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Raman analysis of DLC coated engine components with complex shape: Understanding wear mechanisms

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ABSTRACT

Hydrogenated amorphous carbon (a-C:H) films were deposited on flat samples and engine components using an industrial scale reactor. Characterization of the coating allowed validating its application on engine parts due to high hardness (32 GPa) and high level of adhesion achieved using sublayers. The original approach of this work concerned the use of Raman analysis not only on flat samples after tribometer tests but also directly on coated engine parts with complex shape (like cam/follower system), in order to understand wear mechanisms occurring in motorsport engines. As wear could lead to a coating thickness decrease, a particular attention was paid on the Raman signal of the sublayers. Among the different values extracted from Raman spectrum to characterize structural organization, the value of G peak intensity appeared as a criterion of validity of analyses because it is directly linked to the remaining thickness of the a-C:H layer. For flat samples tested on ball-on-disc tribometer, structure of a-C:H film observed by Raman spectroscopy in the wear track remained stable in depth. Then, a-C:H coated engine components were studied before and after working in real conditions. Two different wear mechanisms were identified. The first one did not show any structural modification of the bulk a-C:H layer. In the second one, the high initial roughness of samples ($R_t = 1.15$ µm) lead to coating delaminations after sliding. Massive graphitization which decreases drastically mechanical properties of the coatings was observed by Raman analyses on the contact area. The increase of the temperature on rough edges of the scratches could explain this graphitization.

1. Introduction

With high wear resistance and very low friction coefficient, hydrogenated amorphous carbon (a-C:H) coatings have a promising future in consumer automotive application to reduce friction losses and to increase lifetime of the mechanical parts. Tribological properties of these films depend mostly on the hydrogen content and the proportion of sp^2 to sp^3 carbon bonds [1,2]. Raman spectroscopy is widely used to observe carbon bonding on a-C:H coated flat samples [3,4]. Many authors have already characterized tribological behavior of a-C:H films under different conditions using tribometers [5–8]. Some of them have linked their results to structural modifications observed by Raman spectroscopy [7,8]. Even if laboratory tests can give precious information, they are not able to simulate the real operating conditions encountered in engines. So the only way to evaluate the stability of a-C:H films is to coat mechanical parts that will be used in motors. Besides the difficulty to obtain a coating with good quality, uniformity and adhesion, mechanical parts present complex shapes that forbid the use of several techniques of characterization. For example, nanoindentation measurements require a smooth plane surface below the nanoindenter and remaining DLC (diamond-like carbon) layer after wear tests has to be thick enough to obtain a reliable value of coating hardness. On the other hand, Raman spectroscopy is a non destructive and non intrusive method which is very useful to observe changes in the DLC coating structure induced by tribological tests [7,8]. Taking some precautions, it should be possible to perform Raman analysis on mechanical parts with curvature radius before and after working.

This paper presents original results of Raman analyses on real engine components. A special attention is given on the methodology to validate these measurements. After the presentation of the main properties of the a-C:H film studied in this work, the observation of structural modifications of the coating on plane sample after tribometer test is presented. Finally Raman analyses are also performed directly on real engine parts with complex shapes after working in real engines.

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2. Experimental part

a-C:H commercial films were deposited onto AISI M2 polished flat samples and engine parts by plasma enhanced chemical vapor deposition technique (PECVD) using an industrial scale reactor. Followers (antagonist part of the cam) have been chosen as the cam/follower system can be responsible for around 20% of the total energy losses of an engine [9]. Furthermore the wear rate of these parts is high due to elevated contact pressures. The thickness of a-C:H layer on both engine parts and flat samples was around 1.5 µm. Adhesion was improved by sublayers between the steel sample and the a-C:H film consisting of a TiN (1 µm) and a-SiC:H (1 µm). Chemical composition of the DLC layer was determined by elastic recoil detection analysis (ERDA) and Rutherford backscattering spectrometry (RBS). Hardness (H) and Young's modulus (E) were estimated by nanoindentation by the means of MTS Nanoindenter® XP working with a continuous stiffness modulus (CSM). Residual stress in the film was calculated from the curvature of silicon sample strips after deposition, using the Stoney equation [10]. Tribological test was realized with a rotating ball-on-disc tribometer at room temperature without lubrication using uncoated AISI 52000 steel balls sliding against DLC coated flat samples. Unlubricated conditions have been chosen because cam/follower systems operate in boundary lubrication regime in which the oil film thickness does not avoid direct contacts between surfaces [11]. Raman spectroscopy was used to investigate the structure of a-C:H films. Raman analyses were performed with a Jobin Yvon spectrometer (model T64000) in backscattering mode, using the 514.5 nm line of an argon ion laser. Owing to the curvature radius of the mechanical parts, X50 objective with long working distance has been used. With its large numerical aperture (0.55), this objective fixed a depth penetration to a value around 2 µm that is higher than DLC thickness. Spectra acquired were fitted by using two Gaussian peaks labeled G and D [3,4]. Two values extracted from the curve fitting are used: full-width at half maximum of the G peak ($FWHM_G$) and ratio between intensities of the two peaks I_D/I_G. $FWHM_G$ increases as disorder increases, i.e. clustering decreases, furthermore clear correlation between $FWHM_G$ and mechanical properties has been already shown [3,4]. On the other hand I_D/I_G is generally used as a measure of the sp^2 phase organized in clusters [12].

