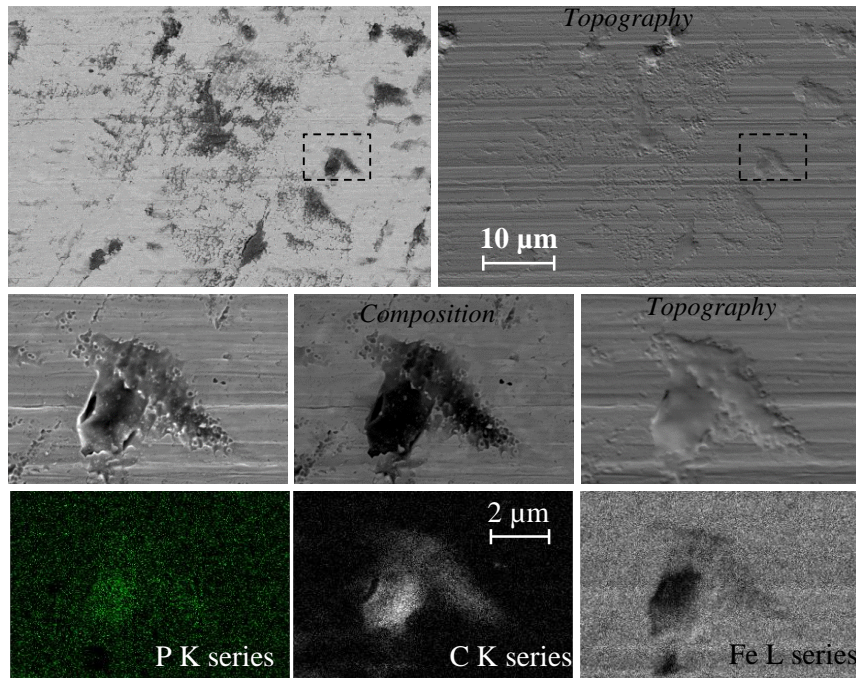


Figure 8: SEM images of the track after sliding test where 5 cycles were performed. Topographic and composition images (back scatter electrons) were indicated. Bottom row: EDS mapping of P, C and Fe, respectively.

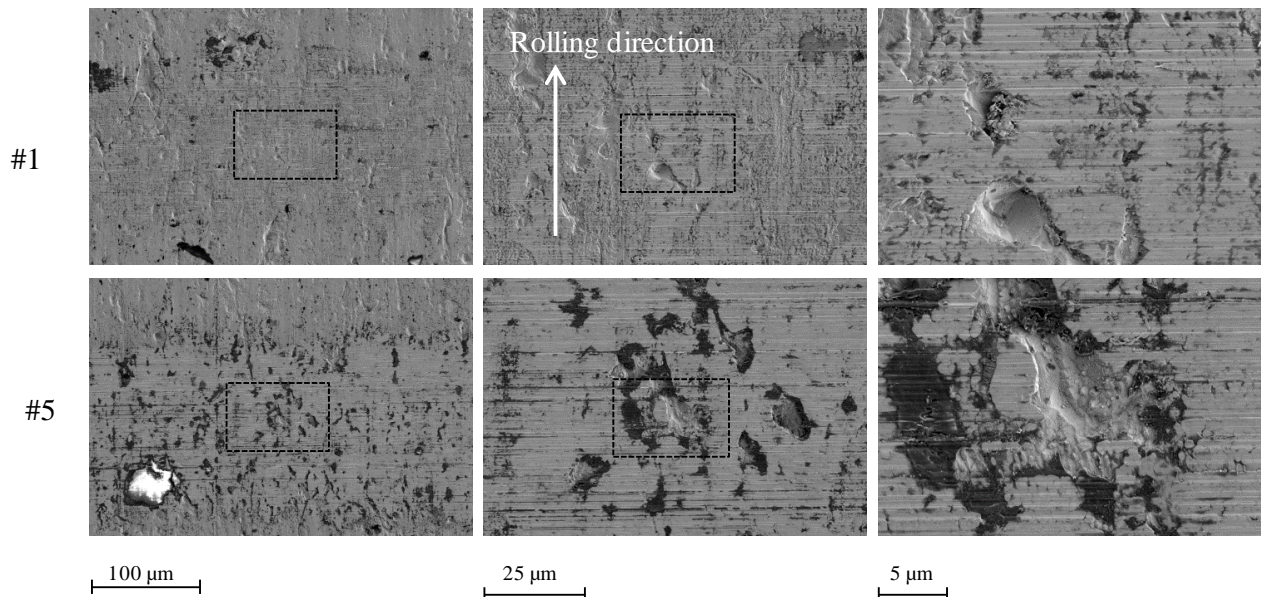


Figure 9: SEM images of the track after sliding test (linear track of 10 mm length, $V=0.01\text{m}\cdot\text{min}^{-1}$, $P=10\text{N}$ leading to a Hertzian mean contact pressure of 680 MPa). Sliding direction is perpendicular to the roughness (perpendicular to the cold rolling direction). 1 pass or 5 passes were performed in the same track.

