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ScienceDirect
Procedia Materials Science 9 (2015) 246 – 253
Procedia Materials Science
www.elsevier.com/locate/procedia

International Congress of Science and Technology of Metallurgy and Materials, SAM – CONAMET 2014

Comparison of tribological properties of stainless steel with hard and soft DLC coatings

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Abstract

Stainless steels are widely used in chemical, petrochemical and food-processing industries due to their good anticorrosion properties. However, they generally exhibit poor tribological properties which limit their applications in tribocorrosive conditions. Surface modifications, like diamond-like carbon (DLC) coatings, can be an optimal technological solution to overcome this problem. These films have attracted considerable attention because of their outstanding mechanical and tribological properties, but they have a major drawback that is their high internal stresses and low thermal stability. The internal stresses and film hardness depend on the ratio sp^2/sp^3, therefore, the film can be classified as hard or soft-DLC coatings depending on this ratio. In this work, different stainless steels (EN14301, EN14435 and EN12316) samples were DLC-coated by plasma assisted chemical vapor deposition. Hard and soft a-C:H:Si films (silicon containing amorphous hydrogenated carbon) were obtained. The films were characterized by wear and adhesion tests; the results show an increase of the practical adhesion at higher film thickness and this improvement would be more effective for harder substrates. Pin-on-disc tests showed that soft-DLC films tend to develop a better tribological behavior than hard-DLC films and it is not influenced by the film thickness or the type of stainless steel substrate. The influence on the tribological behavior of test parameters, such as slide velocity and load, varies with the coating type.

Peer-review under responsibility of the Scientific Committee of SAM–CONAMET 2014
Keywords: Diamond-like carbon; stainless steel; tribological properties

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Peer-review under responsibility of the Scientific Committee of SAM–CONAMET 2014
doi:10.1016/j.mspro.2015.04.031

1. Introduction

As Peckner and Berstein (1977) noted, stainless steels are widely used in the chemical, petrochemical and food-processing industries due their favorable corrosion properties. However, they exhibit generally poor tribological properties that limit their applications to use in tribocorrosive environments, as quoted by Casteletti, Neto and Totten (2008). Surface modifications, like diamond-like carbon (DLC) coatings, can be an optimal technological solution to overcome this problem.

Erdermir and Donnet (2006) pointed out that DLC films offer a wide range of exceptional physical, mechanical, biomedical and tribological properties that make them scientifically fascinating and commercially essential for numerous industrial applications. Certain DLC films are extremely hard and resilient, while tribologically these films provide some of the lowest known friction and wear coefficients. Because of their excellent chemical inertness, these films are resistant to corrosive and/or oxidative attacks in acidic and saline conditions. The combination of such wide range of outstanding properties in just one material is rather uncommon, so DLC films can be attractive because of the multifunctional application needed for advanced mechanical systems. In fact, these films are now used in numerous industrial applications, including razor blades, magnetic hard discs, critical engine parts, mechanical face seals, scratch-resistant glasses, invasive and implantable medical devices and micro-electromechanical systems.

A major drawback of DLC coatings is their high internal stress and low thermal stability. The high intrinsic stress generated in these films causes serious problems leading to its poor adhesion and delamination from the substrate, as Forsich, Heim and Mueller (2008) acknowledged. According to Erdermir and Donnet (2008), a catastrophic film failure can be avoided by minimizing elastic energy stored in the film, i.e., by reducing the product ($\sigma^2 \cdot t_f$), where σ is the stress and t_f is the thickness. A significant reduction of residual stresses in thin films for a given film/substrate structure is not always possible for practical reasons. Therefore DLC films are very thin and, when they are coated in soft materials like stainless steels, plastic deformation will occur with high loads and will lead to the DLC films flake off (Ueda et al. (2007)).

Silicon doped diamond-like carbon layers have been an interesting field of DLC because they have a great potential for solving some of the inherent problems. Silicon incorporation in the DLC films reduces stress, increases the adhesion to steel substrates and the thermal stability (Forsich et al. (2008)), and hence allows the production of thicker coatings.