Finally, Raman analyses were performed on DLC coated followers which have run in different motorsports engines where antagonist cams were also coated with DLC.

3. Results and discussion

3.1. a-C:H characterization

The main characteristics of the a-C:H film used in this work are shown in Table 1. Due to a hardness of 32 GPa and a hydrogen content around 32 at.%, this DLC film could be classified in the hard a-C:H films in the ternary phase diagram proposed by Robertson [1]. Nevertheless mechanical properties mentioned by Robertson for these kinds of films are generally lower (H ~ 20 GPa). In accordance with hardness, compressive stress in the a-C:H layer is high but sublayers allow reaching good level of adhesion as shown by the scratch test result (>30 N).

Table 1
Main characteristics of a-C:H film.

Characteristics	DLC layer
Hardness (GPa)	33 ± 2
Young's modulus (GPa)	246 ± 14
H content (at.%)	32 ± 1.0
Density (g cm^{-3})	1.6
$FWHM_G$ (cm^{-1})	176.0
I_D/I_G	0.47
Scratch test (N)	>30
Residual stress (GPa)	-3.7 ± 0.3

As depth resolution of Raman analysis is higher than a-C:H layer thickness, it is necessary to verify that the Raman responses of sublayers (especially a-SiC:H) and a-C:H layer do not interfere in the 850–1900 cm^{-1} range. In Fig. 1, Raman spectra of the DLC layer and the sublayers stack on flat sample are presented. Raman spectrum of sublayers is obtained with a devoted sample where elaboration process has been stopped just before DLC deposition. Sublayers present a broad band around 1500 cm^{-1} but its intensity is weak in comparison with the one of a-C:H layer. However, it is important to evaluate the influence of the sublayers when the thickness of DLC layer decreases. A Calotest is performed with a steel ball and abrasive solution to obtain a ball crater where thickness of the coating decreases when approaching the center of the crater. Raman analyses are conducted on different positions i.e. for different remaining thickness as presented in Fig. 2. Evolution of $FWHM_G$ and G peak intensity (I_G) are reported in Fig. 3. I_G decreases slightly until position four (where a 0.1 µm a-C:H thickness remains) and then falls to the value already measured for sublayers. $FWHM_G$ is constant on the first four positions before increasing at the last two positions. It means that sublayer Raman signal is not significant if there is more than 0.1 µm of a-C:H on the surface. Evolution of I_D/I_G ratio (non-presented here) confirms this tendency. The remaining thickness of DLC is not directly available locally after a wear test. Thus, the validity criterion of the Raman analysis should be the value of I_G which is directly linked with the remaining thickness of the a-C:H layer. Based on the results presented, values of $FWHM_G$ are only validated if the I_G is higher than 70% of a reference value obtained for a minimum a-C:H thickness of 1.5 µm. For coated engine components, this reference of I_G is taken on a position of the surface which has not been in contact with antagonist parts. This procedure takes advantage of the non destructive property of Raman spectroscopy.

3.2. Raman analysis of worn DLC films

Fig. 4 presents the Raman spectra of the DLC film before wear test and of the remaining DLC in the wear track after rotating ball-on-disc tribometer tests on flat samples. Structure of the bulk coating in the wear track remains similar to as deposited a-C:H structure. Thus mechanical properties of the coating stay constant after sliding and graphitization phenomenon does not occur in depth. Formation of a very thin transfer film is observed on the contact area of the steel ball. Raman spectrum of this tribofilm shown in Fig. 4 presents a very graphitic character. This tribofilm is well-known to be responsible for the very low friction coefficient of DLC films [13]. Indeed, as graphite is very easy to shear, the tribofilm promotes the reduction of the friction

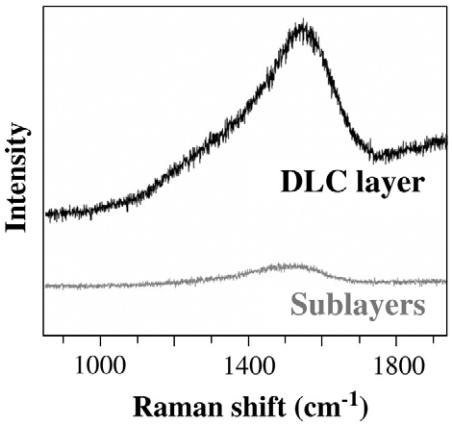

Fig. 1. Raw Raman spectra of a-C:H film and sublayers.