

Mechanism of tribo-chemical reactions of ionic liquids on titanium alloys

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ABSTRACT

In this paper, the tribological, the tribo-chemical reaction mechanisms and desorption properties of three ionic liquids (ILs), [Bu₃MeP][Tf₂N], [Bu₃MeN][Tf₂N] and [Bu₃MeP][(MeO)₂PO₂], in contact with titanium and under vacuum conditions are studied with the CATRI © UHV Tribometer developed by IK4-TEKNIKER [1].

The two ILs containing the bis(trifluoromethanesulfonyl)amide anion presented lower coefficient of friction compared to that having the dimethyl phosphate anion. The tribodesorption study revealed that it is required an induction period to decrease the friction coefficient. The end of this period is accelerated in the case of trifluoromethane ionic liquids by the CF₃⁺ release. Hence, the CF₃⁺ reacts with the titanium surface generating a titanium fluoride tribolayer that could act like a catalyst to generate the tribodesorption of ionic liquid cation fragments (CH₃⁺, C₂H₅⁺, C₃H₇⁺, C₄H₉⁺). The XPS analysis confirmed the generation of a boundary film, comprising of sulfide and inorganic fluoride, and being possibly the responsible of decreasing the friction coefficient. The [Bu₃MeP][(MeO)₂PO₂] ionic liquid required a long induction period, it did not form any tribolayer and no reduction of friction coefficient, yielding instead a high abrasion and adhesion mechanism. Thus, it can be concluded that bis(trifluoromethanesulfonyl)amide anion is more effective than dimethylphosphate in generating a surface protective film on the titanium surface under the selected test conditions and the testing methodology seems to be useful to understand the tribodesorption mechanism.

KEY WORDS: ionic liquids, tribo-chemical reaction, mechanisms, vacuum tribometer

1. INTRODUCTION

Ionic liquids (ILs) are room temperature molten salts consisting of large, asymmetric organic cations and usually inorganic anions. Due to the large amount of possible combination and their lubrication capacity [2], ILs have attracted the attention of many tribologists, especially of the field of vacuum tribology, since properties such as high thermal stability, extremely low vapor pressure and high ion conductivity make them excellent candidates for vacuum applications. However, the number of related papers are still limited [3], [4].

Most of the works related to ionic liquids tribology are focused on the relationship between the chemical structure and tribological properties of the ILs [5] [6] [7] [8]. But although there is a good knowledge about the lubricating properties of most common combination of cation and anions, the reaction mechanism and decomposition of ionic liquids is not yet clearly understood.

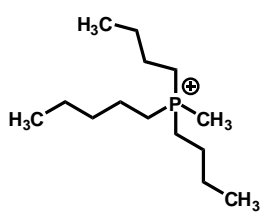
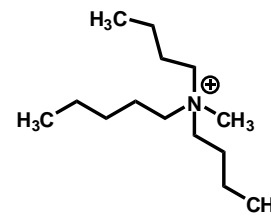
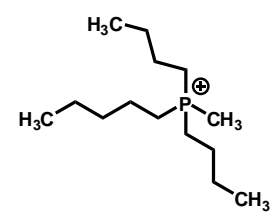
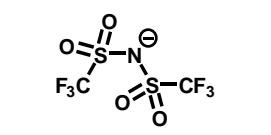
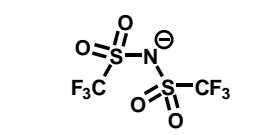
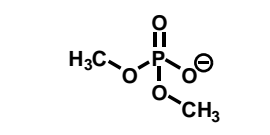
In this work, tribological and tribodesorption characterization of three ILs, for vacuum application is presented. The tribochemical reactions and decomposition mechanism of each ILs is discussed.

2. EXPERIMENTAL DETAILS

Materials

Three kinds of ionic liquids were selected in order to investigate the effects of cation and anion components on friction and wear. Table 1 lists the full names and the chemical structures (hereafter referred to as [Bu₃MeP][Tf₂N], [Bu₃MeN][Tf₂N] and [Bu₃MeP][(MeO)₂PO₂]).

Table 1: Molecular structures of the lubricants.

		IL 1	IL 2	IL 3
Name		Tributylmethylphosphonium-bis(trifluoromethane sulfonyl)amide	Tributylmethyamonium-bis(trifluoromethane sulfonyl)amide	Tributylmethylphosphonium - dimethylphosphate
Abbreviation		[Bu ₃ MeP][Tf ₂ N]	[Bu ₃ MeN][Tf ₂ N]	[Bu ₃ MeP][MeO) ₂ PO ₂]
Chemical structure	Cation			
	Anion			

The tribological test configuration used for the experiments was “Ball on Disc”. In particular, balls with diameter of 3 mm made of Si₃N₄ and discs with diameter of 14 mm and 4 mm thick were used for the test. The material chosen for the disc counterpart was a titanium Grade 5. This titanium alloy is commonly referred to as Ti-6Al-4V because it is composed of titanium alloyed with 6% aluminium, 4% vanadium, 0.25% iron and 0.2% oxygen. These materials were selected due to the reactivity of the titanium and the hardness of the ceramic in order to accelerate the decomposition process of ionic liquids during the tribotests. The specimens were subsequently cleaned in three different solvents (toluene, isopropanol and petroleum ether) for 10 min each, using an ultrasound bath, before and after the experiments. Fresh metal specimens were used for each experiments.

Characterization methods and Test rigs

Thermogravimetry. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/DSC 1 instrument (Switzerland) in the temperature range between 25 and 500 °C at a heating rate of 10°C/min.

Tribological investigations. The tribological performance was evaluated using the CATRI © UHV Tribometer (IK4-Tekniker, Spain) for linear oscillating motion in a ball on disc configuration. This tribometer is illustrated in [Figure 1](#) and has been described elsewhere in detail [49]. The test conditions chosen are summarized in [Table 1](#). Each experiment was performed twice in order to confirm repeatability.