In a paper published by Erdermir and Donnet (2006), it was revealed that the unique tribological behavior of DLC films may vary a great deal from one type to another. Test conditions and environments can also play a major role in their friction and wear performance. In particular, the friction values reported for various DLC films span the range of 0.001-0.7. As far as wear performance is concerned, certain DLC films are very soft and easily scratchable, while others are extremely hard and resistant to wear (the normalized wear rates of such films are as low as 10^{-11} mm^3 $N^{-1}m^{-1}$). Such a large disparity in friction and wear properties of the DLC films appears to stem from complex combination of intrinsic or film-specific factors and extrinsic or test-condition-specific factors.

Therefore, this work deals with the adhesion and tribological properties of hard-DLC and soft-DLC (a-C:H:Si) coatings, with a thickness range of 1.5-28 μm, on different stainless steels substrates. The variation of these properties with test parameters, such as normal load and sliding speed, has been determined.

2. Experimental

The a-C:H:Si films (silicon containing amorphous hydrogenated carbon) of different thicknesses were deposited by means of plasma assisted chemical vapor deposition technique (PACVD). During the process, H_2 and C_2H_2 were used as precursor gases. Silicon doping was accomplished by using hexamethyldisiloxane (HMDSO); the HMDSO gas flow deposition was lower in the soft-DLC films production than in the hard-DLC films production. The deposition rates for the thin films were ~2 μm/h, and ~1 μm/h, for the thicker films. The temperature deposition was 400 ºC to produce soft-DLC films of 780 Vickers Hardness (HV), and 550 ºC to produce hard-DLC films of 2000 HV. The process was carried out in a semi industrial facility at the University of Applied Sciences in Wels, Austria. The film thickness was measured with a home-made Calotest with a 20 mm in diameter ball.

EN 14301, of 159 Brinell Hardness (HB), EN 14435, of 213 HB, and EN 12316, of 253 HB, stainless steels were selected as substrate materials. Prior to film deposition, the samples were grinded and mirror-polished to a surface roughness of approximately $R_a = 0.05$ µm, and cleaned with isopropanol.

The cohesive and adhesive failures of the films were characterized using a scratch test method (CSEM REVETEST). The normal load on the scratch stylus was increased continuously from 1 N to 51 N at a rate of 3 N/s, which corresponds to a table translation speed of 10 mm/min. The damage was assessed by microscopic examination of the scratch track and by monitoring changes in acoustic emission during the test. A two-level critical scratch load was selected: a critical load, L_{C1}, was defined as the load at which first observable failure occurs, that tends to coincide with cohesive cracking/failure in the coating, and the other, L_{C2}, was defined as the load at which subsequent adhesive failure or spalling occurs (practical adhesion).

Tribological tests were carried out in a pin-on-disc tribometer (TRIBOtechnic) with a 100Cr6 ball, 1.5 mm in diameter, as counterparts. Different sliding speeds (0.05, 0.15 and 0.30 m/s) and normal loads (1, 5, 7 and 12 N) were tested for investigation. These tests were performed at relative humidity (RH) about 45% and at room temperature. The samples were cleaned with isopropanol before each pin-on-disc test.

The film wear rate, K_{film}, was calculated using the equation

$$K_{film} = \frac{S}{F_n \cdot n} \tag{1}$$

where S is the sample wear track section which was measured by confocal microscopy (Leica DCM 3D), F_n is the normal load applied and n the number of cycles, which was set in 3200.

The counterpart wear rate, K_{pin}, was calculated using

$$K_{pin} = \frac{(h^2 + 3 \cdot a^2) \cdot h}{12 \cdot F_n \cdot n \cdot R} \tag{2}$$

where a is the worn cup diameter of the counterpart which was measured by a microscope, R is the radius track and h is the height of the worn cup which was calculated as

$$h = r - \sqrt{r^2 - a^2} \tag{3}$$

where r is the counterpart radius (0.75 mm).

3. Results and discussion

3.1. Cohesive and adhesive failure

The specific type of damage that occurs for a given coating/substrate system in a scratch test depends on the properties of the coating and the substrate. The first cohesive failures that appeared in EN 14301 and EN 14435 samples coated with thick soft-DLC films were conformal-cracks [Fig. 1(a)], which defined the critical load L_{C1}. On the other hand, when these films were deposited on EN 12316 samples (the harder substrate), the first cohesive failures were the so called Chevron-cracks. Both failures were followed by the so called Hertz- cracks at higher loads (ASTM C1624, 2010).

