THE CHALLENGE OF DLC COATINGS CHARACTERIZATION[1]

Yves Gachon[2]
Hervé Delorme[3]
Eros de Araújo Neto[4]
Paul Kay[5]

Abstract

Hard layers implemented by PVD and PECVD technologies to protect surfaces against tribological stresses leading to wear, energy losses, corrosion or adhesion is confronted with many technical difficulties primarily related to the smoothness of the studied structures. If some specific tools were developed to measure the thickness of the layers, their hardness, Young modulus, and to evaluate their adhesion on a given substrate, the majority of these tests appears to be extremely insufficient to identify the ideal layer for a given application. In addition to the existence of numerous traps around basic tests of the surface treatment which can easily lead to erroneous conclusions, even aberration, the surface stresses combine a great quantity of parameters which it is not possible to comprehend separately and which are generally highlighted by a progressive increase in the complexity of the tests, for more realism, but to the detriment of the cost of the tests and accuracy of the conclusions.

Kew words: PVD; DLC; Tribology.

O DESAFIO DA CARACTERIZAÇÃO DOS REVESTIMENTOS DLC

Resumo

Filmes finos duros tem sido executados por tecnologias PVD e CVD visando a proteção superfical contra as tensões tribológicas. Esses esforços podem conduzir ao desgaste (abrasivo e/ou adesivo), consumo de energia, corrosão, entre outros e, essas tecnologias são deparadas com muitas dificuldades técnicas, primeiramente relacionadas com a espessura das estruturas estudadas. Se algumas ferramentas específicas são desenvolvidas para medir a espessura, a dureza, o módulo de Young e para avaliar a adesão da camada em um dado substrato, a maioria desses testes mostram-se extremamente insuficientes para identificar a camada ideal para uma dada aplicação. Existem numerosas particularidades a cerca dos testes básicos de engenharia de superfície, as quais podem facilmente conduzir a conclusões errôneas, até aberrações. Em adição, tensões superficiais combinam com uma grande quantidade de parâmetros, os quais não é possível tratar separadamente e que são geralmente acrescidos por um aumento progressivo na complexidade dos testes, visando a proximidade com a realidade, mas estes em detrimento dos custos destes e da acuracidade da interpretação e conclusões.

Palavras-chave: PVD; DLC; Tribologia.

1 *Technical contribution to 64th ABM Annual Congress, July, 13th to 17th, 2009, Belo Horizonte, MG, Brazil.*

2 *HEF R&D France. service Mécanique des Surfaces et Tribologie, ZI sud, rue Benoît Fourneyron, 42166 Andrézieux Bouthéon Cedex. YGachon.hefrd@hef.fr*
3 *HEF France*
4 *Techniques Surfaces do Brasil*
5 *HEF USA*

INTRODUCTION

Since the nineties, the hard and thin films implemented by PVD (Physical Vapour Deposition) or PECVD (Plasma Enhanced Chemical Vapour Deposition) have been highly developed and used because they represent a huge potential for the improvement of the tribological performances of the mechanical components. Indeed, these coatings generally outclass the traditional/conventional processes for surface hardening thanks to their intrinsic properties (hardness, modulus) and their resistance to the usual wear tests as well. Vacuum deposition technologies are today at a strategic stage of their development. Thanks to the research efforts and development undertaken so much in academic world than industrial, the processes from now on are well mastered. For components, one can produce in a consistent reproducible way coatings from 1 to 5 µm thickness, of architecture with an increasing complexity at costs in constant fall thanks to optimization of the processes (filling and architecture of the equipment, handling of the parts…). However, architecture definition and properties of these innovating films on real parts still concerns empiricism as there is a lack of theoretical means to size and design the layers as well as suitable methods to predict their durability.

SEEKED INFORMATIONS

Once we got rid of the pitfalls related to an insufficient adhesion or a too low abrasive resistance, the hard thin films will collapse in the majority of the cases due to complex tribological stresses. What is at stakes for the tribo-mecanic characterization of the vacuum deposition is multiple. Issues are located not only at the level of research, of the development but also of the industrialization of these surface treatments.

What is before-all missing in the research area is the comprehension of the mechanisms by which hard layers interact with their environment (substrate, lubrication, counterpart…). Taking into consideration the multiple physicochemical parameters of interaction between the thin layers and their environment then makes it possible to concentrate the research efforts on the interfaces quality or/and on the tenacity of the coatings allowing a significant increase of their endurance in use.