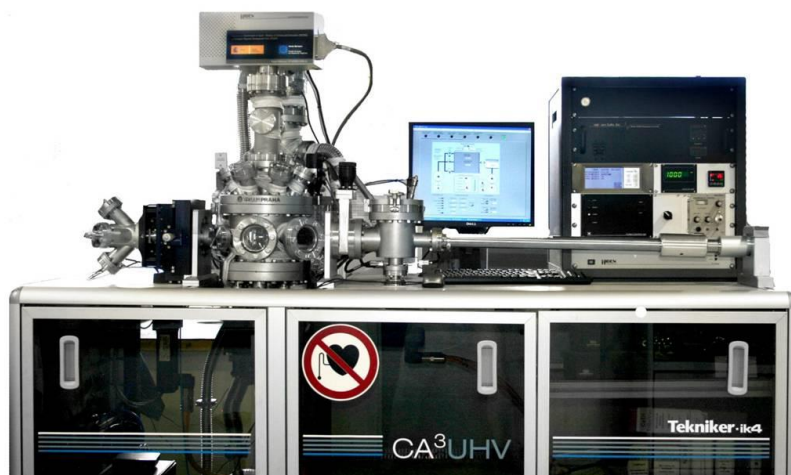


Figure 1. CATRI © UHV Tribometer, IK4-TEKNIKER.

Table 2: Tribological test conditions.

Test Conditions	
Applied load	10 N
Maximum Hertzian stress	1,9 GPa
Sliding velocity	3 mm/s
Oscillation amplitude	3 mm
Test temperature	Room temperature
Cycles	1000
Environment	1×10^{-5} Pa

Tribodesorption measurements. The molecular and fragments ions coming from the tribosystem during the tribological test were monitored by a Fast Response Quadrupole Mass Spectrometer (Q-MS) from Hidden (UK). The Q-MS can measure in two ways: Bar Mode and Multiple Ion Detection (MID) Mode. The Bar Mode displays a histogram of peaks and is used for the identification of chemical components and the determination of some parameters for MID analysis, while MID mode is suitable for quantitative analysis of trace fragments. As it was described above, each tribological test was carried out twice and therefore, each ionic liquid was analyzed using the two modes. The first test was monitored using a Bar Mode for determining the main decomposition fragments, while the second repetition was carried out using a MID analysis of some specific fragments.

The quadrupole mass spectrometer detector is closed to the friction zone of the specimens. Even so, during the tribodesorption measurements, the main pumping valve of the main chamber remains closed so that the gas fragments cannot escape, and only a small orifice is open in order to avoid excessive increase in the pressure. Air was pumped out from the main chamber until reaching ultra-high vacuum regime (around 1×10^{-7} Pa), and then the tribodesorption experiments were carried out in high vacuum regime (around 10^{-6} Pa) by closing the pumping valves.

Surface analysis. The wear scars were examined using a DM 2500 MH Optical Microscope from Leica (Germany) and images were obtained with a magnification of x20. Moreover, the topographies of the worn surfaces were analyzed using an Eclipse ME600 Confocal Microscope from Nikon Instruments Inc. (Germany), and disc wear volumes were calculated from these topographies using a Matlab script developed in IK4-TEKNIKER.

An additional surface analysis was performed on the disk surface after sliding tests using a Thermo Fisher Scientific Theta Probe (East Grinstead, UK) equipped with a monochromatic Al K α X-ray source ($h\nu=1486.6$ eV) and a hemispherical analyzer in order to characterize the chemical composition of it. The measurements were performed at a base pressure of 2×10^{-9} Pa. The elemental and chemical composition of the wear track surfaces on the discs was obtained by spot analysis with an X-ray beam of 100 μ m diameter at a pass energy of 200 eV for the survey spectra and 50 eV for the high resolution spectra. The spectra were analyzed with the Advantage Data System software (East Grinstead, UK), using Gaussian-Lorentzian peak fitting.

3. RESULTS AND DISCUSSION

The thermogravimetric analysis of the lubricants is shown in [Figure 2](#). It can be seen that the two ionic liquids containing bis(trifluoromethanesulfonyl)amide anion have better thermal stability than that containing dimethylphosphate. In particular, the onset temperature for IL 1 and IL 2 were 392 °C and 387 °C, respectively. IL 3 started losing weight around 300 °C.