The first cohesive failures in EN 12316 and EN 14435 samples coated with thick hard-DLC films were Hertz-cracks [Fig. 1(b)], while in EN 14301 samples (the softer substrate), coated with the same films, were Chevron-cracks.

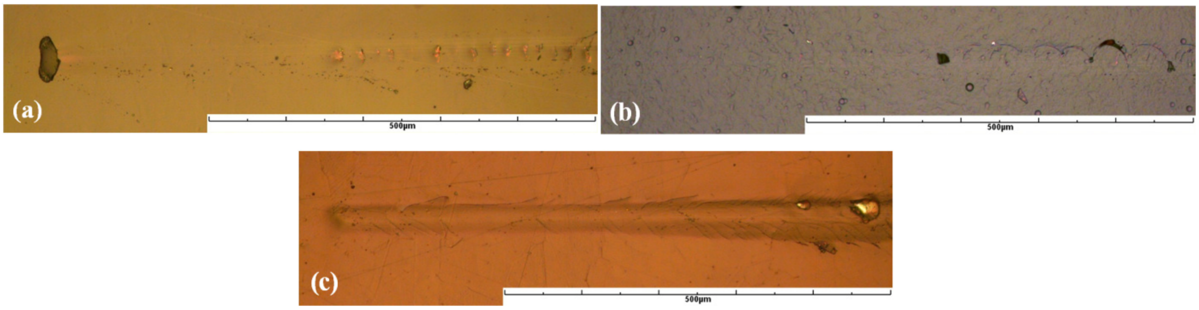

Fig. 1. Scratch microscopy (200x). (a) EN 14301 coated with 25 µm soft-DLC; (b) EN 12316 coated with 23 µm hard-DLC; (c) EN 14301 coated with 2.3 µm soft-DLC.

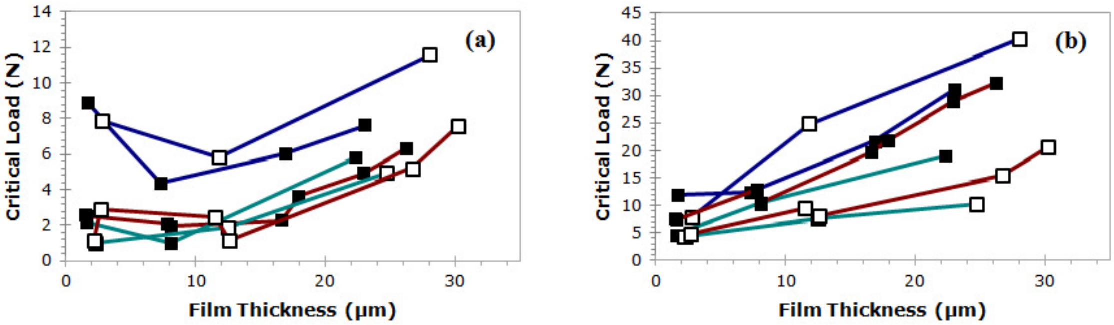

Fig. 2. Critical loads as a function of the film thickness. Films: □ Soft-DLC and ■ Hard-DLC. Material substrates: — EN 14301, —EN 14435 and —EN 12316. (a) First cohesive failure, L_{C1}; (b) Practical adhesion, L_{C2}.

On the other hand, the first cohesive failures in thin films, soft-DLC and hard-DLC, were Chevron-cracks [Fig. 1(c)]. In thin hard-DLC films, these cracks were followed by Hertz-cracks.

In Fig. 2(a) the L_{C1} dependency on film thickness is depicted and it can be seen that L_{C1} tended to decrease with thickness until ~10 µm and then increased at a rate of 0.3 N/µm. It is noted that these values seem to be more dependent on the material substrate than on the type of coating, therefore EN 12316 coated with soft-DLC exhibited the highest value of L_{C1}.

During the scratch test the adhesive failure modes of the soft-DLC films were independent of the substrate material but they were dependent on the film thickness. The adhesive failure mode for thin films was chipping from cracks, with an increase in the film thickness; it changed to wedging spallation and even thicker coatings failed by gross spallation. The adhesive failure mode in EN 14301 samples coated with hard-DLC films was also dependent on the film thickness. The same behavior was observed in EN 14435 samples coated with hard-DLC films, with the exception of the gross spallation which was not presented in any case. However, the adhesive failure mode in EN 12316 (harder substrate) coated with hard-DLC films was wedging spallation and it was independent of the film thickness.

