

# **Tribological investigations of silicon nitride lubricated by ionic liquid aqueous solutions**

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Water-lubricated ceramic components are promising material combinations for tribological applications because they are wear-resistant and can exhibit low coefficients of friction under different loads. The aim of the work was to show in model tribological experiments with silicon nitride that the lubricating properties of water can be improved by adding water-soluble ionic liquids. The geometry used and the experimental parameters were selected to approximately simulate a piston ring/cylinder liner contact. We found that the addition of 1 % IL tributyl methyl phosphonium acetate[P4441][OAc] leads to a reduction of the maximum friction work by 58 % compared to pure water lubrication and even by 96 % compared to oil lubricated steel. It was shown that suitable running-in conditions and sufficient cooling by the lubricant at an early stage are important prerequisites for achieving low friction and wear values. In addition, the chemical interaction of water and IL with silicon nitride strongly affects the tribological behavior. As increasing demands on sustainability (green tribology) become more and more important due to environmental aspects, this work provides important insights for the development of novel water-based lubricant systems.

Keywords: Silicon nitride; running-in, wear mechanisms, water-based; ionic liquids; tribochemistry, EHL

Subject classification codes: Additives, EHL, Lubricants, Friction, Wear

## **Introduction**

Improving the energy efficiency of mechanical systems is one of the key factors in reducing global energy consumption [1]. Reciprocating piston engines, such as micro-scaled combined heat and power (CHP), are very efficient for generating energy with combined heat and power [2]. Using the waste heat, an efficiency of up to 90 % (based on the calorific value of the fuel) can be achieved [3]. However, CHPs must meet specific requirements such as long service life and maintenance cycles as well as high electrical efficiency. These properties are dependent on wear and friction in the

piston/piston-ring/cylinder group. In established systems, the mechanical parts are made of light metal, cast iron, spheroidal graphite iron or alloyed steels and lubricated with engine oil [4]. Typical coefficients of friction (COF) in the upper part of the cylinder liner are about 0.01 to 0.15 [4]. An overview of the evaluation of piston dynamics, lubrication and tribological performance showed that gas emissions and the efficiency of combustion engines can be improved most cost-effectively by reducing friction [5]. To optimize the friction behavior, piston rings were coated with PVD [6] and ceramic [7] and manufactured from TiSiCN nanocomposite [8]. In addition, the honing process of ceramic-coated piston rings and cylinder liners was investigated for their influence on wear [9]. Various concepts of all-ceramic piston engines without lubricants, with solid or with oil-based lubricants were investigated, but tribological aspects were not primarily considered [10].

With regard to the effect of water in the combustion chamber, many studies have been continuously carried out since 1977 which showed a high benefit for efficiency and lower emissions [11]. For example, water can be used to cool the combustion chamber before ignition [12]. The studies in [13] show that at water content of 15 % in the fuel, the best engine performance is achieved by the higher effective mean pressure and cooling of certain engine parts. These studies describe the positive effect of water injection into the combustion chamber for temperature control or to improve combustion efficiency and exhaust gas composition. However, it should also be noted that water can cause corrosion in conventional combustion engines [13], which could be neglected by the use of ceramics. Gates and Hsu investigated the boundary lubrication behavior of silicon nitride with alcohols [14], phosphorus-containing organic compounds [15], sulfonate, phenate and salicylate compounds [16] and discussed the effect of oxygen compounds [17]. They show that tribochemical reactions lead to the

formation of specific interfaces in the wear scar which strongly influence the tribological behavior. Investigations on water lubricity and on the wear mechanisms of silicon nitride ( $\text{Si}_3\text{N}_4$ ) describe that tribochemical wear causes the formation of an amorphous protective layer which leads to a reduction of friction and wear [18]. The formation of silica  $\text{Si}(\text{OH})_4$  is activated by friction as a function of contact pressure, sliding speed, humidity [19] and temperature [20]. This results in an ultra-smooth surface and a very thin hydrodynamic lubricating film is formed even at very low sliding speeds [18]. Coefficients of friction lower than 0.002 were measured for hydrodynamic lubricant sets. These are unique system properties which promise excellent application possibilities for bearing and sealing applications. It is assumed that lubrication can be partially hydrodynamic due to the ultra-smooth surface and partial boundary lubrication due to a hydrated colloidal silica layer. Soft and soluble layers of oxides or hydroxides form on traces of wear in humid air and water, which smoothes the surface [21]. The reaction film formed during rubbing, mostly as a result of mechanical-chemical reactions, should consist of colloidal silicon dioxide with an outer diffusion layer [22]. Wan et al. [23] found out that the addition of water can improve the tribological high-temperature properties of steel compared to  $\text{Si}_3\text{N}_4$  due to tribochemical reactions. These investigations show the high sensitivity of the ceramic water system to various tribological parameters and test conditions. Due to its system properties, silicon nitride is a promising material which offers excellent application possibilities for plain bearings and sealing tasks with water-based lubrication [18]. Since 2001, ionic liquids (ILs) have been at the center of specific tribological investigations. Some researchers have shown that aqueous lubrication systems can also be successfully improved with the aid of ILs [28], [29]. Tribological tests with a mixture of water with 2-methyl-

[C<sub>1</sub>C<sub>2</sub>im] BF<sub>4</sub>/PF<sub>6</sub> improve the bearing capacity and reduce the coefficient of friction for Si<sub>3</sub>N<sub>4</sub> [30].