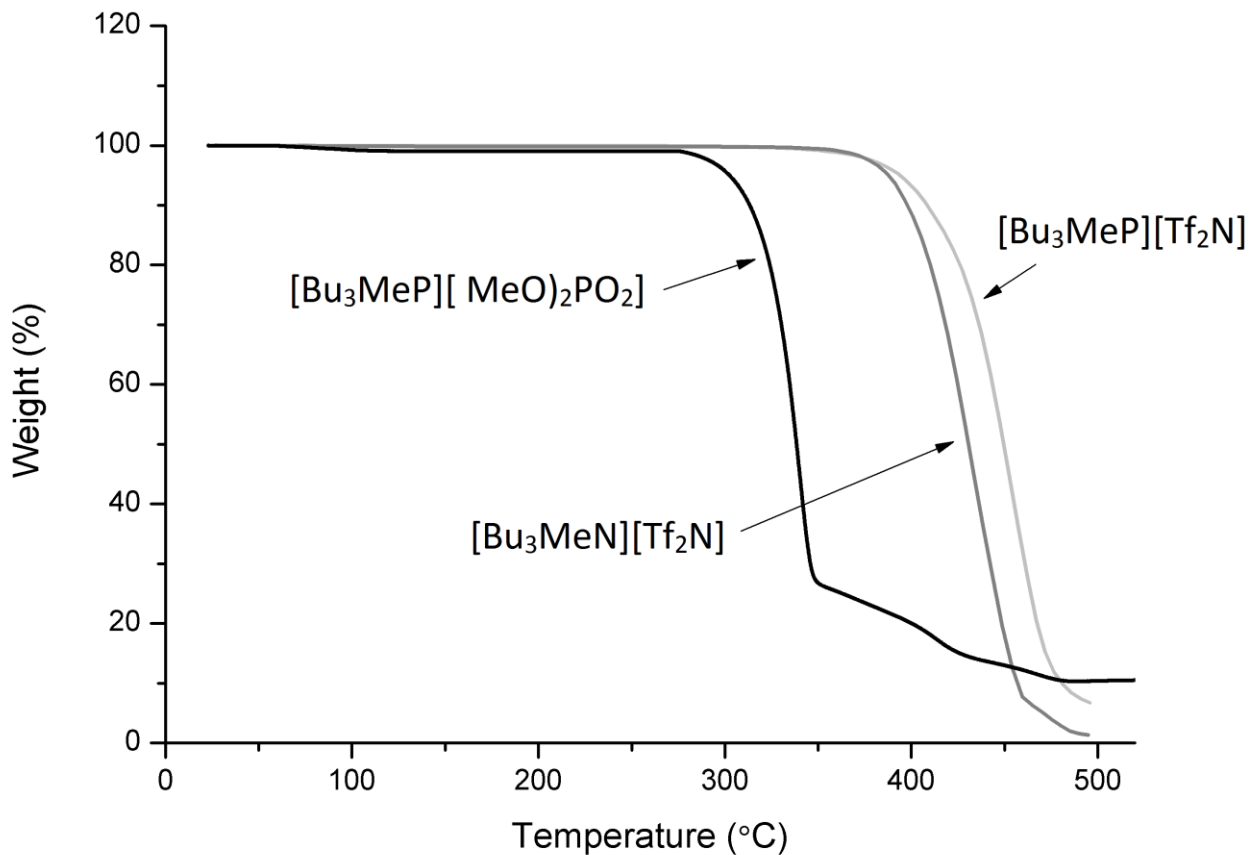


Figure 2: Thermogravimetric analysis diagram of the lubricants.

Tribological Behaviour

Figure 3 shows the average friction coefficient of the steady state regime for each ionic liquid during the tribotests. From previous studies, it was demonstrated that phosphonium phosphate exhibits excellent tribological behavior in combination with steel [10][11], this did not happen in combination with titanium. Actually, the [Bu₃MeP][(MeO)₂PO₂] provided the highest friction among the three lubricants with values exceeding 0.26 while both the other two ionic liquids containing bis(trifluoromethanesulfonyl)amide exhibited lower coefficient of friction with values of 0.1 and 0.11, respectively.

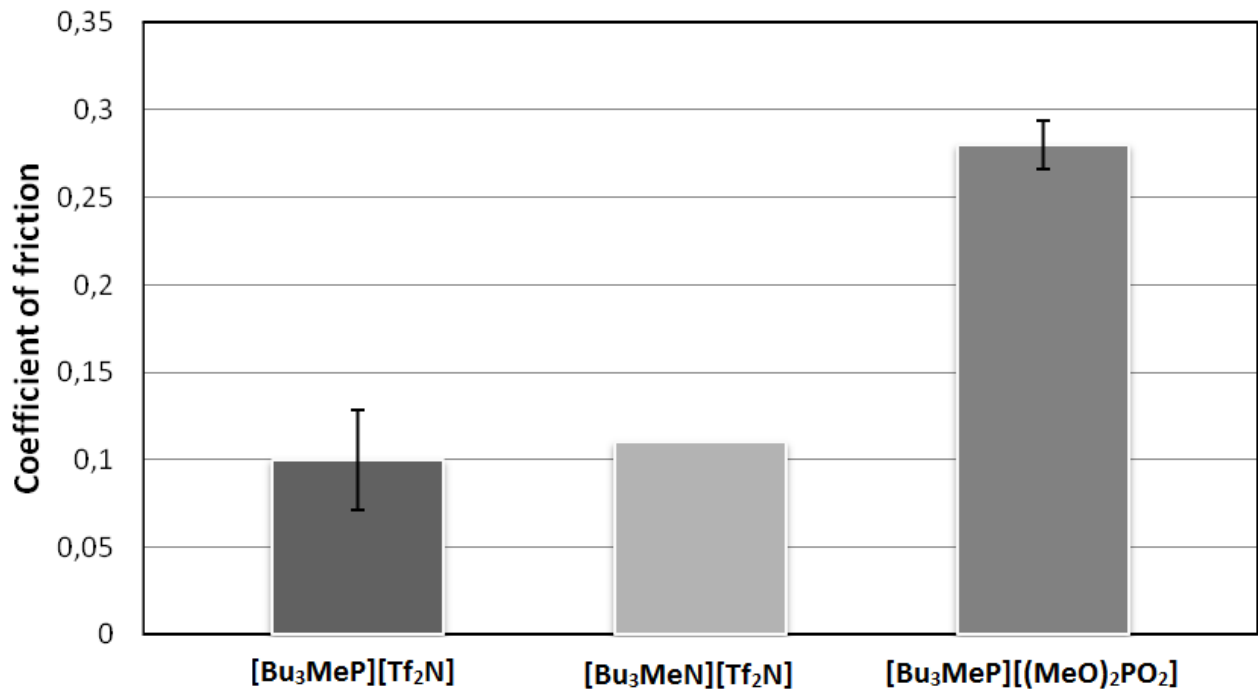


Figure 3: Average of coefficient of friction of the steady-state regime.

In terms of wear, it can be observed that the higher friction exhibited by the IL 3 is accompanied by more severe wear. As matter of fact, the optical analysis of the worn surfaces shows that in this case the wear scar is characterized by high abrasion and adhesion while it seems negligible the influence of chemical reactions on the surface (see [Figure 4](#)). On the contrary, on the disc wear scars of IL 1 and IL 2, it was possible to observe some light sign of chemical reaction was appreciable. [Figure 5](#) shows the wear volume of the disk using each ionic liquid.

