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Choumad Ould, Teddy Tite, Christophe Héau, Anne-Sophie Loir, Christophe Donnet, et al.. Tribological behavior of DLC film models in base oils: Analysis of influence of sp<sup>3</sup>/sp<sup>2</sup> ratio and hydrogen content. Tribology International, 2024, 194, pp.109446. 10.1016/j.triboint.2024.109446 . hal-04487888

**HAL Id: hal-04487888**

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Submitted on 4 Mar 2024

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# Tribological Behavior of DLC Film Models in Base Oils: Analysis of Influence of $sp^3/sp^2$ Ratio and Hydrogen Content

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## ABSTRACT

DLC coatings have been proven in formulated oils used in the automotive industry. The development of electric cars and its consequences on the future of the internal combustion engine makes it increasingly necessary that these coatings take their place in other applications where lubrication is generally of lower quality such as for example strips cold rolling where DLC shows significant potential both for production and finishing cold rolling. As a result, the interest of the behavior of these coatings in base oils takes on a new dimension.

In this study, we explore the influence of the composition and the  $sp^3/sp^2$  ratio on tribological behavior of DLC coatings in mineral and synthetic base oils. Hydrogenated DLC films deposited by conventional PECVD with various levels of hydrogen measured by Elastic Recoil Detection Analysis (ERDA) and non-hydrogenated DLC films deposited by PLD in the nanosecond mode (ns-PLD) and by cathodic arc evaporation, thus allowing to have different  $sp^3/sp^2$  ratios confirmed by Multiwavelength Raman spectrometry, are tested and compared. The tests are performed on a ball-on-flat device with coated balls to better evaluate wear level.

The behavior of highly hydrogenated DLC is of particular interest; with a very high level of durability in both base oils and friction level which comparatively varies between low and very low depending on the base oil.

## KEYWORDS

DLC coatings;  $sp^3/sp^2$  ratio; Hydrogen content; Base oils; Friction; Durability

## INTRODUCTION

Human activity is made of relative movement, thereby leading to an omnipresence of friction in the different aspects of life, playing varied roles, which range from a driving effect where friction is the essential means of accomplishment of the task (as in the case of strips rolling and braking, etc.), to an undesirable accompanying effect to be reduced as much as possible, because it is a source of energy losses and environmental pollution as in many industrial and locomotive activities [1] [2]. Friction is the consequence of surfaces interaction between the two contact partners and the lubricant. An interaction where the nature of the surfaces plays an important role leading to significant research activity on surface modifications [3-5] and coating films [6 - 8]. The completion of researches of this latter field has led to the use of different thin layers in various tribological applications.

In the last three decades, DLC has become a major element of the friction reduction system and a central ally in the fight to reduce energy consumption in the automotive industry [9 - 11] and its environmental consequences. The thickness of the deposited layer determines its cost and influences its mechanical properties, generally leading to layers less than 5  $\mu\text{m}$  thick. This low thickness gives the wear resistance of the layer a particular dimension because it determines the durability of the layer and therefore the longevity of the friction reduction device. We mean by the durability of the layer: its resistance to various mechanical and chemical interaction phenomena with the other contact-partner and the lubricant that may cause its reduction during use (wear, oxidation,...).

The steel/steel/lubricant contact partnership is known and the roles of oils and different additives are clear [12-14]. The introduction of DLC into this tribological partnership generates a new configuration requiring a great deal of analysis and optimization of roles. The multiplicity of DLC makes this analysis much more complex. Indeed, many DLC families exist and whose properties vary due to different parameters ( $\text{sp}^3/\text{sp}^2$  ratio, hydrogen content, doping or not by metallic or non-metallic elements) [15].

The control of the tribological system DLC/steel/lubricant requires understanding the role that each element plays and the influence of its modification on the tribological performance of the system, in particular the nature of the DLC (hydrogen content,  $\text{sp}^3/\text{sp}^2$  ratio) and the constituents of the lubricant. Lubricants used in most tribological applications are often formulated oils composed of a mixture of a mineral and a synthetic oils to which is added a package of additives among them, two play an important role in the tribological behavior: friction modifier and antiwear additives.

Understanding the behavior of DLC coatings in base oils is important for several reasons;

-it is a necessary step for understanding the effects inherent to additives and for evaluating their usefulness according to the conditions and partners of contact;

-in many industrial applications, the oil plays a double role, it is used for lubrication of course but also for cooling, which requires large quantities requiring to remain within reasonable costs to use a much less successful formulation, much less additived than that used in the automotive industry;

-additives are consumables whose exhaustion rate varies according to the conditions and the partners of contact, making the behavior in the base oils increasingly decisive with the aging of the lubricant.

In this study, we analyze the influence of the hydrogen content and the  $\text{sp}^3/\text{sp}^2$  ratio on the tribological performance of DLC lubricated with a mineral base oil (Group III) and a synthetic base oil (PAO6). Four coatings: two hydrogenated DLC with different hydrogen contents and two non-hydrogenated DLC at different levels of  $\text{sp}^3$  are studied.

## **MATERIALS AND CHARACTERIZATIONS**

In this study, the coatings were deposited on the 100Cr6 steel balls and the counter part was a mirror polished HSS steel flat (0.85%C, 6%W, 5%Mo, 4%Cr, 2%V). Four different DLCcoatings were used:two hydrogenated DLC (a-C:H) films containing 20% and 36% of hydrogen deposited by PACVD and two non-hydrogenated DLC films one of a very high hardness deposited using cathodic arc evaporation (CAE) and the other of a lower hardness deposited by Pulsed Laser Depositionin the nanosecond mode (ns-PLD). The coatings were characterised using calotest for thickness, a CSM scratch tester for critical load, a Fisher microhardness tester for elastic modulus and hardness and Nanosurf AFM was used to determine roughness. Finally Multiwavelength (MW) micro-Raman experiments were carried out to determine the  $\text{sp}^3/\text{sp}^2$  ratio of the samples. The spectral resolution was  $\sim 4 \text{ cm}^{-1}$  and the laser power on the sample was set below 3 mW to avoid any deterioration of the materials. The scattered Raman signal was measured with AramisJobinYvon confocal spectrometer equipped with a charge-coupled device (CCD) camera.