Thicker coatings have a general tendency to produce lower L_{C2}, because higher residual stresses are produced in thicker coatings. With higher residual stresses, lower applied loads will reach to the practical adhesion stress levels and produce coating damage. However, hard thicker films can also provide greater load-bearing capacity, if residual stresses are not too high. This is particularly important for hard, brittle coatings on soft, ductile substrates where considerable substrate deformation can occur before delamination failure. Under these conditions, the critical load for spallation may increase with coating thickness, as it was in this case [Fig. 2(b)].

Considering practical adhesion (L_{C2}), for a given substrate material, different type of coatings exhibited different behavior. Hard-DLC films tended to develop higher values of L_{C2} than the soft-DLC films, when the material substrates were EN 14301 and EN 14435 (soft and medium substrates). The opposite occurs when the material substrate was EN 12316 which had the highest hardness of the tested materials. The practical adhesion behavior is summarized in Table 1.

Table 1. Practical adhesion behavior.

Material substrate	Substrate hardness	Type of coating	Practical adhesion
EN 12316	high	Soft-DLC	Higher
EN 12316	high	Hard-DLC	↓
EN 14435	medium	Hard-DLC	
EN 14301	low	Hard-DLC	
EN 14435	medium	Soft-DLC	
EN 14301	low	Soft-DLC	Lower

3.2. Friction and wear

During the pin-on-disc tests, soft-DLC films tended to have a better behavior than the hard ones, i.e. lower coefficient of friction and lower wear rate of coatings and counterparts, with the exception of the tests carried out at 12 N, at which this kind of coating developed higher coefficient of friction and higher coating wear rates. This can be explained by the fact that an increase in the normal load enhanced the transfer layer in the hard-DLC, but on the contrary, it deteriorated the transfer layer in the soft-DLC, as shown in Fig. 3. The formation of this carbonaceous transfer layer on the sliding surface reduces the friction coefficient and the wear rates (Erdermir and Donnet (2008)).

The results of the tribological tests (coefficient of friction, coating wear rate and counterpart wear rate) were not influenced by the film thickness or the material substrate. However, these variables with the type of coating defined the maximum load without fail. Thin films (1.5-3 µm) failed by delamination at 5 N when the samples were coated with hard-DLC [Fig. 4(a)], but they failed by excessive wear at 12 N when the samples were coated with soft-DLC [Fig. 4(b)].

In some cases, an increase in the film thickness allowed the coated samples to work at higher loads. Tests at a normal load of 5-7 N were carried out without fail by all the soft-DLC films but for hard-DLC films it was necessary a minimum thickness of 8 µm in the case of the EN 12316 and EN 14435 substrates, and 22 µm for the soft EN 14301. Furthermore, tests at 12 N were carried out without fail by soft-DLC films with a minimum thickness of 12 µm for EN 12316 substrates and 29 µm for EN 14435 (EN 14301 coated with these films failed by delamination during the tests), and by hard-DLC films with a minimum thickness of 22 µm for the three substrate materials. However, at this normal load, these hard-DLC films worked without fail in tests carried out at 0.05 m/s and they failed by delamination at higher sliding speeds.

Taking into account the successful tests, an increase in the normal load from 1 N to 12 N in hard-DLC produced: a decrease in the coating wear rate, from 4.6×10^{-6} to 4.0×10^{-6} $mm^3 (N{\cdot}m)^{-1}$, a decrease in the counterpart wear rate, from 2.83×10^{-6} to 1.69×10^{-6} $mm^3 (N{\cdot}m)^{-1}$, and an increase in the stationary friction coefficient, from 0.09 to 0.18.