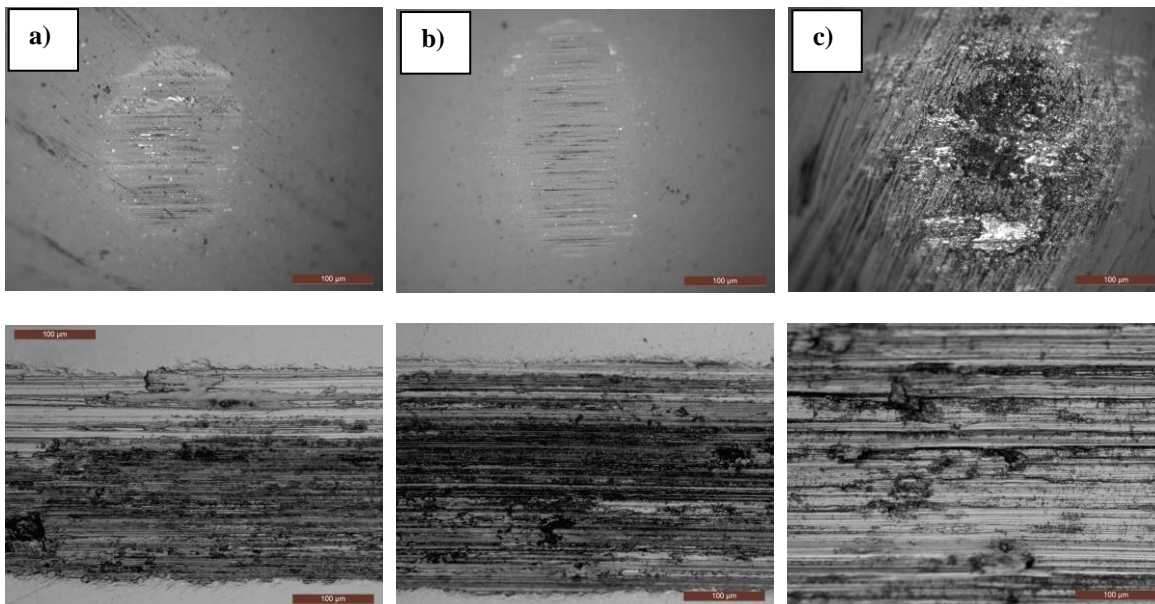
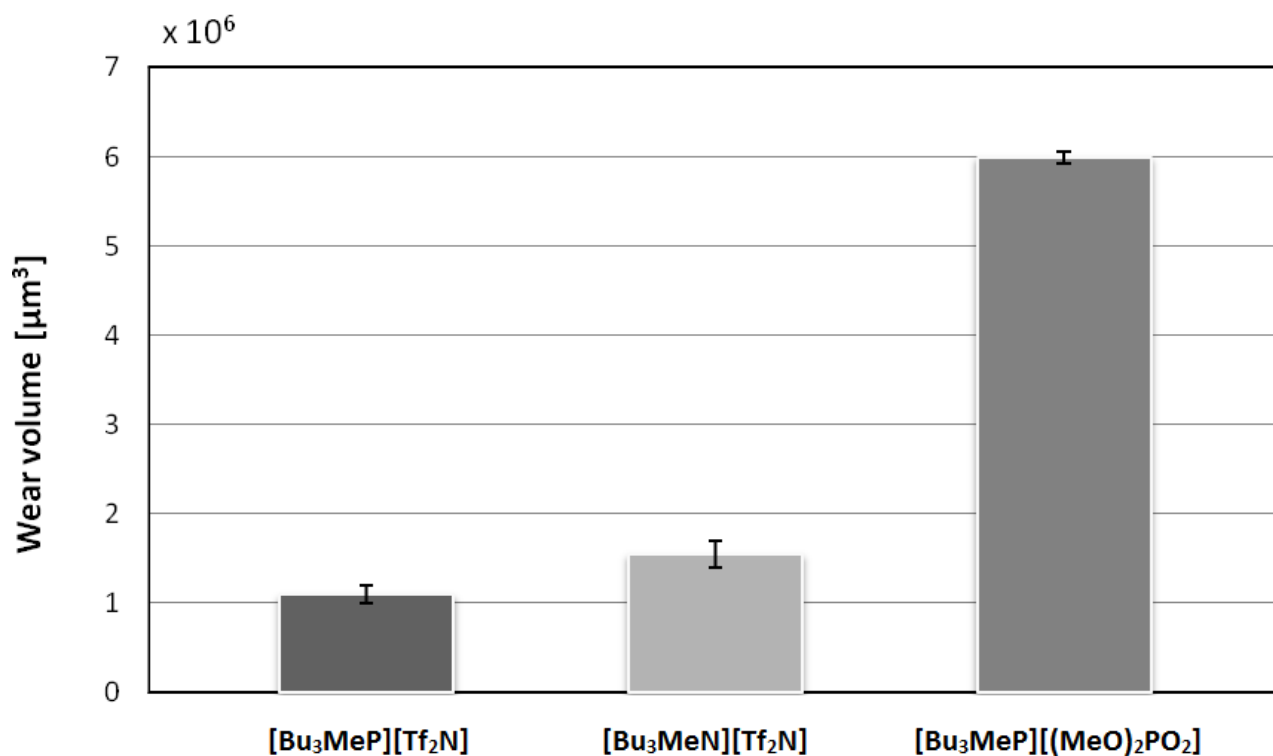


Figure 4: Images of wear scar of ball and disk obtained by the optical microscope for:

(a) $[\text{Bu}_3\text{MeP}][\text{Tf}_2\text{N}]$, (b) $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ and (c) $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$.



(b) Figure 5: Average wear volume on the disc specimen.

In this case, it seems that the role played by the anion for reducing friction and wear is much more important than the role played by the cation. The ionic liquids having the same anion [Tf₂N] showed similar friction and wear performance, even though [Bu₃MeP][Tf₂N] exhibited a slightly lower coefficient of friction and smaller size of wear scar than that for [Bu₃MeN][Tf₂N].

Comparing instead ionic liquids having the same cation, [Bu₃MeP][Tf₂N] showed much lower coefficient of friction and wear scar than that for [Bu₃MeP][(MeO)₂PO₂].

Figure 6 shows the total pressure increment during the test for each ionic liquid. The intensity of the picks increased after certain induction period. For all ionic liquids examined, the total pressure increased when the sliding started and decreased when sliding stopped.