Own preliminary work showed that externally or galvanically induced electrochemical potentials can improve the tribological behavior of the ionic liquid aqueous solution of steel systems [31], [32], silicon carbide and diamond-coated silicon carbide [33], [34]. In addition, it was found that their tribological properties strongly depend on the chemical structure of IL [35]. Therefore, ILs have a high potential for the development of environmentally friendly lubrication systems called "green lubricants" [36], [37]. The reference to green tribology consists in the development of an environmentally friendly and low-wear lubricant. ILs influence the tribosystem Si<sub>3</sub>N<sub>4</sub> in water by reducing running-in times [30], [38]. Current studies on the tribochemistry of silicon-based materials and ILs are published in [39]. The aim of this work is therefore to show in model tribological experiments with silicon nitride that the lubricating properties of water can be improved by the addition of special ionic liquids. The experimental parameters were chosen to approximate a contact between piston ring and cylinder liner. As the increasing demands on sustainability become more and more important for environmental reasons, this work provides important insights for the development of novel water-based lubrication systems.

## **Experimental**

An oscillating test arrangement was selected for the tribological tests. This simulates approximately the motion of a piston engine, whereby the HU width is significantly smaller than in the real application. The testing machine used is from Optimol Instruments Prüftechnik GmbH (Optimol SRV IV). Figure 1 shows the test configuration schematically. The linear wear rate is measured during the test with a capacitive measuring system. The friction force is measured with a piezo force

measuring element. Each COF value is the maximum measured over a period of one second. Since the sliding velocity oscillates sinusoidal, the COFs represent the peak values at the reversal point. The temperature control and heating takes place directly under the test object by means of a thermocouple sensor. In order to evaluate the temperature values, the temperature between the specimens was also measured before the tests.

Gas pressure sintered silicon nitride with the manufacturer's designation SN-GP of FCT Ingenieurkeramik GmbH (Table 1) was used as test material for base and counter samples. This material was chosen because it is used in mechanical engineering and bearing applications. The contact surfaces of the samples were given a surface quality by grinding with a surface roughness  $R_a$  of approx.  $0.3 \mu\text{m}$ . XPS measurements show that the ceramic has high carbon content within the first 200 nm (Figure 2a). From 200 to 1000 nm there is a high oxygen concentration and a lower proportion of nitrogen and silicon. The contact surfaces were cleaned with ethanol before the tests. The intermediate media used were tributylmethylphosphonium acetate [P4441][OAc] (purity > 97 %, halide < 1 %, water: 0.15 %) and tributylethylphosphonium diethylphosphate [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] (purity > 98 %, water: 0.17 %), which contain some impurities due to synthesis (Figure 2, Co. Iolitec GmbH). These ILs were chosen because they differ essentially in their anion (acetate and diethyl phosphate), which leads to different viscosities  $\eta$  ( $\eta = 113 \text{ mPa}\cdot\text{s}$  for [P4441][OAc] and  $\eta = 405 \text{ mPa}\cdot\text{s}$  for [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] at 25°C) and both are soluble in water. A cation with alkyl chains was chosen to give the water an oily character for lubrication. However, care had to be taken that the alkyl chains were not too long in order not to reduce the polarity too much. The ILs were diluted with water ( $w_{\text{IL}} = 1 \text{ mass } \%$ ,  $\eta_{\text{water}} = 0.93 \text{ mPa}\cdot\text{s}$  at 25 °C), increasing slightly the viscosity to  $\eta_{1\%[\text{P4441}][\text{OAc}]} = 0.97 \text{ mPa}\cdot\text{s}$  and  $\eta_{1\%[\text{P4442}][(\text{EtO})_2\text{PO}_2]} =$

0.96 mPa·s at 25 °C. To compare the ceramic tribosystem with a conventional tribosystem, tests were performed on hardened and polished 100Cr6 samples with SAE 10W-40 engine oil ( $\eta = 179$  mPa·s at 25°C).

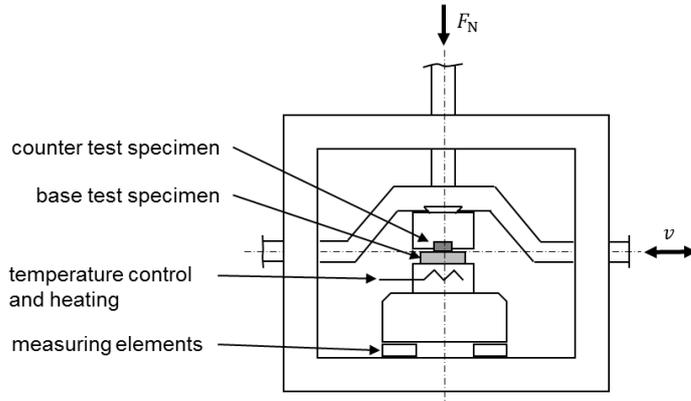


Figure 1. Schematically illustration of the oscillating test setup with applied normal force  $F_N$  and velocity  $v$  in sliding direction (according to DIN 51834-1:2010-11).

Table 1. Material properties of the basic and counter test specimens.