The Raman spectra of DLC films show several common bands in the 1000-2000  $\text{cm}^{-1}$  region, the so-called G and D bands, which lie at around 1560 and 1360  $\text{cm}^{-1}$ , respectively for visible excitation, and the T band, seen for UV excitation at around 1060  $\text{cm}^{-1}$ . The G band is due to the in-plane vibrations of the  $\text{sp}^2$  carbon in both rings and chains, and D band is due to the breathing mode of  $\text{sp}^2$  atoms in rings [16]. The T band is due to the C-C  $\text{sp}^3$  vibrations. Figure 1(a)-(d) shows the Raman spectra of the DLC samples at three laser wavelength ( $\lambda=633, 442$  and 325 nm). The D and G bands were fitted using Lorentzian and Breit-Wigner-Fano (BWF) functions. We used another Lorentzian for the T band, when present. A D band was observed for all the samples, except for the non-hydrogenated DLC sample deposited by CAE (Fig. 1(a)-(d)). According the correlation between the G peak dispersion and the degree of topological disorder [17], we found hydrogenated DLC sample with 40%H has a higher a  $\text{sp}^3$  fraction ( $\sim 57\%$ ) than the one containing 20%H ( $\sim 44\%$ ). This is due to the higher C-H bonds fraction and the dependence of the the  $\text{sp}^3$  fraction on the (C-C+C-H)  $\text{sp}^3$  content. For the non-hydrogenated DLC samples deposited by CAE and ns-PLD, a  $\text{sp}^3$  fraction around 83 and 33% has been estimated, respectively. The fact the CAE sample has a higher  $\text{sp}^3$  fraction is confirmed by the absence of the D band, as well as the presence of the T band. Since the density and Young's modulus mainly depend on the C-C  $\text{sp}^3$  content, CAE sample is expected to be harder than the ns-PLD sample. Because the C-C  $\text{sp}^3$  bonds will be embedded in a softer C-H  $\text{sp}^3$  matrix, DLC 36%H is expected to be softer than DLC 20%H. These results are confirmed by microhardness measurements. Further investigations need to be done to achieve a better control of the  $\text{sp}^3/\text{sp}^2$  ratio of ns-PLD DLC samples.

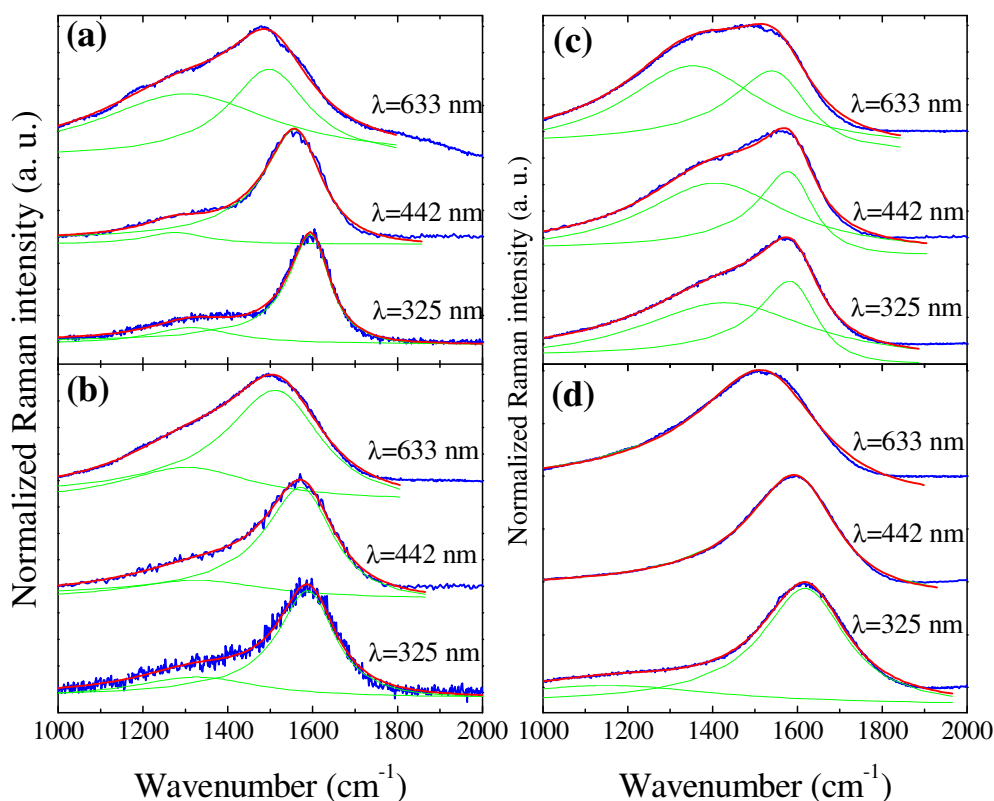


Figure 1. Raman spectra at different laser wavelength of hydrogenated DLC with 40%H (a) and 20%H (b) and of non-hydrogenated DLC deposited by ns-PLD (c) and cathodic arc evaporation (d). Fitting curves are represented in thin solid lines.

The table 1 reports the main characteristics of the coatings.