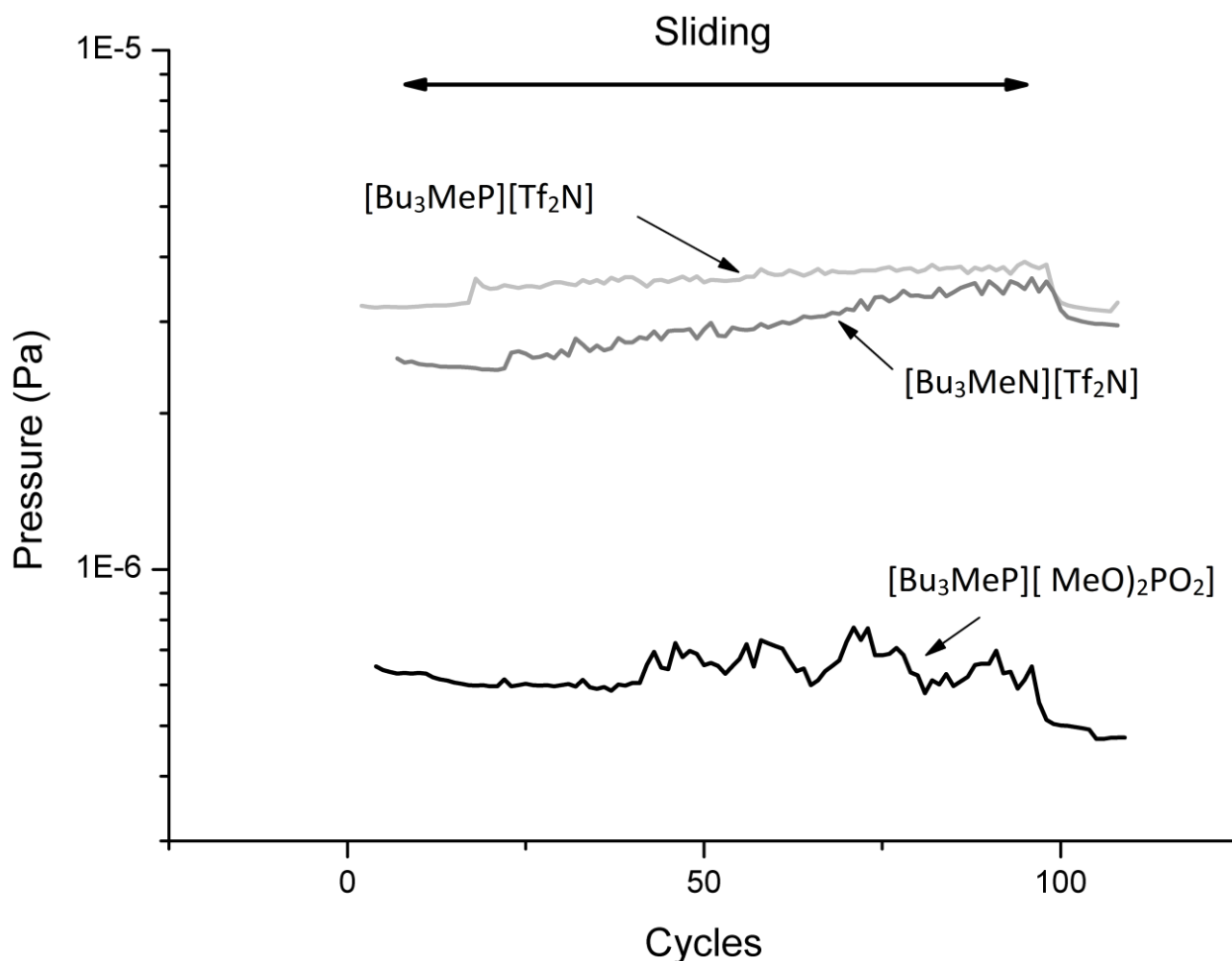
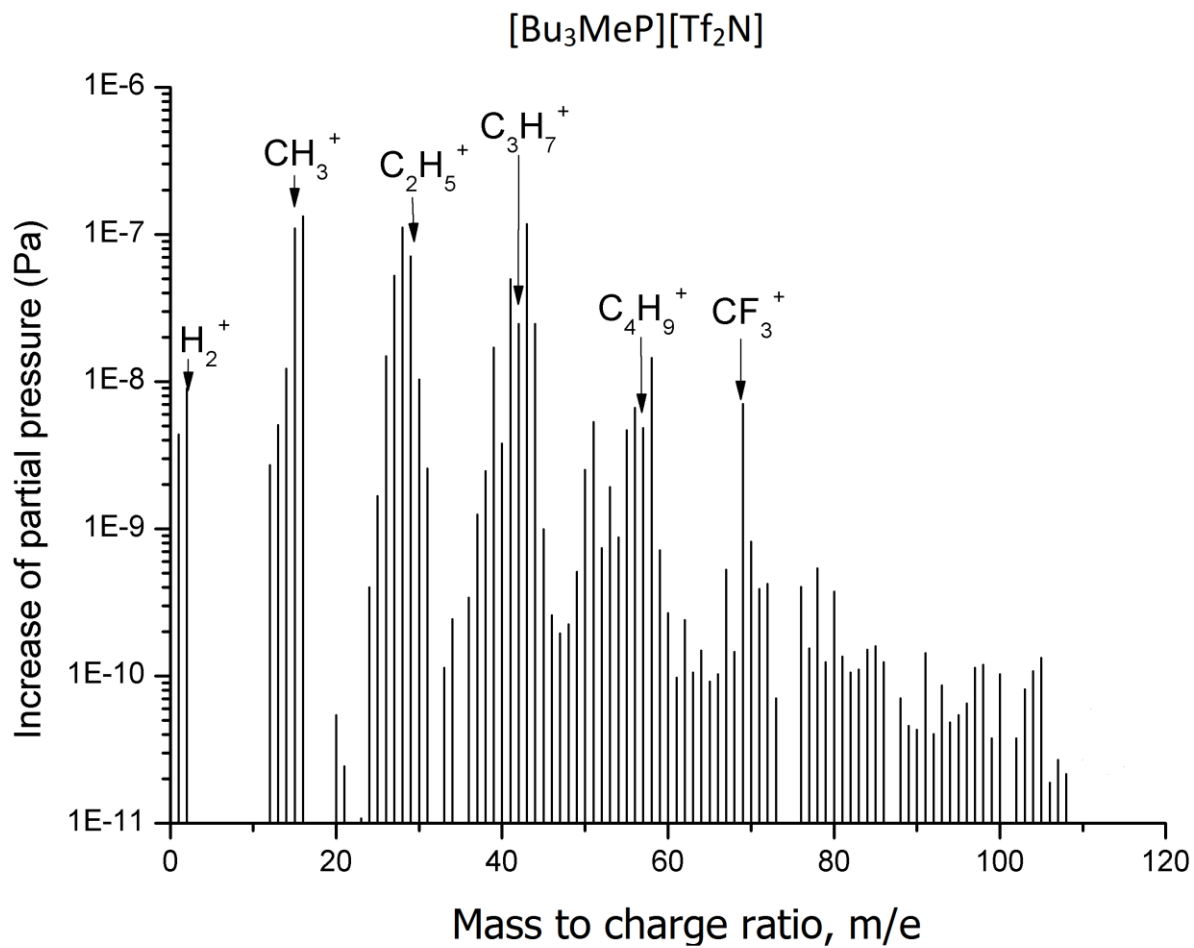