Si <sub>3</sub> N <sub>4</sub> cylinder/disk	
manufacturing process	gas pressure sintered
sinter additives	Y <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub>
secondary phase fraction in %	10
density $\rho$ in 10 <sup>3</sup> kg/m <sup>3</sup>	3.18 to 3.40
Vickers hardness in GPa (DIN EN 843-4)	15
bending strength $\sigma_B$ at 25 °C in MPa (DIN EN 843-1)	730
R <sub>a</sub> in $\mu\text{m}$	0.39
Steel 100Cr6 ring/disk	
ring hardness (HRD)	60
ring R <sub>a</sub> in $\mu\text{m}$	0.22
disk hardness (HRD)	62
disk R <sub>a</sub> in $\mu\text{m}$	0.05

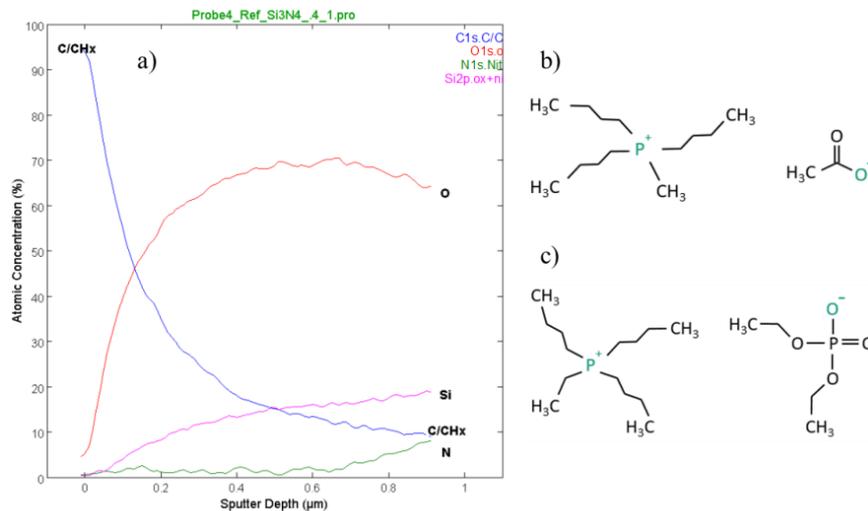


Figure 2. Reference XPS-spectra of  $\text{Si}_3\text{N}_4$  ceramic sample (a). Ionic liquids: (b) tributyl-methyl-phosphonium acetate [P4441][OAc] and (c) tributyl-ethyl-phosphonium diethyl-phosphate [P4442][(EtO) $_2$ PO $_2$ ].

Tribological test methods outside of engines for the system "piston ring/cylinder liner" were developed in [40]. The authors provide parameter settings for an application-oriented load spectrum to simulate the tribological behavior in the upper part of the cylinder liner of a piston ring/cylinder liner. The settings used in this paper refer to the work of Woydt and Kelling [40] (Table 2). The surface contact used in this paper permits an application-oriented contact pressure of approx. 2 MPa, which corresponds to the references in the literature [41], [42]. The maximum slide way pressure between piston skirt and cylinder liner is approximately equal to the contact pressure between piston ring and cylinder liner at a combustion pressure of approximately 1.5 MPa to 6 MPa. In order to achieve a defined plane-parallel contact and to identify suitable running-in conditions for the tribological system, the contact surfaces were rubbed at 5 MPa and 0.08 m/s sliding speed without lubrication. The friction tests were then carried out at 30 °C and 100 °C contact surface temperature. Permanent lubrication was provided by a reciprocating diaphragm pump.

Table 2. Used test procedure for simulating piston ring/cylinder liner contact.

	test procedure [1]	applied test method
ambient medium	hot oil bath (180 °C)	laboratory air/lubricant
motion mode	oscillating or continuous	oscillating
normal force $F_N$ in N	50	50
contact pressure $p_N$ in MPa	-	2
mean sliding velocity $v$ in m/s	0.3	0.24
maximum velocity in m/s	-	0.38
frequency $f$ in Hz	-	60
oscillation stroke $s_{\text{stroke}}$ in mm	-	2
contact surface temperature $T$ in °C	180	30, 100 °C (dry 150 °C)
test duration $t$ in h	approx. 22	16
sliding distance $s$ in km	approx. 24	13.8

The surface topography of the wear track was analyzed microscopically on different scales with light microscopy (digital microscope VHX-500F, Co. Keyence) and laser scanning microscopy (Color 3D laser microscope, VK-9700K, Co. Keyence) as well as scanning electron microscopy (Supra 40 VP, Co. Zeiss). Using X-ray photoelectron spectroscopy (XPS, Leybold MAX 100; argon ion sputtering with sputtering rate: 2.5 nm/min; 1 kV; 500 nA; diameter check point ~ 2mm), the material composition of the tribologically stressed boundary layer was investigated in order to identify possible interactions of the lubricant with the contact surface of the test specimen.

## Results

In a first step, the surfaces were tribologically pre-treated to obtain a smooth and defined plane-parallel connection between the upper and lower specimens. Stricter tribological test conditions were therefore selected than in the friction tests to simulate the piston ring contact with the cylinder liner in order to shorten the test time. As shown in Figure 3a, high wear occurs at a higher contact pressure of approximately 5 MPa and

low sliding speed of 0.08 m/s, compared to 2.5 MPa at 0.24 m/s. These results show that the running-in conditions can be changed by contact pressure and sliding speed so that the process only takes 1.5 h (Fig. 3b).