During the development stage of a given layer, this question of the comprehension of the way the layers behave is added to a problem of quantification of these properties in order to more finely tune the coating parameters. For a given chemical composition (target, reactive gases …), the modification of some key parameters of the coating makes it possible to appreciably modify the microstructure of these layers and thus to tailor their mechanical properties around a median value (hardness, adhesion, Young modulus …). The adaptation of a surface treatment to a given application can thus go through the research of the properties of an optimal layer for this application. After these various development levels of the coatings, characterization of the layers is to be implemented at the production stage to guarantee the consistency of the properties batch after batch.

Various characterization tools/means are available as well at the academics as at the industrialists. Two points however will be noticed:

- Despite an increase in number of materials characterization means is observed at the academics, these tests remain generally difficult to implement and the relevance of extracted information is not guaranteed. Thus, the main part of the industrialists do not take the plunge and remain focussed on some basic tests of which the representativeness is often criticisable.

- Multiplicating the tribological tests adapted to the hard thin films and to precise friction conditions leads to an significant amount of information of which it is still extremely difficult to extract the essential for the user and the one implementing: which is the best deposition for a given application?

This paper illustrates the problems of the characterization of the thin layers for the one implementing the coatings from a purely mechanical point of view, disregarding the chemical aspect of the coatings (chemical compatibility, temperature in use, surface energy…) that makes the issue even more complex.

EXISTING CHARACTERIZATION MEANS

Thickness Measurement

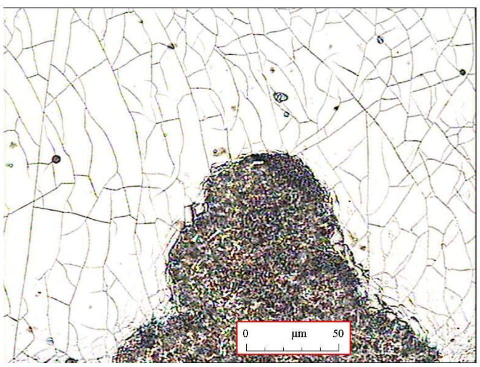
Even if this requires quite specific measuring devices compared to the traditional thermo chemical treatments, the thickness measurement of the coatings does not represent in general a technical issue. In addition to the methods using ultrasonic waves for the ranges of a few microns, there are methods easily accessible to the industrialist, non-destructive (x-ray fluorescence) as well as destructive like step height measurement using a profilometer (requiring a specific preparation before deposition), and measurement using a crater-ball test (Calotest™) using a large diameter ball that provides a tenth of a micrometer precision reading provided the surface roughness is smooth enough. This test is probably the most commonly used, it has the advantage of requiring a simple and low cost, easy to use equipment. In addition to the thickness measurement of the layers or multi layers, this test can also be used to evaluate the behaviour of a layer regarding abrasion and the interfaces quality. However, increased thicknesses or precise thicknesses cannot be considered as a proof of improved behaviour of the coatings in use. These tests must thus necessarily be supplemented by information on the mechanical properties of these coatings.

Instrumented Micro Hardness

The micro-indentation seems to represent the keystone of the industrial characterization of the hard thin films. By applying a sufficiently low load, it is possible to evaluate the hardness of the layers independently from the properties of the substrate and to deduce some intrinsic properties of the layers such as the reduced Young modulus, or/and to evaluate the fraction of energy elastically restored after indentation… These tests have the advantage of presenting notions well understood by the user of the layers, as they refer to concepts of mechanics of volumes. It is however necessary to keep a critical eye on it as it represents many traps and many shortcomings.

To characterize the mechanical properties of a layer without affecting the substrate, the criterion of the tenth is a general admitted rule: the maximum indentation depth at the time of the measurement shall not exceed the tenth of the coating thickness. When measuring hardness of a few micrometers thick layers, the maximum penetration of the indentor is thus of the same order of magnitude as the roughness of surfaces. According to the same criterion of the tenth, the quality of measurements can be guaranteed only when the depth of the indentation is ten times larger than the height of the roughness profile (Rz parameter). These two rules lead to sometimes contradictory constraints, even on polished surfaces (Ra = 0,02 µm, Rz = 0,2 µm), which makes difficult a precise measurement of the micro hardness of the thin films: either the depth of the indentation exceeds the tenth of the thickness of the coating, then the substrate partly affects the reading, or measurement is affected by the