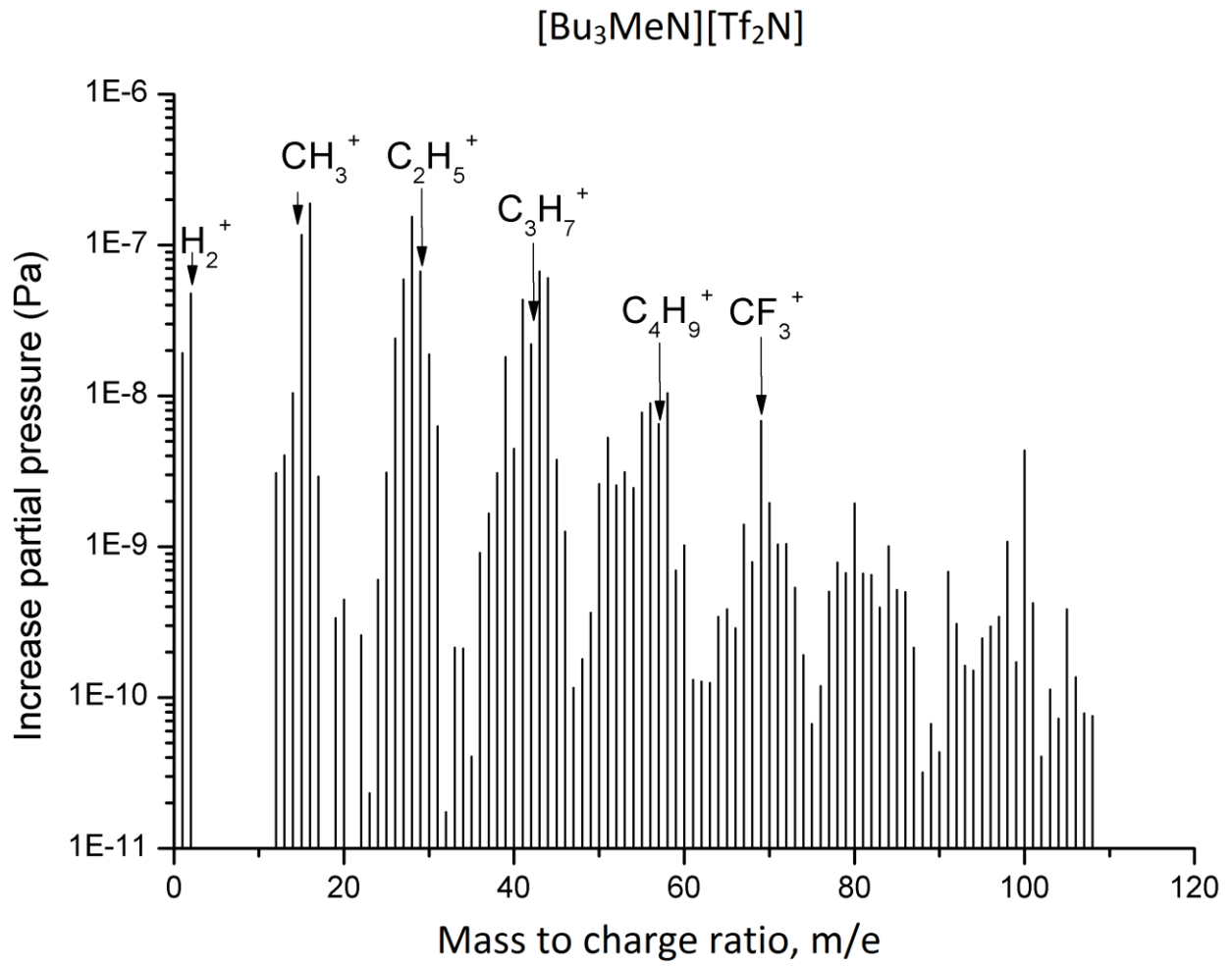