**Table 1: Characteristics of coatings.**

Coating	Roughness of flat Ra ( $\mu\text{m}$ )	Thickness in $\mu\text{m}$	Scratch test Critical load in N	Elastic modulus in GPa	Vickers microhardness In Hv	Coating $\text{sp}^3$ %
High hydrogenated DLC (36%H)	0.02	2.5	39	96	1270	57
Low hydrogenated DLC (20%H)	0.02	2.5	30	230	3400	44
Unhydrogenated DLC high $\text{sp}^3/\text{sp}^2$ ratio	0.02	3.0	25	386	5400	83
Unhydrogenated DLC low $\text{sp}^3/\text{sp}^2$ ratio	0.02	2.0	26	214	2000	33

**TEST DEVICE AND PROCEDURE**

Tribological tests were carried out using ball-on-flat device, a linear alternative friction test (Fig. 2). For all tests presented here, the ball has a diameter of 10 mm and the applied load is 5 N generated a mean contact pressure of 0.54 GPa and at the beginning of the test, a contact area of about 100  $\mu\text{m}$  of diameter. The mean value of the sliding speed between the ball and the flat surface is 0.035 m/s and the track length is 10 mm with a total number of cycles of about 15000. The ball-on-flat device is immersed in a small tank filled with lubricant and the temperature in the oil during tests was 110 °C. In this study, two different base oils lubricants were used: mineral base oil (Group III) and polyalphaolefin base oil (PAO6). Both base oils are among the most used in formulated oils. During the test, the mean friction coefficient is recorded. The ball and flat were examined after the tribological test using optical microscopy, to determine the ball contact diameter and the friction track width on the flat.

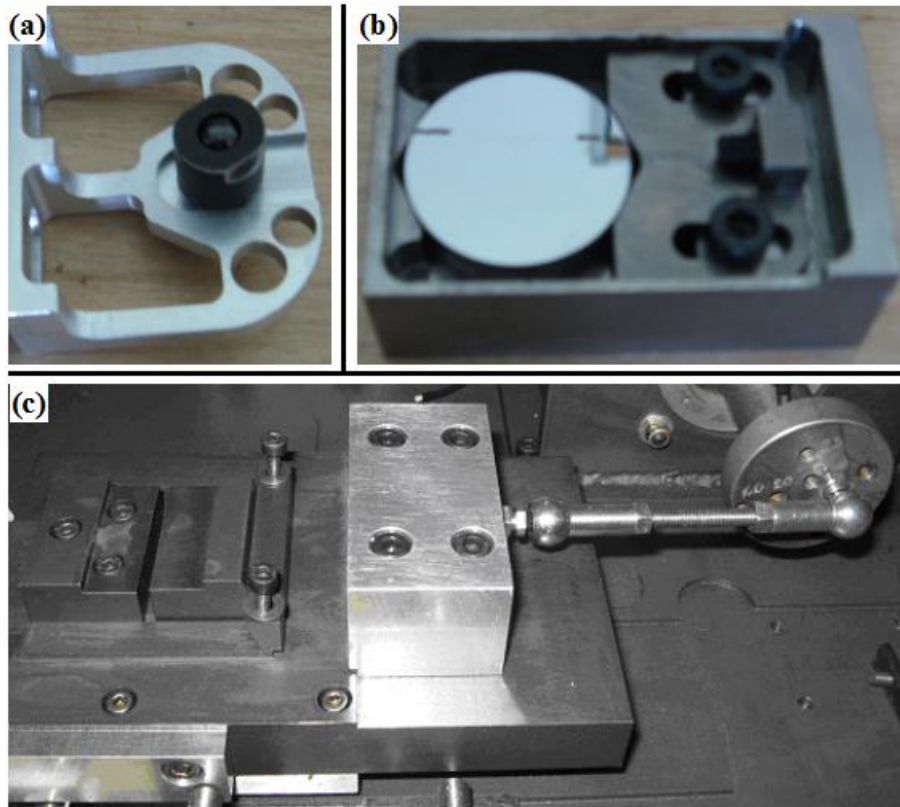


Figure 2. The ball-on-flat test device used for tests: ball support (a), flat support (b) and drive mechanism of the flat (c).

## RESULTS

The different tests were carried out at the same load (5N), at same oil temperature (110 °C) and with the same speed evolution during the cycle for all coatings to allow the comparison of their tribological behavior, in particular the level of friction and coating durability in same test conditions. To better evaluate the durability of coatings, tests are carried out for 15000 cycles and coatings are deposited on the ball on which the wear kinetic is the highest because its contact surface does not change during the test. The nature of the device (sinusoidal alternating linear) makes the speed changes during the path from zero at the edges to a maximum value at the center and of course the speed was chosen low enough to allow to remain all the test time in the mixed regime. During the acquisition of the friction coefficient, a point per cycle is recorded and this value is an average over the cycle.

In Figure 3, we present the evolution of the friction coefficient during the test for three tests with the same coating (non-hydrogenated DLC deposited by PLD with low  $sp^3/sp^2$  ratio) in a mineral base oil (Group III). The results of these tests show very good reproducibility for tests in base oils. Indeed, the level of reproducibility of the tests in base oils is generally lower than that of fully formulated oils where friction is largely governed by relatively thick tribofilms reducing the effects of random aspect of surfaces of contact-partners.

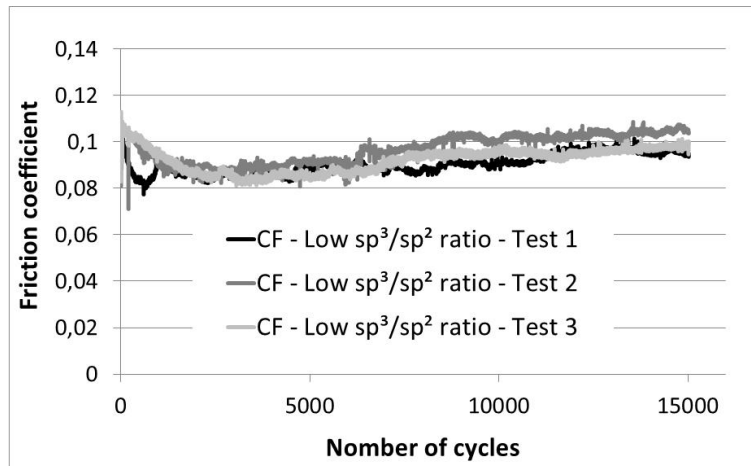


Figure 3. Friction evolution during the ball-on-flat test lubricated by mineral base oil (Group III): reproducibility of test (load 5N and temperature 110 °C).