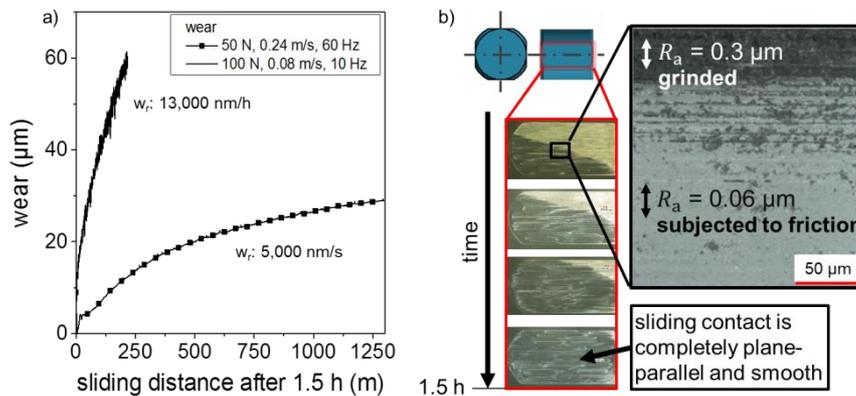


Figure 3: Running-in behavior: a) Comparison of in-situ wear generation at 50 N, 60 Hz, 0.24 m/s, dry, 1.5 h (wear rate: 5,000 nm/h) and 100 N, 10 Hz, 0.08 m/s, dry, 1.5 h (wear rate: 13,000 nm/h); b) Surface analysis of wear scar using laser microscope after different testing times ( $R_a$  between 0.06 and 0.14  $\mu\text{m}$  crosswise to the sliding direction). The roughness values ( $R_a$  between 0.06 and 0.14 transverse to the sliding direction) in the wear track are about three times lower than on the ground surface before the running-in tests. In order to obtain an overview of the system behavior at different contact surface temperatures, the temperature was gradually increased from 182 °C to 336 °C ( $v = 0.24$  m/s,  $F_N = 50$  N,  $p_N = 2$  MPa). If the water supply is too low, the supplied liquid evaporates immediately on the sample surface and no lubrication takes place, which leads to high friction and high wear. By means of a sufficient continuous water supply with the piston diaphragm pump, the temperature in the contact surface could be kept constant at 100 °C by simultaneously measuring the surface temperature and controlling the heating power. The water supply had to start already during the heating phase. Under these conditions, minimum COFs of 0.02 could be achieved at any temperature, interrupted by solid contacts of the friction pairings with short-term

friction peaks. During this mixed lubrication regime, wear leads to a reduction in roughness and the surfaces are adapted to each other (Figure 4).