roughness of the studied parts leading to an important uncertainty of the reading which must be compensated by a large amount of measurements.
Regarding the Young modulus assessment thanks to this method, let us recall on the one hand that the instrumented micro hardness does not make it possible to take into account the anisotropy of the coatings which can be deducted from the sometimes important residual compression stresses and from a sometimes columnar structure. On the other hand, the indentation only gives access to the “reduced” Young modulus, function of the Young modulus and the Poisson's coefficient. No information concerning the Poisson's coefficient is thus available, whereas this parameter can affect the contact mechanics and lead to a different behaviour of the interface. It is thus noticed that important voids remain regarding the determination of the mechanical characteristics of the thin layers and affect the quality of the calculation models which can be proposed to understand the damage mechanisms of these coatings. Finally, the indentation tests make it possible to quantify the resistance of a layer the penetration of a diamond and are not always representative of a real stress and the background reveals that a high hardness is not systematically correlated with a good behaviour in abrasion wear mode.[1] Hard layers can also fail by flaking (fragile behaviour) without showing a significant wear like illustrated in the following figure for a CrN coating.



Coating: CrN
Substrate : AISI M2 62 HRC

Hv (20 mN) = 2200 ± 150
E* = 290 ± 10 GPa

5.10^6 impacts at 250 N,
ball : AFN Z200Cr12 ∅ 20 mm

Figure 1 : Shocks test on CrN

Adhesion Testing: Scratch Testing and HRC Indentation Test

If numerous tests allow to get an evaluation of the adhesion of the layers,[2,3] there does not exist at the present time any method making it possible to define in a rigorous manner adhesion of the layers by defining a limit tensile or shear stress at the interface or its toughness. The scratch tests or HRC indentations (VDI 3198 standard) makes it possible to assess the adhesion of the coating in a rather qualitative way. Regarding the scratch test, one can note the influence of the hardness of the substrate, thickness of the deposited layer, roughness of surface,[4] loading rate, diamond’s speed,[5] wear of the diamond… At the present time, this test is not sufficient to determine whether a coating can afford a given stress. In addition to a critical load estimating the flaking of the layers, this test makes it possible to determine the weak links in the stacked multilayers by an inspection of the shape of the scales: cohesive, adhesive, dimensions of the scales…
For R&D purpose, alternatives are conducted with multiple scratch tests,[6,7] being in fact oligo-cyclic surface fatigue tests (less than 10^4 cycles) and with nano scratch tests,[8] for which the ultra low loads applied make it possible to precisely obtain the maximum shear stress at the precise interface deposition/substrate. However sensitivity of the latter to the roughness of the treated surface leads to the same

problems as for micro hardness measurement. The HRC indentation tests make it possible to define the quality of a layer by a note from 1 to 6. These rather qualitative tests are often mentioned as a quality control tool of the hard coatings but the background showed that the results are not always correlated with the real behaviour of the layer on tests benches. These tests will be also affected by the hardness and the roughness of the substrate, the thickness of the layer and the friction of diamond on the coating.
One will finally reproach these adhesion evaluation tests of testing the coating and the interface by an excessive plastic deformation of the substrate which is not representative of the real use of the components. If it is agreed that wear debris can lead to the scratching of the coating, the dimensions and hardness of this third body must be taken into account to obtain a relevant sorting of the layers. Then, the low thickness of the layers providing no structural functionality to them, they do not influence significantly the deformation of the substrate at the time of a scratch or an indentation with heavy load. Consequently, the deformation of the coating is imposed by the one of the substrate and the coatings are taking advantage of low Young modulus making it possible to reduce the stress under a given deformation.

Residual Stress Measurement

The residual stress measurement for thin films can be carried out by x-rays diffraction (non applicable to the DLC which are amorphous) or by the Stoney method (deflection). These tests give interesting orders of magnitude with generally compression stresses of several tenth to some giga-pascals, but require the realization of specific test coupons and do not allow to look into the influence of the geometry on the evolution of these residual stresses. Also, the influence of the residual compression stresses on the mechanical resistance of the thin film in terms of fatigue is rather complex. Indeed, if an increase of the compressive stresses can be of benefit for the fatigue resistance of the coating itself, it is inevitably accompanied by a tensile stress on the substrate. Thus, an optimal value of the residual compression stresses must exist for a given layer according to the interface and to the substrate.