In Figure 4 we present the results in terms of friction of the tests carried out in the mineral base oil (Group III) for the different coatings. These results show that the highly hydrogenated DLC with a atomic hydrogen content measured by ERDA at 36% is distinguished by a significantly low friction level for lubrication in a base oil without any friction-reducer additive starting at 0.06 and stabilizing at 0.04. For low-hydrogenated DLC (20% H) and non-hydrogenated DLC with low  $sp^3/sp^2$  ratio coatings, the friction increases continuously during the test to stabilize at a value of about 0.095 at the end of test. The coefficient of friction of low-hydrogenated DLC starting with a lower value, it increases faster than non-hydrogenated DLC with low  $sp^3/sp^2$  ratio. For the non-hydrogenated DLC with high  $sp^3/sp^2$  ratio, the coefficient of friction is higher than all the other with a value of 0.1 on a first part of the test before increasing to reach a value of 0.11 of a second part of the test followed by growing instability and a further increase in the friction coefficient.

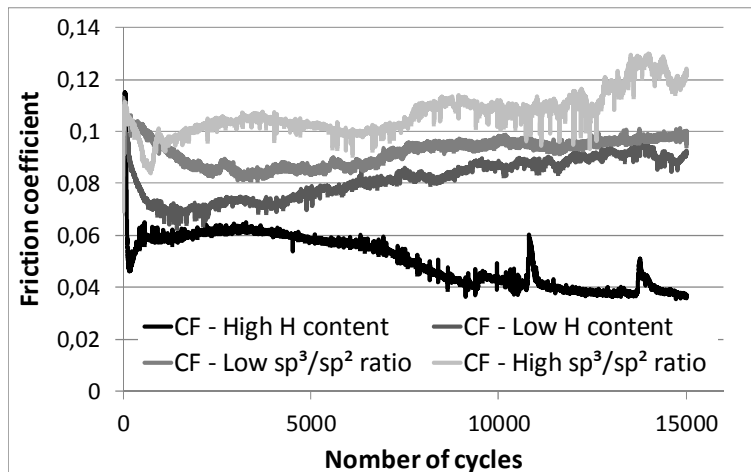


Figure 4. Friction evolution during the ball-on-flat test lubricated by mineral base oil (Group III) for different DLC coatings (load 5N and temperature 110 °C).

The contact surfaces were observed after the tests in mineral base oil and the results of these observations presented in Figure 5 show that for the highly hydrogenated DLC (36% of hydrogen) the contact surface of the ball increases very slightly during the 15000 cycle test, going from an initial diameter of 100  $\mu\text{m}$  to a diameter of 135  $\mu\text{m}$  at the end of the test revealing that the different tribological phenomena generally at work during friction and which cause the reduction in the thickness of the layers were, in this case, very little active or even

completely inhibited giving this coating an exceptional durability in those very lower protective conditions in the absence of the usual protective additives (anti-wear, antioxidant).

For the non-hydrogenated DLC with low  $sp^3/sp^2$  ratio, surface passes from 100  $\mu m$  to 150  $\mu m$  during the test: A weak but significant increase, allowing this coating to have a relatively good durability under these lubrication conditions. For the DLC slightly hydrogenated (20% of hydrogen), the increase in the surface of contact is significant. It passes from 100  $\mu m$  at the beginning of the test to 174  $\mu m$ , corresponding to a consumption of a little more than 0.5  $\mu m$  of thickness of the coating during the test. For the ball coated with non-hydrogenated DLC of high  $sp^3/sp^2$  ratio, its surface of contact passes from 100 $\mu m$  to 353  $\mu m$  at the end of the test and the coating thickness of 3  $\mu m$  is entirely consumed during the test.