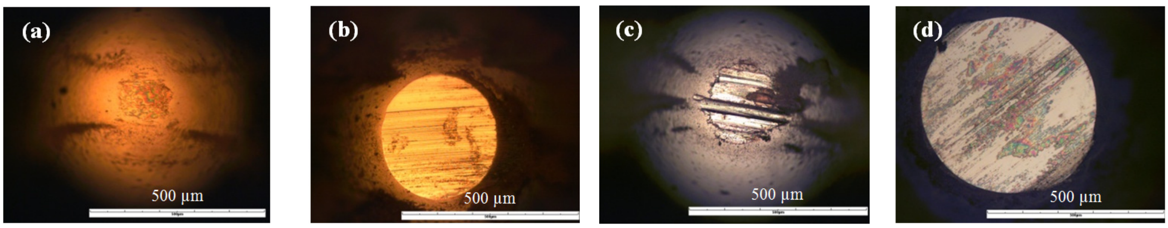

Fig. 3. Optical micrographs (200x) of counterpart wear surfaces sliding against the DLC-films. Sliding speed: 0.05 m/s. Material substrate: EN 12316. Film thickness: 25 µm. (a) Soft-DLC film tested at 1 N; (b) soft-DLC film tested at 12 N; (c) hard-DLC film tested at 1 N; (d) hard-DLC film tested at 12 N.

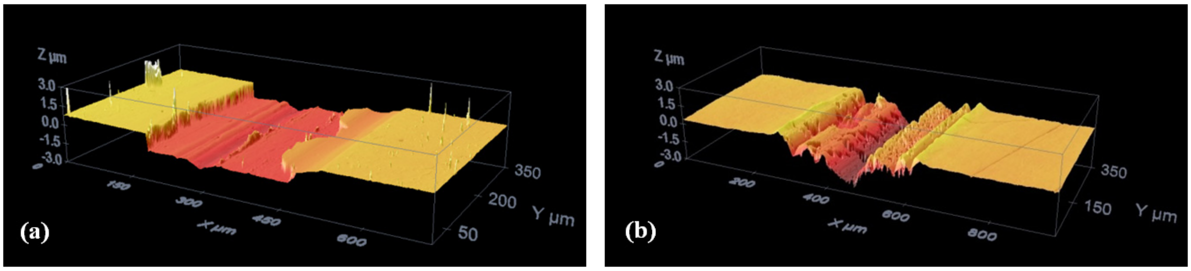

Fig. 4. Topography of the sample wear tracks. Sliding speed: 0.05m/s. Material substrate: EN 14301. Film thickness: 2µm. (a) hard-DLC film tested at 5N; (b) soft-DLC film tested at 12N.

On the other hand, the same increase in the normal load, produced an increase in the coating wear rate of the soft-DLC, from 0.4×10^{-6} to 11.8×10^{-6} mm^3 (N·m)$^{-1}$, an increase in the counterpart wear rate, from 0.03×10^{-6} to 0.63×10^{-6} mm^3 (N·m)$^{-1}$, and an increase in the stationary coefficient of friction, from 0.04 to 0.18.

In addition, an increase in the sliding speed from 0.05 to 0.30 m/s generated a decrease in the coating wear rate in the order of 1×10^{-6} mm^3 (N·m)$^{-1}$, a slight decrease in the coefficient of friction of 0.015 and changes in the counterpart wear rate that depends on the type of coating. When the pin-on-disc tests were running on samples coated with hard-DLC, the counterpart wear rate increased by 0.8×10^{-6} mm^3 (N·m)$^{-1}$, while in samples coated with soft-DLC this parameter decreased by 0.03×10^{-6} mm^3 (N·m)$^{-1}$.

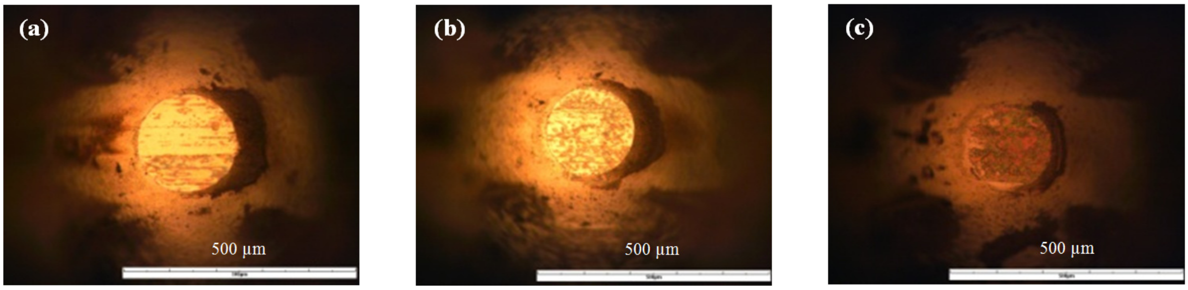

Fig. 5. Optical micrographs (200x) of counterpart wear surfaces sliding against soft-DLC film. Material substrate: EN 14301. Film thicknesses: 25 µm. Normal load: 7 N. Sliding speed: (a) 0.05 m/s; (b) 0.15 m/s; (c) 0.30 m/s.