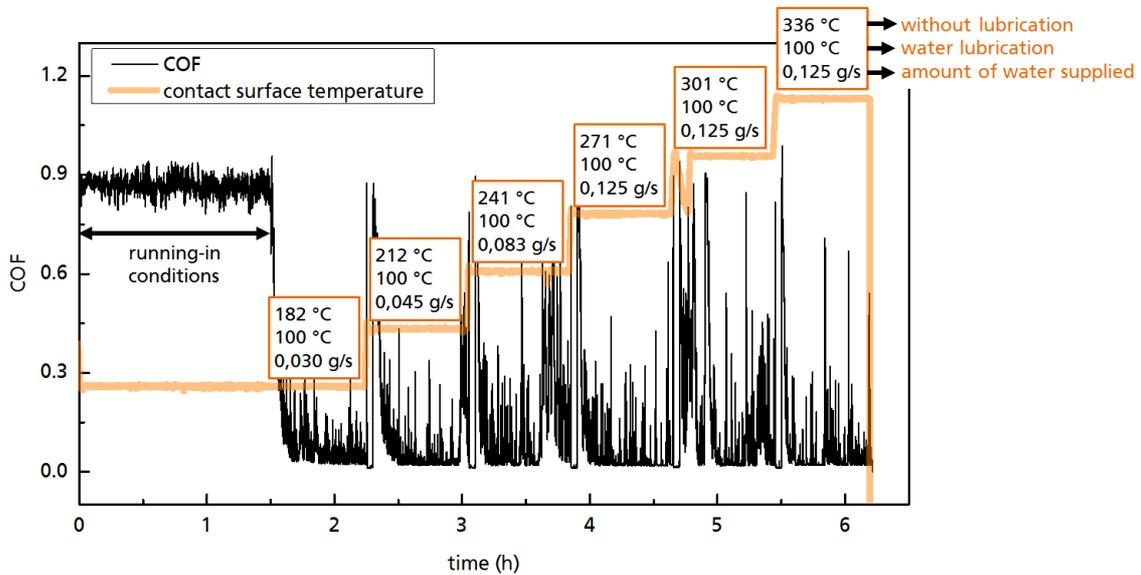


Figure 4: Coefficient of friction at different contact-surface temperatures between 182 °C and 336 °C using test parameters:  $v = 0.24$  m/s,  $F_N = 50$  N,  $p_N = 2$  MPa. After identification of running-in parameters and amount of water supply friction tests were carried out at 30 °C and at a surface temperature cooled to 100 °C (surface temperature would be 150 °C without cooling) with the test procedure given in Table 2. The quantity of intermediate medium supplied to cool the contact surface from 150 °C to 100 °C was about 0.03 g/s. Figure 5 shows the friction behavior of the different systems with 16 h test time depending on the intermediate medium and the temperature. Within the tribosystem 100Cr6/10W-40 there are no friction spikes and the COFs are between 0.08 and 0.16 depending on temperature and test time whereas lower COF was measured at 30 °C. The ceramic tribosystem lubricated with pure water shows a running-in behavior at any temperature. Friction spikes occur at 30 °C until the end of the test. With [P4441][OAc], the running-in time is the shortest. At 100 °C a COF of 0.028 is reached after 2 minutes and only very few and low friction spikes occur. With this tribosystem, the lowest COF ( $\mu_{\text{end}} = 0.021$ ) was measured. Using

[P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] at 100 °C there are three severe rises of COF. Since the COF values illustrated in Figure 5 represent the static friction values or COF values at the reversal point, without hydrodynamic influences, the maximum friction work  $W_{f,max}$  can be calculate by integration of COF over sliding distance. Figure 6a illustrates the calculated  $W_{f,max}$  of the friction tests with different lubricants (according to Figure 5). While at 30 °C the intermediate medium has only little influence on the friction work  $W_{f,max}$  of the ceramic tribosystems, it is significant at 100 °C. In case of intermediate medium tributyl-methyl-phosphonium acetate [P4441][OAc] 58 % less maximum friction work was measured compared to the pure water system and 96 % less friction to the conventional steel/oil tribosystem. With the load spectrum used, wear was too small to measure with the Optimol detection cell for the Si<sub>3</sub>N<sub>4</sub>/water as well as steel/oil systems.

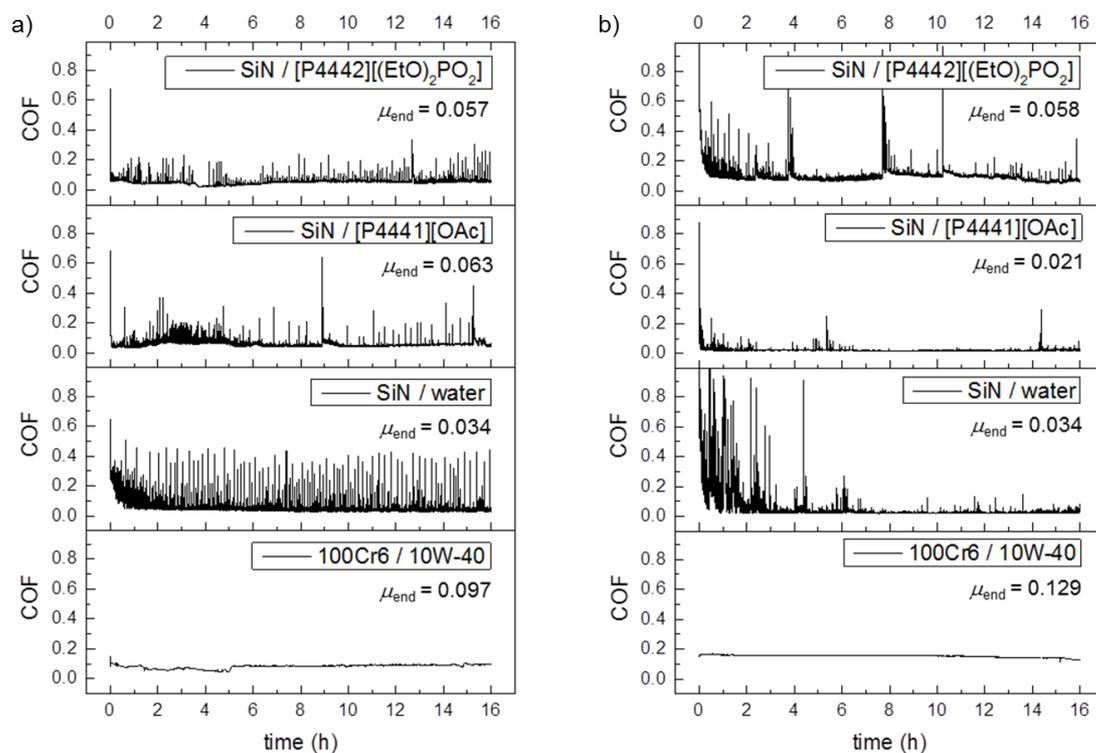


Figure 5: Coefficients of friction with the conventional tribosystem (100Cr6/10W-40) compared with the ceramic tribosystem using different intermediate media distilled

water, [P4441][OAc] and [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] at a) 30 °C and b) 100 °C contact surface temperature. Load spectrum:  $v = 0.24$  m/s,  $pN = 2$  MPa,  $t = 16$  h.

Wear rates are illustrated in Figure 6b. In contrast to dry lubrication conditions (Figure 3) wear rate is much lower and in the range of <200 nm/h for tests at room-temperature. In the 100°C tests, the wear rate can no longer be measured because the wear is below the resolution limit and temperature effects interfere with the measurement.