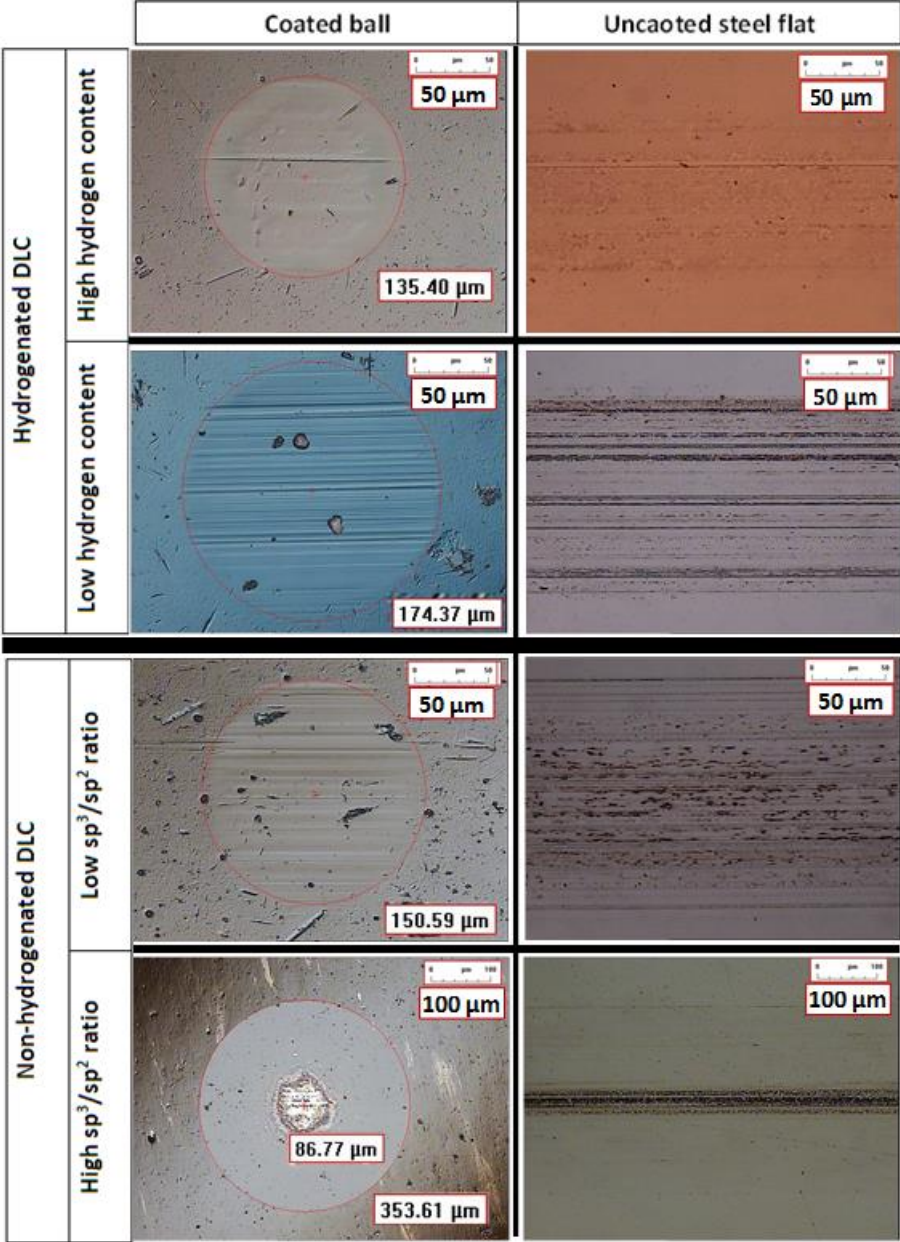


Figure 5. Surfaces of DLC ball and steel flat after tests lubricated by mineral base oil (Group III) for different DLC coatings,(load 5N, temperature 110 °C, 15000 cycles).

These coatings were tested with synthetic base oil without additives (PAO6). The evolution of the friction coefficient during the test for the different coatings is shown in figure 6. Highly hydrogenated DLC has a stable



coefficient of friction and relatively low of the order of 0.064, but higher in the average than its value with the mineral base oil (Group III). The slightly hydrogenated DLC has a higher coefficient of friction of about 0.08, but relatively stable, no evolution during the test in contrast to its behavior with the mineral base oil in which it is constantly increasing. The friction evolution curve of the non-hydrogenated DLC with low  $sp^3/sp^2$  ratio is characterized by the presence of three distinct parts: a first part with a friction coefficient of about 0.1; a second part where the coefficient of friction gradually decreases to join the low hydrogenated DLC at a value of about 0.08 before stabilizing at this value during the third part of test, knowing that this coating is deposited on a layer of slightly hydrogenated DLC to improve its adhesion. The coefficient of friction during the test with the ball coated with non-hydrogenated DLC of high  $sp^3/sp^2$  ratio drops sharply during the first thousand cycles, before stabilizing for a relatively short period at a value of about 0.06, followed by a rapid increase and second stabilization at a value of 0.1.

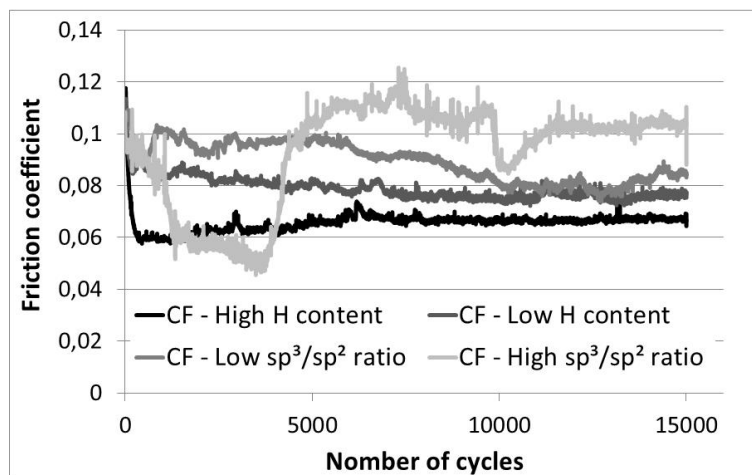


Figure 6. Friction evolution during the ball-on-flat test lubricated by polyalphaolefin base oil (PAO) for different DLC coatings (load 5N and temperature 110 °C).

The observations of the ball and the flat after tests with synthetic base oil allow to evaluate the durability of these coatings in these lubrication conditions and to correlate the evolution of friction coefficients during tests with these of contact surfaces (Fig. 7). The contact surfaces of the two hydrogenated DLC change only very slightly during the test from 100  $\mu\text{m}$  to about 135  $\mu\text{m}$ . Therefore, these two coatings have a high level of durability with synthetic base oil. The contact surface of the ball coated with non-hydrogenated DLC with low  $sp^3/sp^2$  ratio significantly increased reaching 200 $\mu\text{m}$  at the end of the test. The layer with low thickness at this place of the ball (0.6  $\mu\text{m}$ ) is consumed during the test driving to a contact between the sub-layer of slightly hydrogenated DLC and the flat, which explains the gradually transition on the curve of the coefficient of friction after 6000 cycles from the value of 0.1 to the value of the friction coefficient with the slightly hydrogenated DLC, which is of the order of 0.08 and stabilized at this value until the end of the test. The contact surface of the ball coated with non-hydrogenated DLC with high  $sp^3/sp^2$  ratio increases very sharply to 383 $\mu\text{m}$  at the end of the test and the DLC layer is consumed revealing the substrate that what explains the strong and fast increase in the coefficient of friction.

Both non-hydrogenated DLC coatings have been fully consumed during the test. A considerably faster consumption for DLC with high  $sp^3/sp^2$  ratio whose 3  $\mu\text{m}$  thick layer is consumed entirely during the first 3500 cycles of test against 0.6  $\mu\text{m}$  during the first 6000 cycles for the DLC with low  $sp^3/sp^2$  ratio. Note that the highly hydrogenated DLC has a very good level of durability with both base oils, that of slightly hydrogenated DLC is much better in the synthetic base oil and the two non-hydrogenated DLC have a higher level of durability with the mineral base oil. The figure 8 summarizes the consumption rates of the tested coatings lubricated by mineral and synthetic base oils.