Roughness Measurement

The whole question of the definition of the surfaces roughness in mechanics is reported to the surface treatment. When communication restricts oneself with some usual parameters of roughness (Ra, Rt, Rz, Rsk…) there exists a multitude of parameters to define the roughness among which it is difficult to sort the ones determining the mechanisms of friction, of lubrication… The surface analysis for the thin films is strongly linked to the amplitude of these roughness as those are often not negligible compared to the coating thickness scale.
The characterization means usually used in R&D make it possible to be finely look into the microstructure of the layers, their chemical composition (AFM, Raman, ERDS…) and their mechanical properties in particular thanks to acoustic analysis. All these tools make it possible to more and more finely describe the coatings carried out by PVD but this large quantity of available information does not make it possible yet to define how these coatings fulfil their tribological functionalities. Experience shows that good performances on characterization test cannot systematically be correlated with a good behaviour in use or in field test.

COMPARING CHARACTERIZATION TESTS TO TRIBOLOGICAL EXPERIENCE

Tribological tests show that the layers description using some basic mechanical properties is not sufficient to foresee the friction behaviour of these coatings or treatments. Tribology also takes into account the chemistry of surfaces and the wear mechanisms, and the coefficient of friction will mainly depend on the nature of the antagonist (counterpart), on the lubrication, on the mechanics of the stress (shock, friction, bearing, fretting…). These points can easily be illustrated by some tests.
The following table summarizes some friction tests carried out on a DLC coated coupon, considered for its low coefficient of friction and its great hardness. The comparison of the various coefficients of friction highlights different affinities of this coating towards the tested antagonists.

Table 1: Coefficient of friction of DLC vs different antagonists, dry condition

Dry friction test Cylinder M2 (62HRC, Ra = 0,07 µm) + 3 µm DLC Vitesse de glissement 0,5 m/s pendant 1 h	
Antagonist (Ra = 0,1 µm)	Coefficient of friction By the end of test
DLC	0,12
steel (XC38)	0,25
Aluminium (AU4G)	0,12
Bronze (UE12P)	0,35
Hard chrome	0,5 (seizure)

Remarkably low coefficients of friction are observed for DLC/DLC and DLC/Aluminium couples, but these coatings are clearly not suitable for friction tests versus copper alloys and a hard chromium plating. Regarding the influence of the environment, the literature related to tribology provides many examples dealing with the influence of the relative humidity or with the oxygen partial pressure on friction: fretting tests on TiN coating reveal for example that the coefficient of friction is divided by 4 when the relative humidity of the environment goes from 10% to 80%.[11]
The following graph illustrates the influence of the environment on a DLC coating during tribological pin on disc tests implemented under ultra-high vacuum by LTDS (CNRS UMR 5513) highlighting a coefficient of friction remarkably lower in the vacuum (in red) that in a nitrogen atmosphere at atmospheric pressure (in green) or in air (in blue).

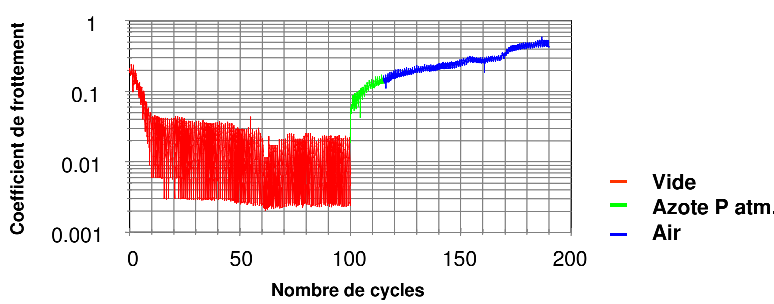


Figure 2: Friction test of a DLC coating under vaccum, nitrogen & l'air.

The influence of the environment is generally explained by tribochemical reactions supported by the important surface heat flows generated by friction (typically in the range of 10^7 W/m ²).