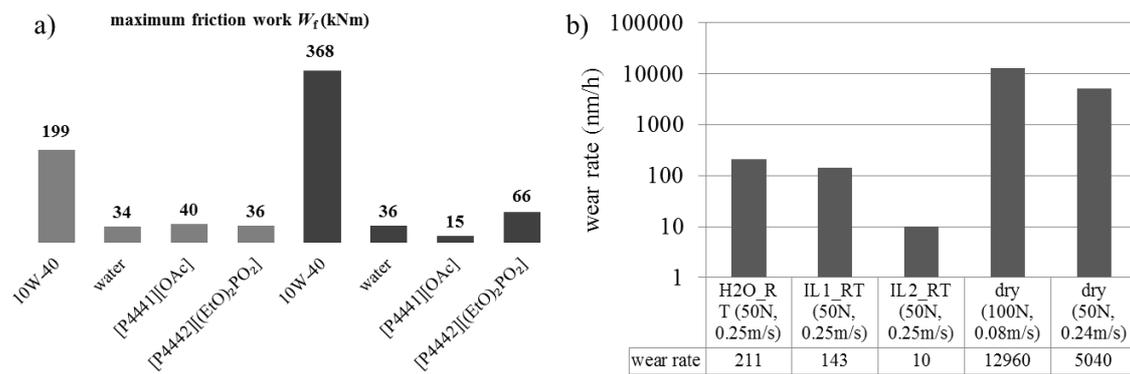


Figure 6: a) Maximum friction work at 30 °C and 100 °C with the conventional tribosystem (100Cr6/10W-40) and the ceramic tribosystem using the different intermediate media distilled water, [P4441][OAc] and [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] within the first 5 h, last 5 h and the whole testing time. Load spectrum:  $v = 0.24$  m/s,  $pN = 2$  MPa,  $t = 16$  h; b) Wear rate at the end of the friction test (no values for tests at 100 °C as wear rate is too low for measuring system)

Figure 7 shows the surface profiles after friction tests with [P4441][OAc] at 30 °C and 100 °C contact surface temperature. The surface roughness in the wear tracks measured in sliding direction after the tests is smaller than before the tests. The surface profile in the sliding direction is about one order of magnitude lower than crosswise. The characteristics of the wear tracks examined with SEM are shown in Figure 8. Different wear mechanisms can be observed dependent on the temperature and the intermediate media. Figure 8a shows the wear track after the friction test at 30 °C with pure water. A very homogeneous, smooth surface can be seen and also a cluster on the

surface consisting of small wear particles is visible. Figure 8b and c shows the very smooth surface after friction test at 30 °C with the intermediate media [P4441][OAc] and [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>]. Figure 8d shows the wear track after the friction test at 100 °C with pure water. There are grooves on the smooth surface in the sliding direction and a ditch in the transverse direction filled with a cluster of wear particles. In contrast, after friction test at 100 °C with intermediate medium [P4441][OAc] besides the smooth surface there are wear particles visible (Figure 8e). A particular point on the wear track at 100 °C with intermediate medium [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] is illustrated in Figure 8f in which the silicon nitride crystallites are exposed. Investigations of the distribution of chemical elements on the wear track using XPS reveal that oxides formed to a depth of approximately 50 nm at 100 °C using [P4441][OAc] (Figure 9). The measured ratio of the atomic fractions between nitrogen and silicon deviates significantly from the stoichiometric composition (N/Si = 1.33) up to a depth of approx. 25 nm. Similar oxide layers are not found on any other wear track.

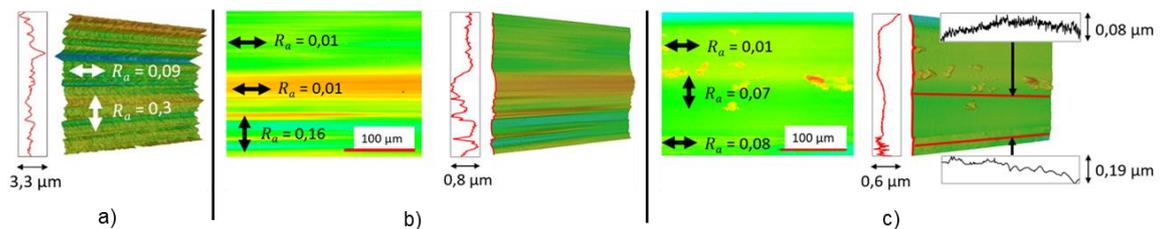


Figure 7: 3D-surface profiles on the counter test specimens of the silicon nitride samples (a) before the friction tests and after the friction tests at (b) 30 °C and (c) 100 °C, measured with laser-scanning-microscopy. The used intermediate medium is [P4441][OAc].