3.3 Effect of roughness

Two important factors that define the friction response of a system are the surface topography and the local chemical composition. The valleys of roughness are thus well-known to be preferential places to accumulate molecules, leading to the development of a tribofilm.

Unidirectional multi-pass scratch tests with a progressive increase of the pass lengths were here performed on two different surface roughnesses: an industrial “2B” roughness and a manually polished substrate. The Fig. 10 illustrates the results obtained for these two drastically different surface states. Concerning the 2B roughness, this one was imprinted during the last rolling-step (skin-pass operation), leading to oriented roughness. The resulting ridges or grooves had thus a specific direction relative to the sheet and hence the sliding direction.

In spite of this surface anisotropy of the 2B sample, friction appears to stay unconditionally isotropic, with the same tribological answer whatever the roughness orientation against the sliding direction: parallel (Fig. 10b) or perpendicular (Fig. 10c). Once again, tribofilm was trapped in the valleys of roughness, independently of the direction relation between the sliding direction and the surface topography (Figs. 9, 11). During the first pass and for the last few mm of each pass, the sliding took place on a virgin grafted surface. As can be seen in the Fig. 10, the friction coefficients measured in these zones, close to 0.15, were very similar whatever the surface textures. According to the previous results concerning this 2B surface state, the tribofilm formation occurred during the first pass, leading once again to low friction coefficient (around 0.08) when increasing the number of passes in the same track.

Concerning the polished substrate, the observation is quite different. Indeed, the friction coefficient continuously increased during each pass. SEM observations of the polished surface (Fig. 12) highlight a significant surface modification during the first pass, mainly characterized by numerous narrow scratches developed at the bottom of the track. These micro-gallings appears to be useful since enabling in the meantime the anchoring of tribofilm (see Fig. 12). Moreover, whatever the initial roughness, micro scratches were formed parallel to the sliding direction due to the micro transfer of material on the ball. A significant amount of tribofilm used these scratches as fixing places (Figures 9, 11 and 13). When surfaces were polished, these scratches formed during the first passes have been essential to the tribofilm formation. The previously seen healing effect used the initial roughness and/or the new roughness created during sliding as foundations of the tribofilm.

Even when initial roughness of both substrate and ball was very low, using a mirror polished stainless steel and a ceramic ball, a few passes were enough, leading to a very low and constant friction coefficient. In Fig. 14 are shown friction results when a Si_3N_4 ball slides on a polished substrate, with a normal load of 50 N, leading to a relatively high Hertzian mean contact pressure of 1.28 GPa. Friction coefficient was stable at an extremely low value of 0.08 after two cycles. It may be reasonable to assume that this excellent low-friction behavior was mainly due to that the scratches developed earlier, during the first passes, were filled by the tribofilm.