The difficulties met by the job-coater to optimize the thin films according to simple mechanical characterization tests is illustrated in the following example, presenting the influence of the thickness of a DLC coating during adhesion test by scratch test then by HRC indentation. The scratch tests provides comparable critical loads for the 1 µm and 2 µm thick coatings and would lead to disqualify the 3 µm thick coating. The HRC indentation test suggests that the thinner the deposition is, the more its adhesion is good, whereas the interface is supposedly being the same one in the three cases

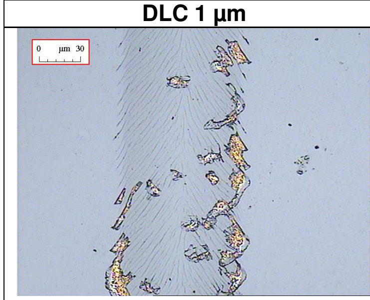
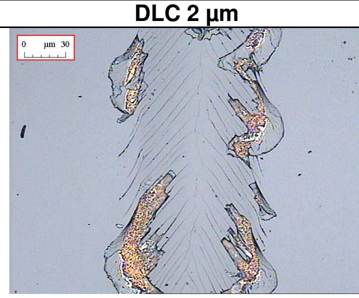
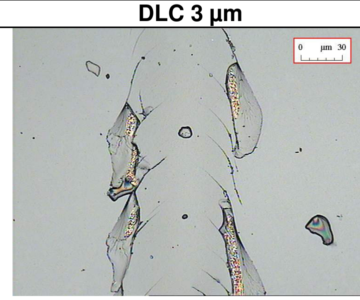
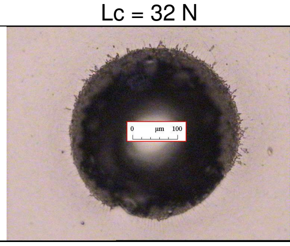
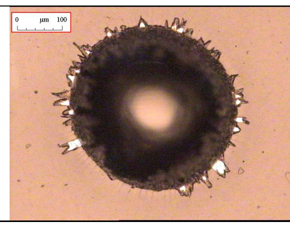
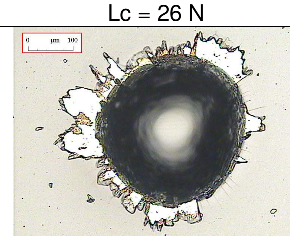
DLC 1 µm	**DLC 2 µm**	**DLC 3 µm**
 Lc = 32 N	 Lc = 33 N	 Lc = 26 N
		

Figure 3: Scratch and HRC indentation tests on a DLC coating

This kind of result can be explained by an increase in rigidity in flection of the layers with their thickness being sensitive under the small radius of curvature of the substrate when running this type of test.

Comparing these mechanical tests to tests on tribometer in lubricated conditions presented on Figure 4, shows that the correlation between the mechanical characterization and the performance in use of the coatings is not commonplace. This graph represents the evolution of the coefficient of friction during a test roller/roller both DLC coated, in an engine oil, with a sliding speed of 1,5 m/s. During this test, the contact pressure increases gradually by steps of 1 hour. The coefficients of friction are very close, but these samples can be distinguished by their mechanical resistance with a brutal rise in the coefficient of friction at the end of the test corresponding to a wrenching of the layer for the 1 µm thick coating (in green), 2 µm thick (in red) and 3 µm thick (in blue). These tests show a clear superiority of the 2 µm thick coating compared to the others which give equivalent results. The mechanical tests of figure 3 do not make it possible to foresee this type of results.

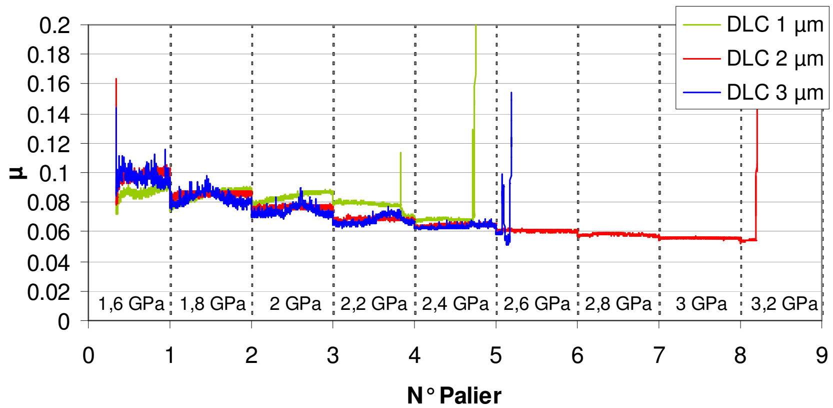


Figure 4: tribological test of a DLC under increasing load

With hindsight, these results can be explained by compromises between a soft wear and a rupture by surface fatigue, by the influence of rigidity in flexion of the coatings according to their thickness… But the occurrence of these various phenomena varies considerably with the tests configuration and cannot be easily anticipated at the present time. These results show the complexity of the development and the optimization of hard thin films. Thus, if the specifications of the end user are summarized most of the time with simple mechanical tests which have the advantage of being able to be realized by whoever working in the mechanics, like indentation, these data are seldom if ever representative of the behaviour in use of the thin films.