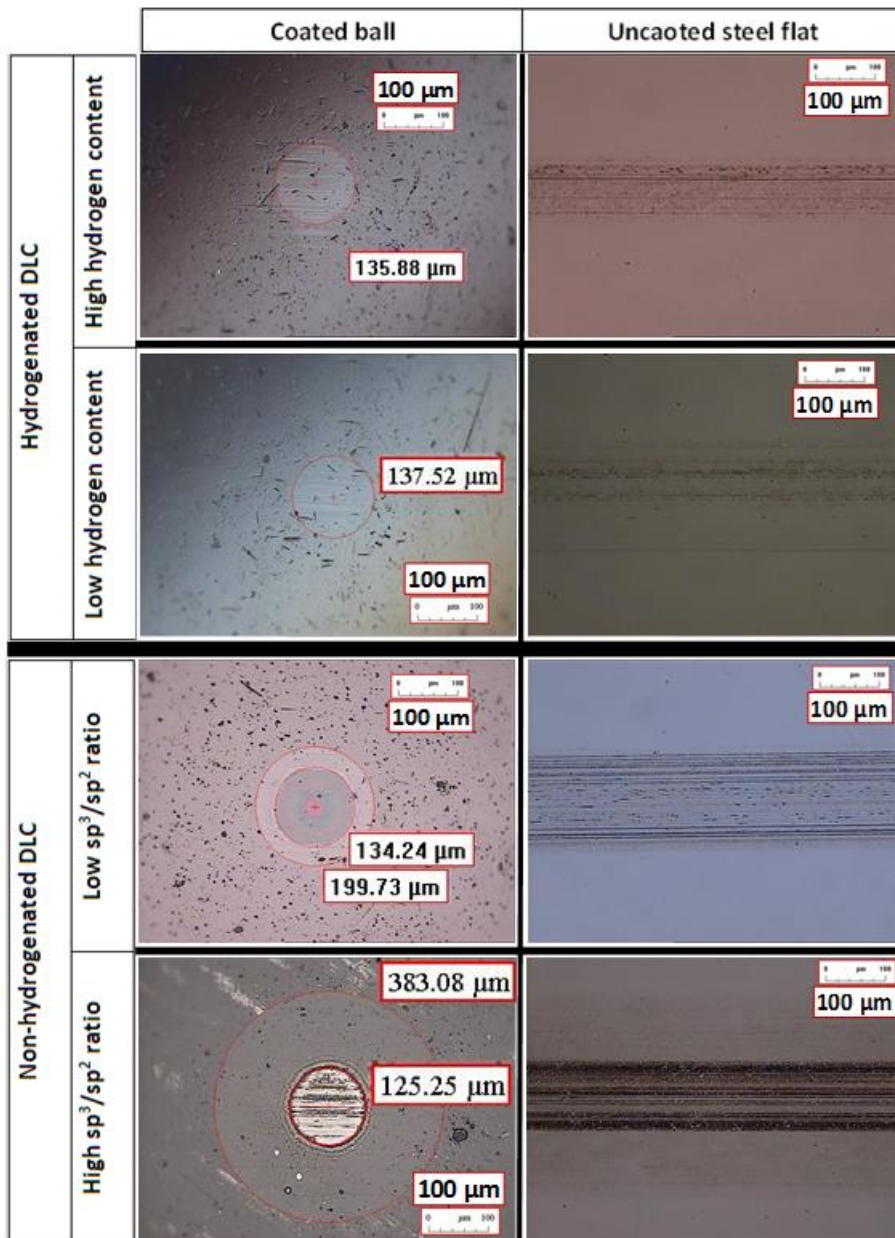


Figure 7. Surfaces of DLC ball and steel flat after tests lubricated by polyalphaolefin base oil (PAO6) for different DLC coatings, (load 5N, temperature 110 °C, 15000 cycles).

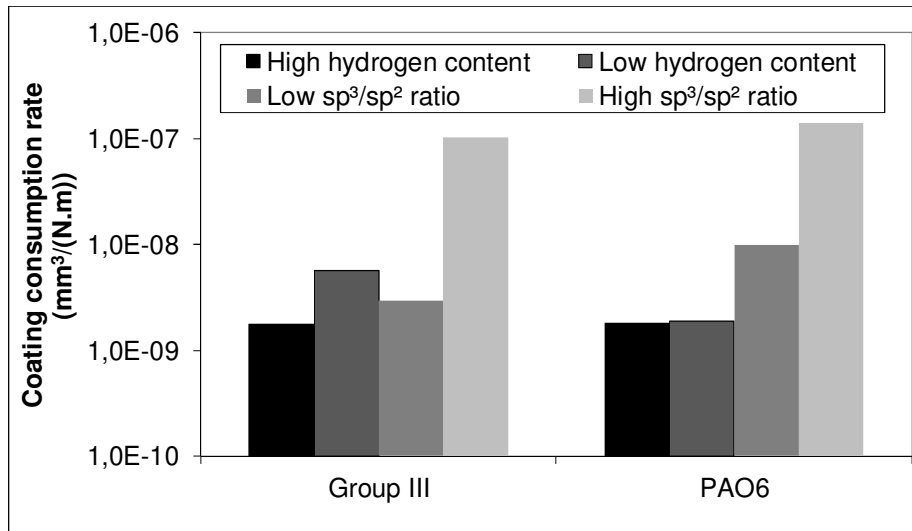


Figure 8. Consumption rate of ball against steel flat after friction tests lubricated with base oils (Group III and PAO6) for different DLC films (load 5N and temperature 110 °C).