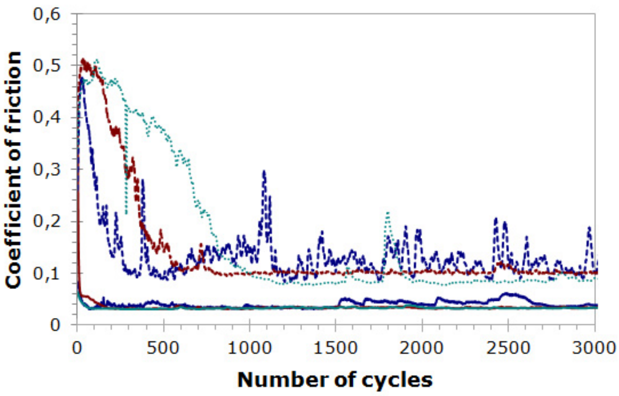

Fig. 6. Coefficient of friction evolution for DLC-films. Material substrate: EN14435. Normal load: 5 N. Dotted lines represent hard-DLC films (8 µm in thickness) and solid lines represent soft-DLC (2.5 µm in thickness). Sliding speeds: — 0.05 m/s, — 0.15 m/s and — 0.30 m/s.

During the pin-on-disc tests, the behavior of the soft-DLC films with an increase in the sliding speed was expected because the sliding speed has been observed to enhance the layer transformation as shown in Fig. 5, where the most compact transfer layer was observed for high sliding speed. The thick layer formation was also observed to decrease the wear rate of the hydrogenated DLC film and the steel spin sliding against the coated surface (Erdermir and Donnet (2008)). In the case of hard-DLC films, the increase of the counterpart wear rate with the sliding speed could occur due the fact that, as shown in Fig. 6, an increase in the sliding speed generated an increase on the time in which the stationary conditions is reached.

4. Conclusion

Scratch tests revealed that the failure mode changes with the stainless steel substrate, the coating type and its thickness.

The practical adhesion of DLC-films could be improved by an increase in their thickness and this improvement would be more effective for harder substrates.

Pin-on-disc tests showed that soft-DLC films tend to develop a better tribological behavior than hard-DLC films (lower coefficient of friction and lower wear rates of coatings and counterparts) and it was not influenced by the film thickness or the material substrate.

An increase in de normal load during the pin-on-disc tests generates, in hard-DLC films:

- a decrease in the coating wear rate,
- a decrease in the counterpart wear rate,
- an increase in the coefficient of friction.

On the other hand, in soft-DLC films this increase in the load produces:

- an increase in the coating wear rate,
- an increase in the counterpart wear rate,
- an increase in the coefficient of friction.

Furthermore, an increase in the sliding speed enhances the layer transformation that results in a decrease in the coefficient of friction as well as in the coating wear rate. The effect of this variation on the counterpart wear rates changes with the type of coating, while in hard-DLC there is an increase, in soft-DLC there is a decrease.

The improvement of tribological properties of stainless steels samples by coating with soft-DLC or hard-DLC films is undeniable, and both kinds of coatings may be used for parts subjected to a wide range of sliding conditions. Nevertheless, soft-DLC films are more recommendable than hard-DLC films because of their better tribological behavior, as mentioned earlier, and when a failure occurs it is not catastrophic. But, at high loads such as 12 N, hard-DLC films develop a smaller coating wear rate that makes them more effective for the wear protection of stainless steels.

It was noted that the coefficient of friction is largely dominated by the formation of transfer layers. This is why in samples that failed by detachment of the coatings and that were able to create such kind of layers, the friction coefficient behavior is the same as that of the samples with coatings without failures. Therefore, immediate changes in friction are not expected when this happens and periodical optical inspections are recommended to avoid wear of the parts.

Acknowledgements

The authors would like to acknowledge the “Plasma Nitriding and PACVD for Surface Modifications” research group of Upper Austria University of Applied Sciences, for the help and support in this research process.

This project would have been impossible without the equipment, the facilities and the financial support of the Upper Austria University of Applied Sciences.

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