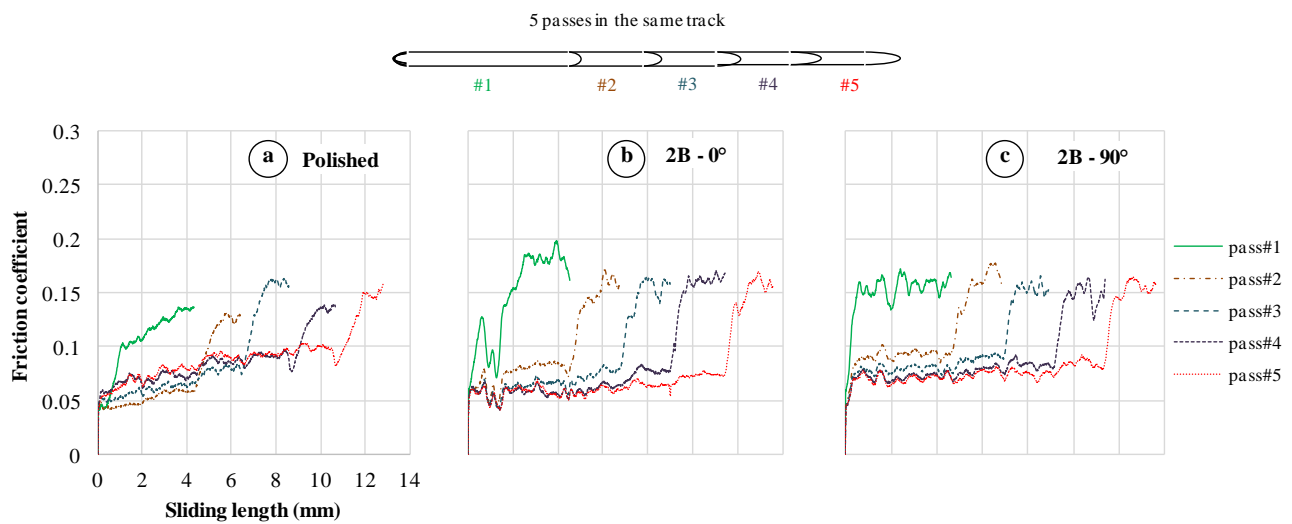


Figure 10: Evolution of mean friction coefficient (linear track of 10mm length, $V=0.01\text{m}\cdot\text{min}^{-1}$, $P=10\text{N}$ leading to a Hertzian mean contact pressure of 680 MPa), versus unidirectional lubricated sliding conditions in alkylphosphonic molecules dissolved in solvent, (CP at [0.001M]). In each of the three cases, five passes, respectively of 4.5, 6.8, 9, 11.5 and 13.5 mm length, were performed in the same track. a) Substrate with very low roughness (Polished; $R_a < 0.1\ \mu\text{m}$), b) and c) Substrate with higher roughness (2B; $R_a = 0.35\ \mu\text{m}$). b) Sliding direction and roughness were parallel c) Sliding direction and roughness were perpendicular.

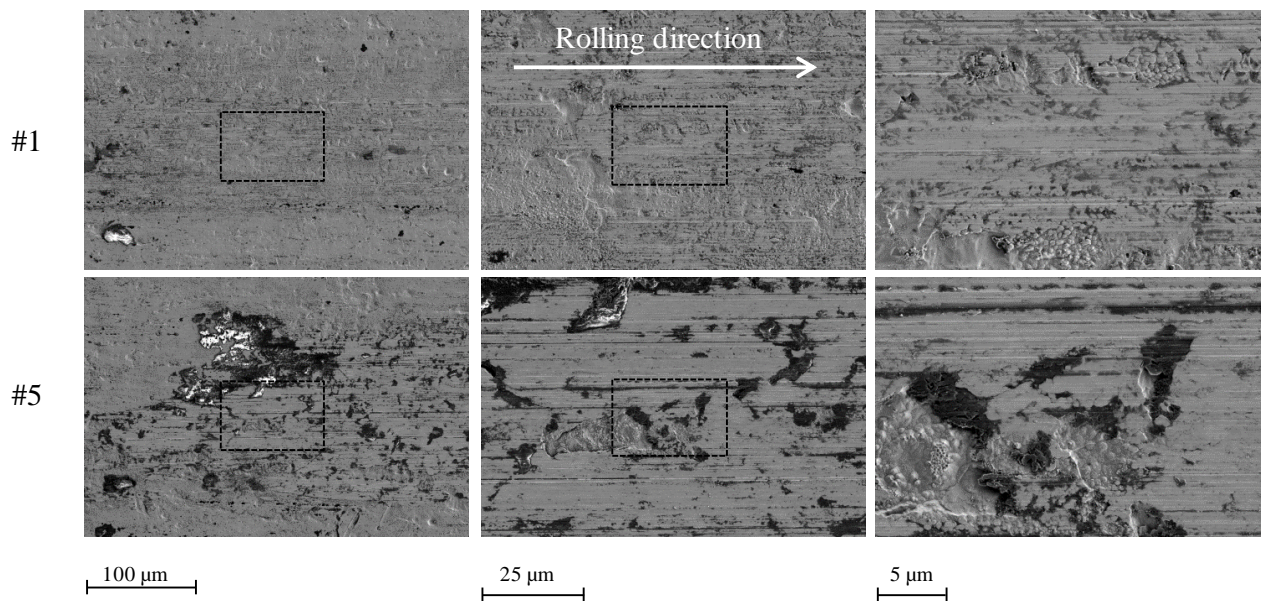


Figure 11: SEM images of the track after sliding test on 2B sample (linear track of 10 mm length, $V=0.01\ \text{m}\cdot\text{min}^{-1}$, $P=10\ \text{N}$ leading to a Hertzian mean contact pressure of 680 MPa). Sliding direction was parallel to roughness (rolling grooves). 1 pass or 5 passes were performed in the same track.