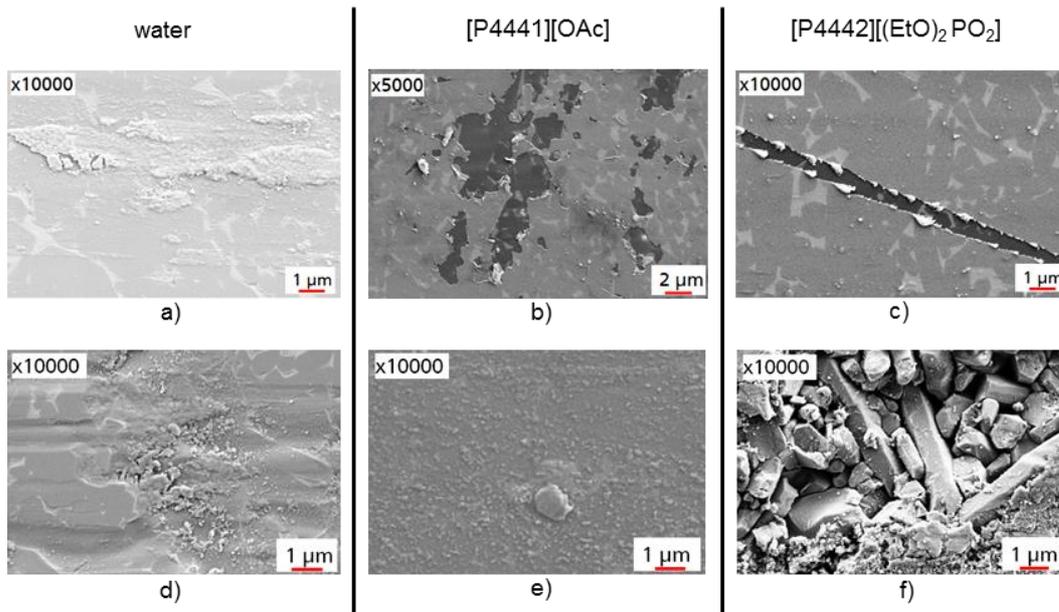


Figure 8: SEM analysis of the wear track at 30 °C (a, b, c) and 100 °C (d, e, f) with the intermediate media distilled water, [P4441][OAc] and [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>].

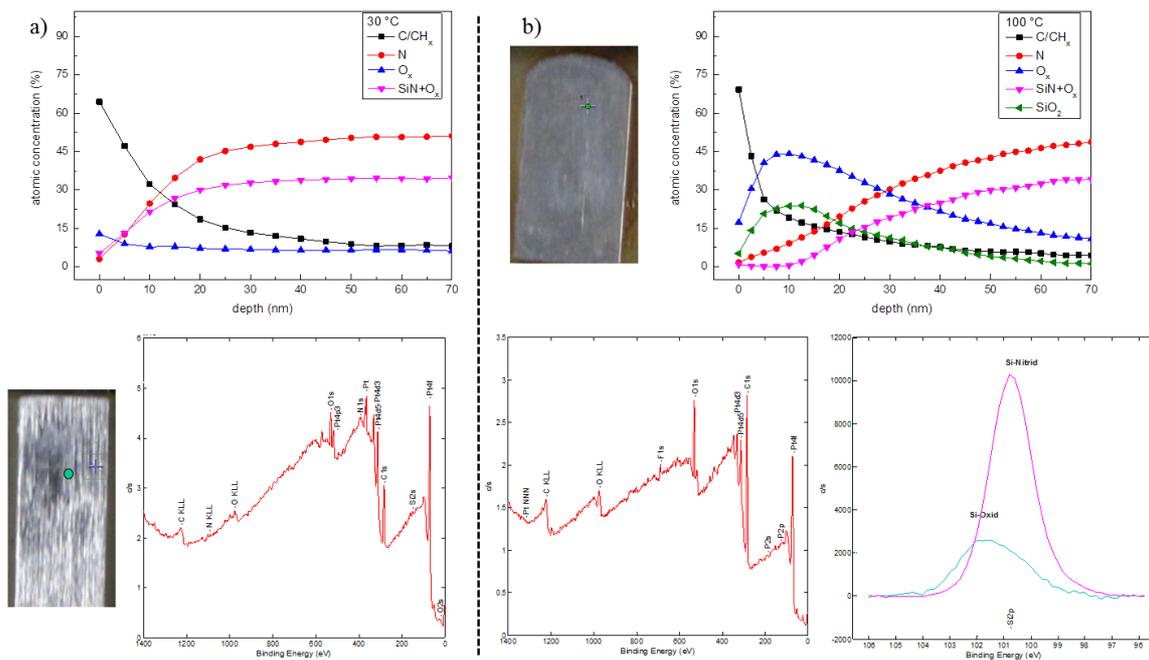


Figure 9: Atomic composition of the surface after the friction tests with the intermediate medium [P4441][OAc] at (a) 30 °C and (b) 100 °C, using XPS sputtering method. At 100 °C a silicon dioxide layer has been detected.