TRENDS OF THE DEVELOPMENTS IN HARD THIN FILMS CHARACTERIZATION

A review of the existing tools for characterization shows that it is not yet possible to determine necessary figures and properties to feed the models in order to correctly design the coatings. The efforts carried out on the characterization of the thin films can be gathered according to five main topics:

Roughness

The experience on tribometer showed that usual roughness parameters (Ra, Rz…) are not any more sufficient to qualify a surface from a tribological point of view. One can then be interested in the contact between real surfaces, taking into account various order of magnitude on the topography of surfaces. It will be noticed that according to the Hertz theory, some topographies can lead to a maximum shear stress precisely located at the interface coating/substrate.

To tolerate initial damages

Inspection of surfaces before tribological tests reveals the existence of defects on the surface for various reasons (voids, scratches, indentations), related for example to the handling of the parts before and after treatment. According to their nature and their location, these defects can lead to a layer damaged by fatigue. Suppressing these defects might not be compatible with markets on which one will rather seek to reduce the costs. It is then possible to consider these defects as inevitable and to work on the coatings architecture and the preparation process in order to obtain a certain defects tolerance of the treatments when used in cyclic conditions.

Characterization of the Adhesion and of the Interface

Efforts are also carried out to quantify the adhesion of the coatings not taking into account the mechanical properties of the substrate. For this purpose work is conducted to implement indentation on the sectioned coating, but which will quickly be a problem for the multi-layer coatings. The characterization at this level is systematically facing the issue of the scale of the considered volume element.

Efforts

Are also carried out to look further/deeper into the mechanical characterization of the thin films. This work, including the characterization tests carried out and listed above aims to propose a description of the tribological role of the hard and thin films. This description goes with the comprehension and the optimization of the surface treatments.

Tribological Tests

At the present time, the best solution to make sure a surface treatment will be a solution to a given tribological need consists in carrying out tests under conditions as close as possible to the real use of the coatings and to take into consideration not only the kinematics of the contact but also the thermochemical interactions between the various components. A panel of tribological tests is elaborated in order to make a transition between the real conditions of use of the parts and the traditional characterization tools mentioned above. If links are still missing to allow to understand the damage mechanisms of the coatings, this approach seems currently the most suitable to adapt the coatings to quite precise conditions of use.

CONCLUSION

The challenge of the thin films characterization, especially related to the small scale thus relates to all the levels: from research, development, to industrialization.

For the researcher, the various existing models require to define limit conditions and materials properties to determine the damaging modes under various stress conditions.

If the researcher can have access to instruments of utmost precision to explore the characteristics of the hard layers and interfaces (MET, AFM, instrumented nano hardness, acoustic microscope, shocks laser…) these various tools are not yet sufficient to feed a hard layers model.

For the coater, the tribological optimization of a coating for a well defined functionality remains still a problem. Thus, the coater is generally limiting the tests to obtain a good flaking behaviour during scratch tests and HRC indentation, a high hardness and a low coefficient of friction. Probably because these mechanical tests are excessively severe, the tribological background shows that these required characteristics are in fact, to a certain extent, neither necessary nor sufficient to guarantee the good behaviour in use of the coatings.

This is why, at the present time, HEF R& D works on the optimization of the hard thin films based on tribological tests according to a progressive approach, illustrated on the diagram hereafter, with a choice of the treatments under test conditions really close to the real conditions in use, and costs are in accordance.