Figure 6: Total pressure increment during during sliding for each ionic liquid.

Figure 7 shows the results of increases in partial pressure (measured in Pascal) for each fragment m/e (where m is the molecular mass and e is the ionic charge) value by sliding in case of $[\text{Bu}_3\text{MeP}][\text{TF}_2\text{N}]$, $[\text{Bu}_3\text{MeN}][\text{TF}_2\text{N}]$ and $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$, respectively. In these images, the x axis shows m/e from 1 to 120, while the y axis shows the increase in Pa as a result of the mechanical action. This increase is defined as the difference between the partial pressure of each m/e value at the instant of maximum total pressure during sliding (Figure 6) and the partial pressure of each m/e before the sliding. The m/e values of 15, 29, 43, and 57 were assumed to correspond to CH_3^+ , C_2H_5^+ , C_3H_7^+ and C_4H_9^+ fragments ions, respectively, released from the cationic components. The m/e value of 69 was assumed to correspond to CF_3^+ derived from the $[\text{TF}_2\text{N}]$ anion. No outgassing of neither oxygen ($m/e=32$) or phosphorous ($m/e=31$) derived from the anion of $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$ was detected.



a)



b)

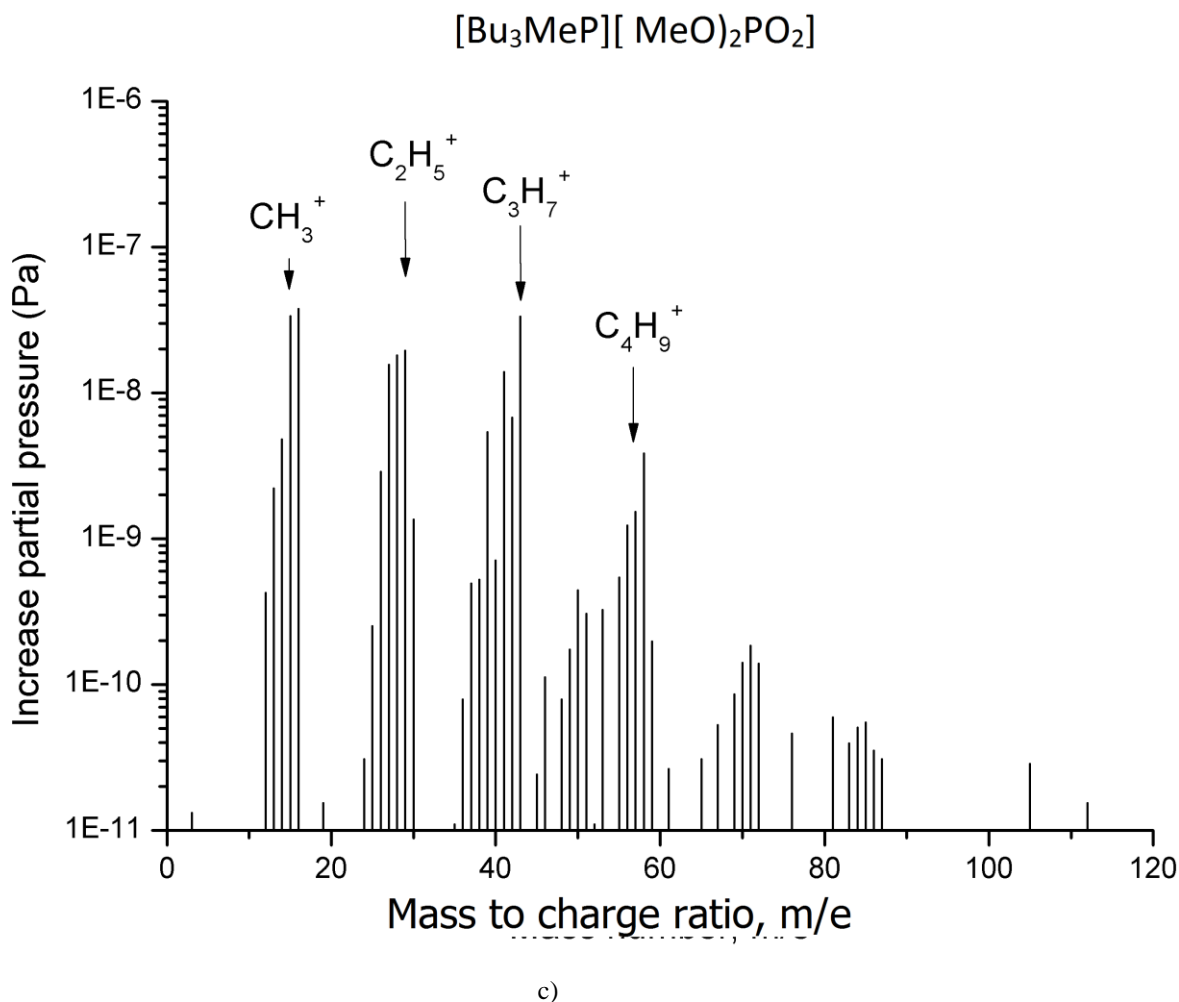


Figure 7: Increasing of fragments partial pressure with sliding for: a) $[\text{Bu}_3\text{MeP}][\text{Tf}_2\text{N}]$, b) $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ and c) $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$.

The time plot for the intensity of these gaseous fragments –that of mass 15, 16, 32, 43, 57, 69 is shown in [Figure 8](#) together with the friction trace in voltage for the test for $[\text{Bu}_3\text{MeP}][\text{Tf}_2\text{N}]$, $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ and $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$, respectively. For IL 1 and IL 2, the partial pressure of all selected gaseous fragments sharply decreased when sliding stopped. For IL 3, these reduction was slightly softer, indicating different mechanisms of decomposition of the ILs.

In case of $[\text{Bu}_3\text{MeP}][\text{Tf}_2\text{N}]$ ([Figure 8](#)), an initial running-in period was observed in the time period of 0-3 min after sliding started, coinciding with the induction period. The end of the tribodesorption induction period is accelerated in the case of trifluorometane ionic liquid by the CF_3^+ release that was detected like a pick in the tribodesorption measurements. During steady-state period m/e values of 15, 29, 43 and 57 derived from the cation were hardly generated. However, outgassing derived from the anion (CF_3^+) was slightly detected during steady state time; it is thought that decomposition of the $[\text{Bu}_3\text{MeP}]$ cation and reaction of the $[\text{Tf}_2\text{N}]$ anion with the track occurred. In the case of $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$, the running-in and the induction periods were similar than those for phosphonium. And similar outgassing behavior also was observed, although for this lubricant, the intensity of CF_3^+ ion during induction period was smaller. After the test stopped, in both cases, all the ion fragments decreased down to initial values.

In the case of $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$, a high friction coefficient was observed throughout the entire testing period. In this case, IL 3· having the worst thermal stability exhibited a longer induction period, concluding that the induction period depends not only on the temperature reached at the contact surface but also on the reactions that take place there. Besides, it was no detected outgassing derived from the anion.