## Discussion

The parameters used for the model tribotest are quite similar to a real cylinder/piston system, but the influences of the combustion gases, pressure and temperature fluctuations as well as the kinematics of the tribological stress are not taken into account. In contrast to the evaluated test configuration in [40], the intermediate medium was added dropwise instead of immersing the samples. Since the sliding velocity oscillates sinusoidal between 0 m/s and 0.38 m/s ( $v_{\text{medium}} = 0.24$  m/s), the coefficient of friction (COF) represents the friction value at the reversal point of the sinusoidal movement (data acquisition rate: 1 per second). It is assumed that the actual COFs over the entire glide path are lower due to increasing hydrodynamic effects at higher speeds. The wear was too low to be measured with the capacitive measuring system used. In the case of tributylmethylphosphonium acetate [P4441][OAc] a COF  $\mu_{\text{end}} = 0.021$  was measured. Application-oriented friction tests were also carried out in [43] for the piston cylinder liner system with a conventional steel tribosystem (continuous sliding, 100 °C, 2.5 MPa). At a comparable sliding speed, the COF was higher than 0.15. A COF of 0.025 was only achieved at 8 m/s. Compared to the COFs in [44] and [43], the COFs achieved with the ceramic tribosystem are more than one order of magnitude lower. There are two possible reasons for the low friction detected. On the one hand, the surface roughness of the sliding surfaces is considerably smoother. The lubricating film thickness in friction tests at 30 °C can be estimated at 300 nm for pure water according to [45]. Since the viscosity changes only slightly with the addition of 1% IL, the decisive factor for the formation of hydrodynamic conditions should be roughness. The layer thickness ratio or lambda ratio describes the relationship between layer thickness and surface roughness. For [P4441][OAc] the lambda ratio is calculated to 1.4 (mixed lubrication) and 3.1 (elastohydrodynamic lubrication) for [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>]. It is also assumed that the formation of an oxide layer observed at 100 °C with

tributylmethylphosphonium acetate [P4441][OAc] at 100 °C reduces friction in boundary lubrication mode. However, it is not clear whether the oxygen originates from the anion of IL or from the air. A higher oxygen concentration in the outer boundary layer indicates increased surface activity. The ionic liquids used differ essentially in their anion. From this it can be concluded that the anion has an important influence on the tribological behavior. In [46] it was determined that the anions of the ILs can be adsorbed on the surface. We assume that the positively charged surface adsorbs the anions of the ionic liquid. Another reason for the different COFs at 100 °C (depending on the intermediate medium) could be that the COFs decrease with smaller surface roughness. Due to the measured low roughness in the wear marks, the tribochemical reactions can be identified as the dominant wear mechanism of the system for all three intermediate media. Since the diameter of the contact surface (8 mm) is greater than half the stroke length (1 mm), the possibility of the third body being trapped in the contact surface could be greater, which cannot be compared to piston/cylinder contacts, depending on the piston skirt length and stroke length. This difference to engine applications with larger glide paths will be eliminated in future application-oriented tests. The following wear mechanisms are present on all wear rails. 1) Surface defects: Fine-grained microcracks break up the surface and small wear particles are formed. 2) Film delamination: Wear particles are first compacted into a smooth top layer and then torn through the contact body by adhesive bonding, resulting in pitting and deposits, stripes and sticky groups of wear particles. 3) Tribochemical reactions by molecular removal of surface irregularities leading to a tribochemical, transcristalline smoothing of the surfaces. Due to the coexistence of these wear mechanisms, boundary and mixed friction can be assumed. At 100 °C the intensity of the tribochemical reactions increases, especially when the intermediate medium [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] is used, in

which the nitride grains are exposed by the dissolution of the secondary phase. It is known that silicon nitride can be etched with phosphoric acid with a water content of less than ten percent by volume [47]. Based on the resolution of the secondary phase observed on the wear track (Figure 8f), phosphorus in ILs should be omitted in further investigations. Another reason for the more intensive tribochemical reactions is certainly the increase in the concentration of IL in the lubricant due to the evaporation of the water and a significantly higher viscosity of IL compared to water. At 100 °C, with IL [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] in the intermediate medium, there is a strong increase in COF (Figure 5). The reason for this is probably the increase in the viscosity of the intermediate medium, which leads to the formation of a film that reaches a critical thickness after a few hours and delaminates, as already described in [48]. IL [P4441][OAc] does not show similar increases as the viscosity is almost four times lower than IL [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>]. It is also worth mentioning that the evaporation of the intermediate medium [P4441][OAc] produced intense odors in contrast to [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>]. Further investigations will concentrate on the lifetime estimation of real components. Using new oscillating test geometry with longer stroke, the entire tribological load spectrum of a cylinder liner contact (combination of low and high speed at higher contact pressures) can be analyzed.

## Conclusions

- Silicon nitride lubricated with a mixture of water with 1% IL has 96% less friction compared to a conventional tribosystem (steel/oil). It was found that tribochemical reactions lead to surface polishing and chemical changes in the near-surface area that reduce the coefficient of friction.

- Suitable running-in conditions and sufficient cooling and lubrication with water at an early stage are important prerequisites for this water-lubricated ceramic tribological system to withstand the load spectrum of a piston engine.
- It was shown that the chemical structure of the anion of the water-soluble ionic liquids used strongly influences the tribological behavior. For tributyl methyl phosphonium acetate [P4441][OAc] a 58 % reduced maximum friction work was measured compared to the pure water-lubricated tribosystem. We assume that the oxidation and interaction with the anions of [P4441][OAc] at 100 °C promotes surface protection and friction reduction in boundary lubrication mode through an oxide layer. In contrast, when using the ionic liquid with diethyl phosphate anion [P4442][(EtO)<sub>2</sub>PO<sub>2</sub>] a higher friction and no oxidation of the surface was measured.
- With the in-situ SRV wear measurement, low wear rates of approx. 200 nm were measured at room temperature when lubricated with water and with the addition of IL. At 100 °C, the wear rates for water/ceramics and oil/steel were below the measurement limit.
- Surface defects, film delamination and tribochemical reactions are observed as wear mechanisms.

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### **References**

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