The wear of the non-hydrogenated DLC with a high  $sp^3/sp^2$  ratio shows that the mechanical properties playing a decisive role in the resistance to abrasive wear had no effect in protecting the coating against the phenomena at work under the test conditions. The work of Lafon-Placette et al. [23] have made an important contribution to the understanding of the tribochemical corrosive wear mechanism responsible for the consumption of the coating, the effects of iron and other metallic elements as well as that of temperature have been identified, analyzed and explained.

In terms of durability, no significant difference between the two hydrogenated DLCs in the synthetic base oil and a hydrogen level of 20% seems largely sufficient to play the same protective effect as offered by an atomic hydrogen level of 36 %, on the other hand with mineral oil there is a significant difference in durability with significantly greater wear of the 20% hydrogenated DLC. This raises the question of the existence or not of an intermediate hydrogen level beyond which the increase in the hydrogen level does not provide additional protection against the wear phenomena at work under these conditions of lubrication. To answer this question, tests were carried out with four hydrogenated DLCs containing 20%, 24%, 28% and 36% measured by Elastic Recoil Detection Analysis (ERDA) technique using  $^4He^+$  ions of 2.2 MeV. Incident current was 2 nA for an analysis surface of a few  $mm^2$  and analysis depth of about  $0.4\mu m$ . Table 2 presents the characteristics of these different coatings. The results presented in Figures 9 and 10 show that the higher the hydrogen level, the better the protection of the coating in the mineral base oil and that bringing the level of hydrogen to a high level around 40% is not without interest.

Table 2. Characteristics of different hydrogenated DLC.

hydrogenated DLC coatings (a-C:H)	Thickness in $\mu m$	Scratch test Critical load in N	Reduced elastic modulus in GPa	Vickers microhardness In Hv	Hydrogen content (at. %) by ERDA
Coating 1	2.5	39	96	1270	36
Coating 2	2.5	39	128	1790	28
Coating 3	2.5	39	190	2820	24
Coating 4	2.5	30	230	3400	20

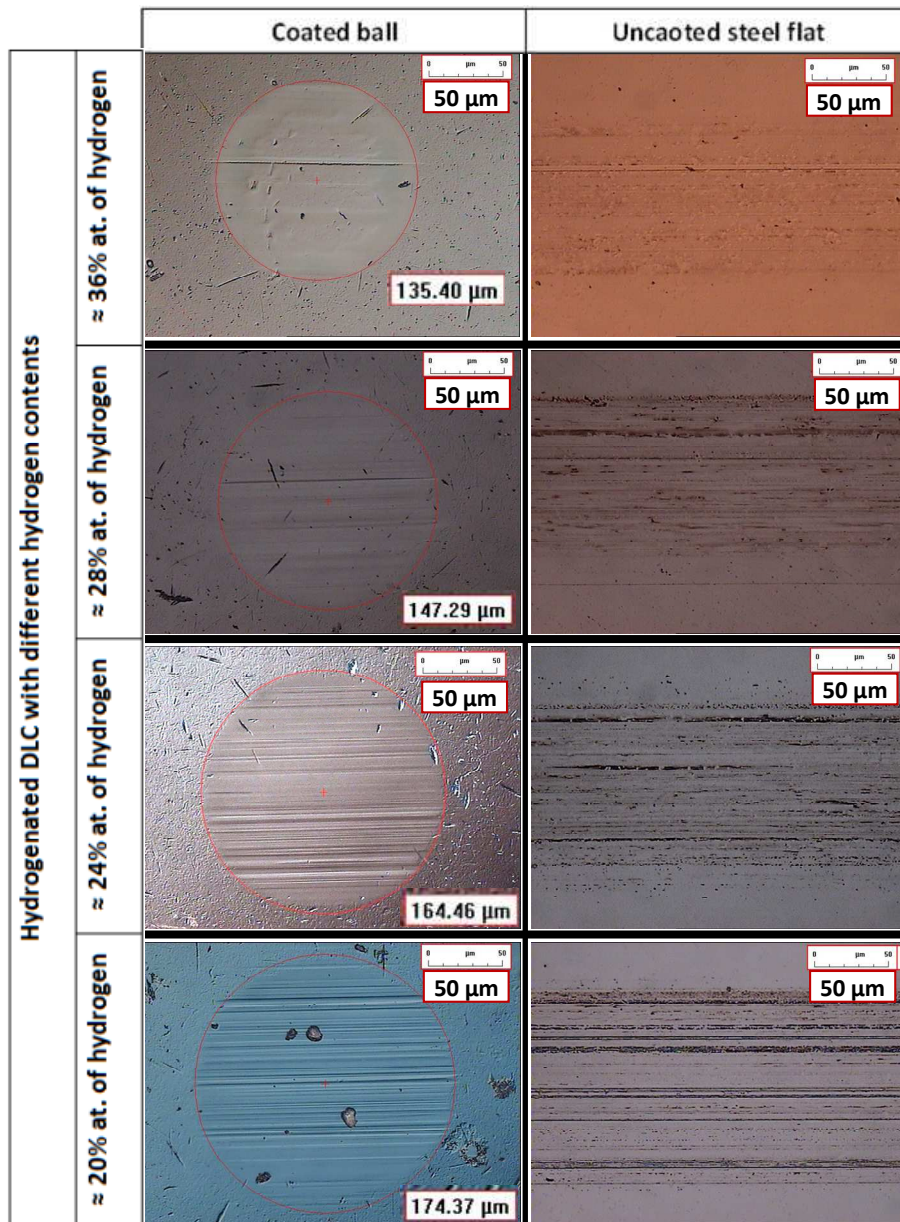


Figure 9. Surfaces of DLC ball and steel flat after tests lubricated by mineral base oil (Group III) for different hydrogenated DLC coatings, (load 5N, temperature 110 °C, 15000 cycles).