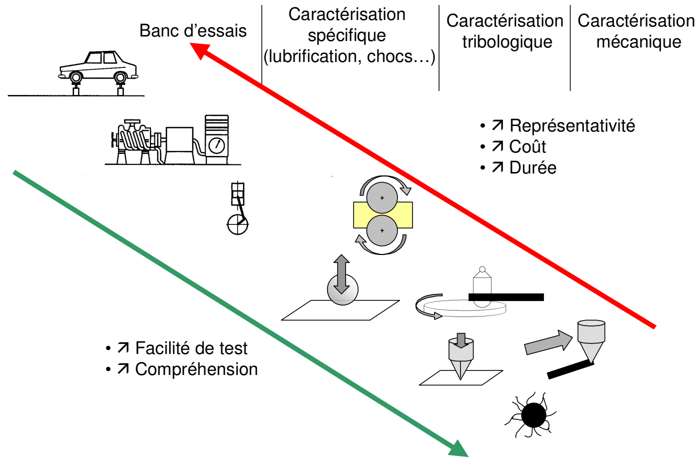


Figure 5: Caracterization of the treatments and coatings

For the end user, the characterization represents a production quality control . At the present time, the majority of the users of PVD coatings are satisfied with indentation tests and are at the origin of the standards relative to these tests. If such tests can constitute good indicators to identify process failures of, they cannot guarantee the quality of the layers. These tests are however very widespread in the technical-commercial discussions between the coater and his customers, which results in optimizing these coatings for this type of test in order to have commercial claims without true scientific value. This generalization of the indentation tests shows the need for the end user to be able to characterize the parts quickly, easily and at the lower cost. The previously illustrated tribological testing solution is not adapted to the quality control for daily routine production as it may require heavy specific equipment to implement and leads to long and expensive fatigue tests providing results sometimes only several days after the treatment of the coupons.

REFERENCES

1 « Etude de l'influence de la composition de couches minces de TiBN sur leur résistance à l'usure par abrasion » - C. HEAU ; N. GUILLON – Journées Internationales Francophones de Tribologie 1997

2 « Les tests d'adhérence appliqués aux revêtements minces : une synthèse bibliographique » - S. BENAYOUN ; J. J. HANTZPERGUE – Matériaux et Techniques n° 10-11-12 (2004) – pp. 23-31

3 « Evaluation of adhesion strength of thin hard coatings » - T. ARAI ; H. FUJITA ; M. WATANABE – Thin Solid Films 154 (1987) – pp. 387-401

4 « Influence of substrate roughness on the scratch adhesion of titanium nitride coatings » C. SUMBRAMANIAN ; K. N. STRAFFORD ; T. P. WILKS ; L. P. WARD ; W. Mc MILLAN – Surface and Coatings Technology 62 (1993) – pp. 529-535

5 « The effect of intrinsic parameters on the critical load as measured with the scratch test method » – N. X. RANDALL ; G. FAVARO ; C. H. FRUNKEL – Surface and Coatings Technology 137 (2001) – pp. 146-151

6 « A multipass/scanning tribometer for on line friction and wear mapping » - A. DARBEÏDA ; J. VON STEBUT ; M. ASSOUL ; J MIGNOT – International Journal of Machine Tools and Manufacture 35 n°2 (1995) – pp. 177-181

7 « Tribological behaviour of N- or O-doped austenitic stainless-steel magnetron sputter-deposited coatings » - P. GUTIER ; A. DARBEÏDA ; A. BILLARD ; C. FRANTZ ; J. VON STEBUT – Surface and Coatings Technology (1999) – pp. 148-155

8 « The nano-scratch tester (NST) as a new tool for assessing the strength of ultrathin hard coatings and the mar resistance of polymer films » - R. CONSIGLIO ; N. X. RANDALL ; B. BELLATON ; J. VON STEBUT – Thin Solid Films 332 (1998) – pp. 151-156

9 « Aspects statistiques de la multifissuration unidirectionnelle des revêtements » - A. MEZIN – Acta metallurgica et materiala 43 n°8 (1995) – pp. 3151-3157
10 « An analytical solution for stress relaxation in cracked coatings » - A. MEZIN – Surface and Coatings Technology 166 (2003) – pp. 160-166
11 « The influence of humidity on the fretting behaviour of PVD TiN coatings » - H. MOHRBACHER ; B. BLANPAIN ; J. P. CELIS ; J. R. ROOS – Wear 180 (1995) – pp. 43-52
12 « Multilayer PVD coatings for wear protection » - H. HOLLECK ; V. SCHIER – Surface and Coatings Technology 76-77 (1995) – pp. 328-336