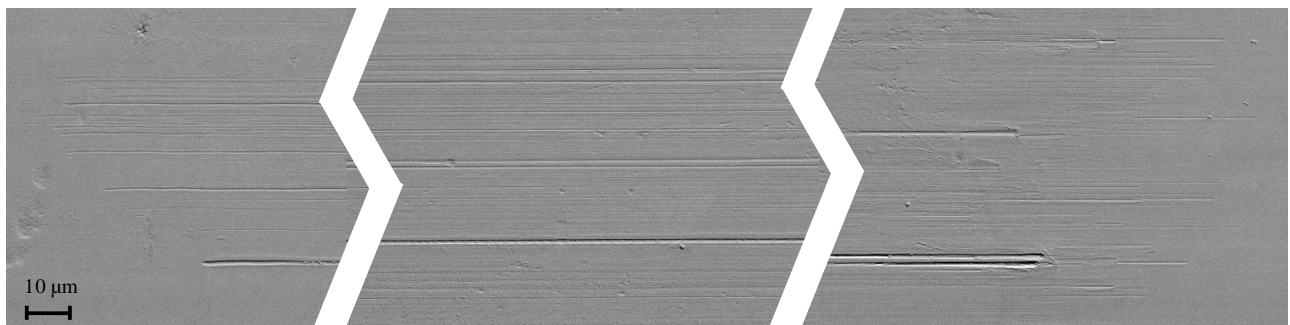


Figure 12: Beginning, middle and end of the track on the polished sample after one pass (back scattering images)

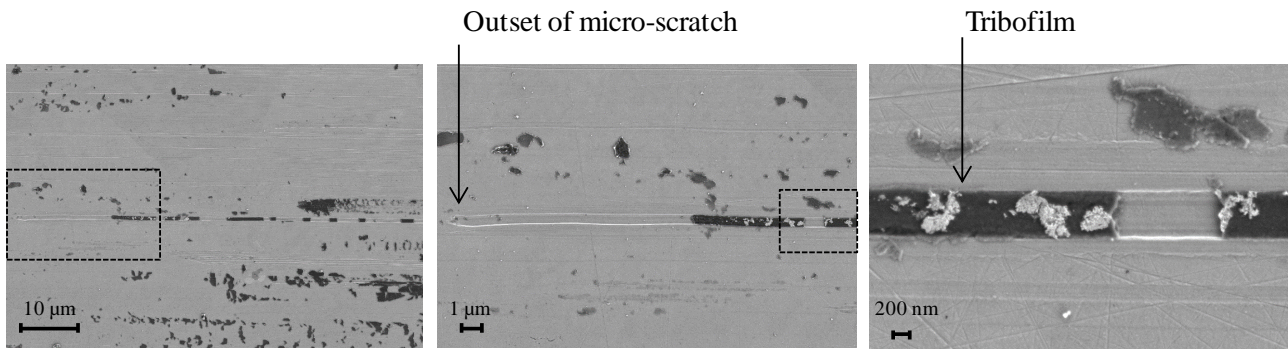


Figure 13: SEM images of the track after one pass (linear track of 10 mm length, $V = 0.01 \text{ m}\cdot\text{min}^{-1}$, $P = 10 \text{ N}$ leading to a Hertzian mean contact pressure of 680 MPa). 2B K41 substrate was polished prior test.