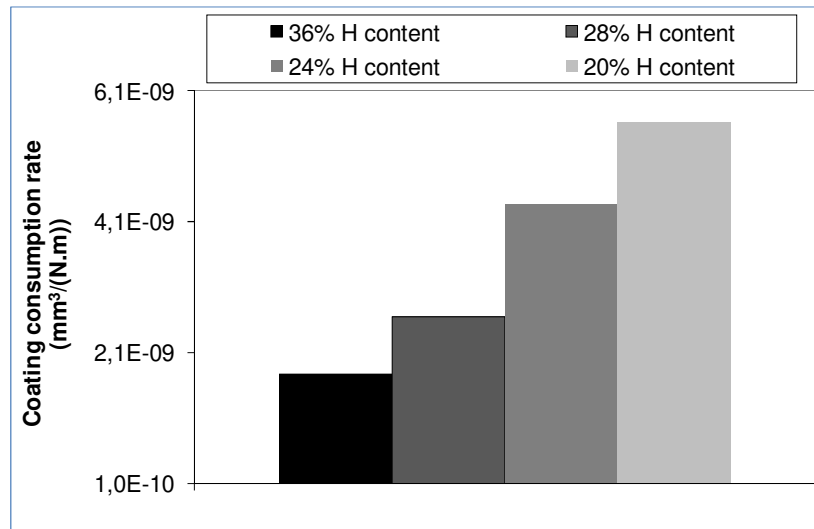


Figure 10. Consumption rate of ball against steel flat after friction tests lubricated with base mineral base oil (Group III) for different hydrogenated DLC films (load 5N and temperature 110 °C).

## DISCUSSION

The tribological behavior of DLCs with steel in formulated oils used in the automotive industry is well known and many studies have been published justifying its wide use in this application. Today with the increasingly large place that the electric car is taking and the decline of the internal combustion engine that it risks to generate, it is urgent to find for DLC, a major product in vacuum deposition industry, outlets in other applications where the oils used are much less additived for the reasons already explained. In rolling of high carbon steel strips, for example, the work we have carried out shows that hydrogenated DLC has real potential to replace hard chromium in this application [22]. The identification of the DLC coating that can be suitable for different families of base oils is a major step on this path.

This study comparing the tribological behavior of four different DLC coatings in two base oils (mineral and synthetic) was allowed to analyze the influence of the hydrogen content and the  $sp^3/sp^2$  ratio on friction and durability of the coating and the performances of these four different DLC coatings are summarized in Table 3. Highly hydrogenated DLC has a particularly interesting tribological behavior with a low coefficient of friction and a high level of durability both in the mineral and synthetic base oil without additives. The combination of a low friction with durability is the objective of the use of coating in different tribological applications because it determines the energy consumption and lifetime of parts and therefore, the economic contribution of coating.

Generally to achieve this objective to have a low coefficient of friction and a high level of durability, an optimization work is done on the lubricants and different additives are tested and associated [18-20]. One of the major obstacles in achieving this goal lies in the fact that the use of anti-wear additives generally generates with DLC an increase of friction. The combination of antiwear and friction reducer often results, with DLC, by canceling the effect of one of them or by a relative durability and a medium friction coefficient in the order of 0.08. However, the results of Haque et al [21] showed that the combination of ZnDTP and Moly-trimer (friction reducer compound having no oxygen in the molecular structure) leads to a good protection of the DLC they have tested and a low coefficient of friction. In this study [21], the DLC is deposited on the flat which makes the evaluation of wear level of the coating difficult and relatively imprecise due to the difference in the kinematic length from one point to another depending it is in the center of the track or on the edges. It should be noted that the DLC studied by Haque et al [21] is a hydrogenated DLC with significant hydrogen content (at. 30% of hydrogen). So the behavior of the highly hydrogenated DLC (at. 36% H) in base oils without additives is particularly interesting for several reasons including the fact that it opens the way for the use of this coating in applications where lubricants used are, for economic reasons, much less complex and less protective than engine oils.

Table 3. Friction and durability performances of different DLC coatings in different base oils.

	DLC coatings performances in mineral base oil (Group III)		DLC coatings performances in synthetic base oil (PAO6)	
	Friction performance	Durability performance	Friction performance	Durability performance
<b>Unhydrogenated DLC high <math>sp^3/sp^2</math> ratio</b>	<b>Low</b>	<b>Very low</b>	<b>Low</b>	<b>Very low</b>
<b>Unhydrogenated DLC low <math>sp^3/sp^2</math> ratio</b>	Middle -	Middle +	Middle -	<b>Low</b>
<b>Low hydrogenated DLC (20% H)</b>	Middle +	Middle -	Middle +	<b>Very high</b>
<b>High hydrogenated DLC (36% H)</b>	<b>Very high</b>	<b>Very high</b>	<b>High</b>	<b>Very high</b>

## CONCLUSION

In this work, we made a comparative study between different DLC coatings to identify the influence of the hydrogen content and the  $sp^3/sp^2$  ratio and the performance of the coatings in friction and durability in a mineral base oil and a synthetic base oil. The results confirm that the increase in the  $sp^3/sp^2$  ratio and its consequences on the mechanical properties improving the resistance to abrasive wear have no protective effect on the coating, on the contrary the  $sp^3/sp^2$  ratio seems to promote the acceleration of phenomena at the origin of the wear of the coating, a wear clearly of tribochemical corrosive nature. These results show that the presence of hydrogen protects the coating with the two base oils but in two different ways; with synthetic base oil, a hydrogen content of 20% provides maximum protection identical to that offered by a high level of 36%; with mineral base oil, the increase in the hydrogen content improves durability, which only reaches the same level as with synthetic base oil at an hydrogen content of around 36%. These results show that highly hydrogenated DLC has a particularly interesting behavior, combining durability (very low wear) with a low coefficient of friction in both families of base oils, paving the way for the use of this coating in applications where the oils for technical and economic reasons are lightly added.

## ACKNOWLEDGEMENT

This work was performed within the framework of the LABEX MANUTECH-SISE (ANR-10-LABX-0075) of Université de Lyon, within the program "Investissements d'Avenir" (ANR-11-IDEX-0007) operated by the French National Research Agency (ANR).

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