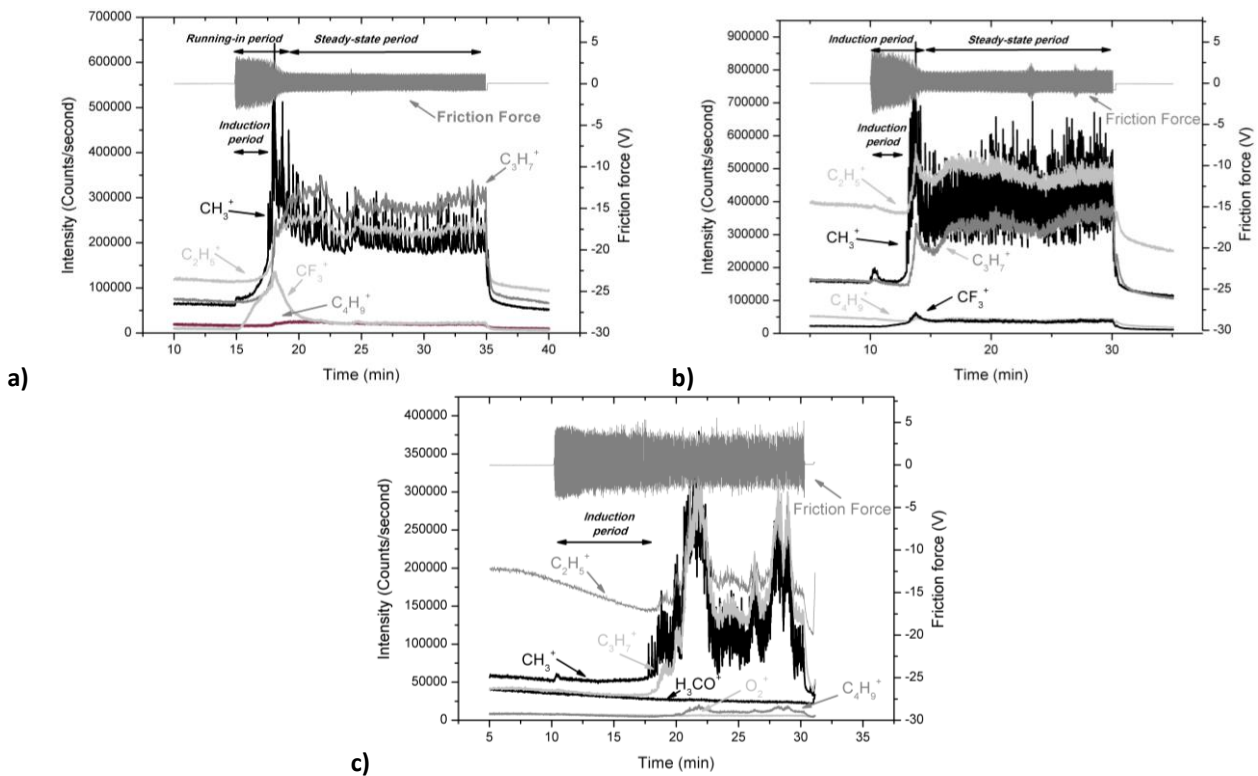


Figure 8: Evolution of different gas fragment intensity and friction force curve in voltage during the test for: a) [Bu₃MeP][Tf₂N], b) [Bu₃MeN][Tf₂N] and c) [Bu₃MeP][(MeO)₂PO₂].

Surface analysis

Figure 5 shows the images of worn surfaces lubricated with [Bu₃MeP][Tf₂N], [Bu₃MeN][Tf₂N] and [Bu₃MeP][(MeO)₂PO₂], respectively. As it was described above, the discs lubricated with IL 3 showed mild abrasive wear and high adhesion, while surfaces lubricated with [Bu₃MeP][Tf₂N] and [Bu₃MeN][Tf₂N] exhibited smoother wear track and chemical attack was appreciable. Therefore, for the interpretation of the chemical surface composition on the discs after the tribometrical experiments, XPS analyses were performed. Sulfide and inorganic fluoride was found inside and outside wear track for IL 1 and IL 2, indicating the reaction of anion with Ti occurred even under static conditions. However, the IL 3, [Bu₃MeP][(MeO)₂PO₂], did not yield a phosphorus-containing boundary film as occurred in reference [1] for steel.

Table 3: XPS analysis results of worn disc surfaces

Sample	Cation	Bu ₃ MeP ⁺		Bu ₃ MeN ⁺
	Anion	(MeO) ₂ PO ₂ ⁻	Tf ₂ N ⁻	
Chemical reaction; XPS analysis	Cation	P was not found	P was not found	P was not found
	Anion	P was not found	Inorganic F, S(II)	Inorganic F, S(II)

4. CONCLUSIONS

In this work, the tribochemical reactions of [Bu₃MeP][Tf₂N], [Bu₃MeN][Tf₂N] and [Bu₃MeP][(MeO)₂PO₂] on titanium surface under boundary lubrication conditions were investigated using the CATRI © UHV Tribometer. Tribochemical decomposition of IL 1 and IL 2 occurred on titanium surface when the surface oxide layer was removed during sliding. In both cases, the induction period observed at the beginning of the tribological tests finalized with the detection of a sharp pick of CF₃⁺. This pick comes from the bis(trifluoromethanesulfonyl)amide anion. This fragment reacts with the titanium surface to form titanium fluoride boundary film that catalyst the tribodesorption of the fragments from the

cation. The boundary film comprising both sulfide and inorganic fluoride, enhanced considerably the tribological properties of the titanium. In the case of IL 3, $[\text{Bu}_3\text{MeP}][(\text{MeO})_2\text{PO}_2]$, the tribotests were characterized by a longer induction period, no desorption of ions derived from anion was detected during the test. XPS analysis showed that there was no phosphorous inside and outside the wear track, indicating that there was no reaction between the titanium and the IL 3. Hence, lubricant may be decomposed due to the temperature reached by friction at the contact. Thus, it can be concluded that bis(trifluoromethanesulfonyl)amide anion is more effective than dimethylphosphate in generating a surface protective film on the titanium surface under the selected test conditions.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

The partners would like to acknowledge the financing to the Austrian Government financing of COMET K2 Excellence Centre of Tribology called X-Tribology to carry out this research collaborative activity. The authors also would like to acknowledge the financing of the EMAITEK Programme by the Basque Country.