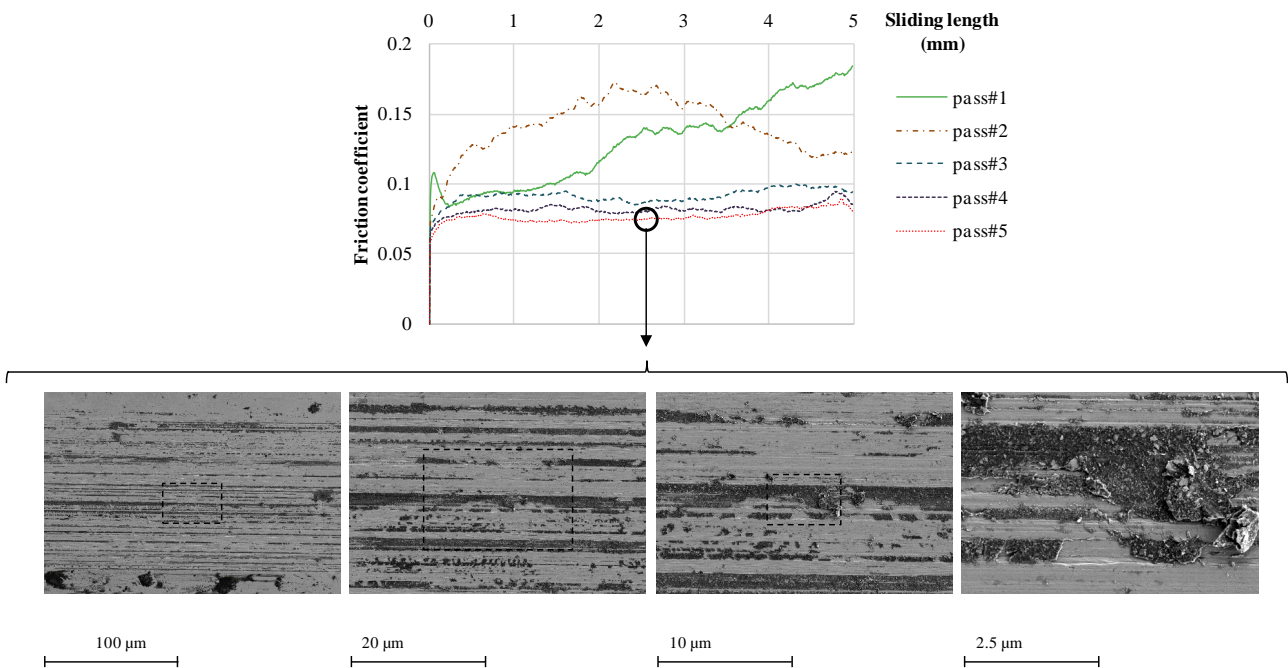


Figure 14: Polished substrate – SEM images of the track after sliding test (linear track of 10 mm length, $V = 0.01 \text{ m/min}$, $P = 50 \text{ N}$ leading to a Hertzian mean contact pressure of 1.28 GPa), performed with a Si_3N_4 ball (very smooth). 5 passes were performed in the same track.

4. CONCLUSIONS

Recent work showed the effectiveness of alkylphosphonic acids to improve friction behavior of metallic substrates and reduce the risk of galling. The possible use of alcohol with alkylphosphonic acids at very low concentration has already been identified as a promising way to reduce the environmental impact of lubrication in copper metal stamping [1, 9]. However, these studies focused on the functionalization of an ideal copper substrate, electrochemically reduced and re-oxidized in a controlled environment.

In the present study we tested how well this new surface treatment could be used for ferritic stainless steel to remedy unfavorable mechanical properties, compared to an austenitic stainless steel.

We found a significant reduction of the friction coefficient and a strongly reduced tendency to metal transfer onto a slider. In addition, the improvements noted in our experiments were unrelated to contact time between surface and molecules, leading to an extremely quick effect of these additives. These findings extend those relating to copper substrates, confirming that the lubricating function of the tribofilm is due to two factors:

firstly molecules grafting on the surface, and secondly accumulation of molecules and transformation initiated by the combined action of applied and alternating contact stresses.

This study therefore indicates that the valleys of roughness are needed for the tribofilm establishment, by accumulating and compacting the molecules in every groove. When the substrate is very well-polished, these anchoring places are reduced. So, a running-in phase leading to micro-scratches is necessary to provide the main sites for strong tribofilm anchoring. Most notably, one of the direct consequences is that these molecules have a strong healing effect. Moreover, the friction behavior becomes isotropic, even when roughness is not. Nevertheless, the tribofilm formation process is a dynamic course and requires a continuous supply of active molecules to compensate for the wear of tribolayers during sliding.

Our results provide compelling evidence for the benefits of using alcohol with alkylphosphonic acids to reduce the environmental impact of lubrication in ferritic stainless steel stamping.

Although these results are very convincing, some interrogations are worth noting. Grafted molecules were favorably impacted by the first contact stresses generating very low friction. That would suggest that grafted molecules form a layered structured under tribological load. Further work should therefore include tribofilm analysis (rheology, thickness, morphology) to provide a better understanding of their formation and function.

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