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Laser texturing of a multilayer DLC from nano-liquid-diamond precursors via microsecond laser pulses

A.Zivelonghi[a*], L.Giorleo[a], M.Gelfi[a], E.Ceretti[a], M.G. La Vecchia[a]

[a]*University of Brescia, Department of Mechanical and Industrial Engineering, Brescia, Italy*

Abstract

Diamond Like Carbon (DLC) coatings have well known mechanical properties, including high hardness, chemical stability, optical transparency and biocompatibility. In addition they are frequently used in multilayer coating systems.
Laser surface texturing of DLC coatings can be a tailoring solution to optimize the coating functional parameters like roughness, wettability, wear, corrosion resistance, etc. Furthermore, compared to mechanical grinding, local laser removal could be a suitable technology for repairing locally damaged coated parts (i.e. worn surfaces, corroded surfaces, etc.)
In the present work, laser surface texturing and controlled laser removal of a multilayer DLC coating obained from nano-liquid-diamond precursors have been studied using a 8W Q-switched laser (λ=532 nm) with microsecond pulses. Textured ablation as well as full planar decoating are shown through proper adjustment of laser texturing parameters.

Keywords: laser ablation, laser etching, laser surface texturing, DLC

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* Corresponding author. Tel.: +39 030 3715538 Fax. +39 030 3702 448
E-mail address: alessandro.zivelonghi@unibs.it

1. Introduction

Diamond like carbon (DLC) films are well known protective coatings due to excellent material properties like high hardness, chemical stability, optical transparency, dielectricity and biocompatibility (Bewilogua and Hofmann 2014, Czyż et al. 2016). DLC also possesses very favourable tribological properties which makes it an excellent low friction different engineering components (Kano 2006, Fontaine et al. 2008).

Moreover, a number of studies have reported that the tribo-mechanical properties can be significantly improved by doping the DLC with various elements like Cr, Si, W, etc. (Chiu et al. 2005; Ban et al. 2002; Forsberg et al. 2013).

Laser ablation processing both of DLC coatings and related metallic substrates is a growing research field in material processing (Konov 2012, Silva et al. 2013). The process is based on laser ablation and is commonly referred in literature as laser surface texturing (LST). It has been recently proven, for instance, that laser texturing of pure DLC and DLC:Si is capable to further reduce the friction coefficient with tungsten carbide and alumina (Shum, Zhou, and Li 2013, Amanov et al. 2013).

It should be pointed out that nowadays one often encounters a complex multilayer coating architecture, with interlayers to improve adhesion, particularly for automotive applications (Renman 2012).

In this context, decoting through laser ablation can be also of interest for those applications requiring repair of locally damaged coated parts. Controlling the ablation depth, however, is critical, particularly for multilayer coating systems. In this case, efficient decoating can only be achieved through controlled laser processing.

In the present work, laser removal of a 6.8 µm thick bilayer DLC + DLC:Cr coating system designed for tribological applications has been investigated. A 8W Q-switched laser source (λ=532 nm) in pulse mode was employed for the experiments (Fig.1).

Different decoating textures were obtained as a function of the different laser parameters. In order to control the decoating depth within the multilayer, energy dispersive spectroscopy (EDS) was employed in combination with scanning electron microscopy (SEM), optical measurements (OM) and calotest.

The paper strategy is as follows. The most influencing process parameters during decoating have been identified through controlled experiments on the laser input parameters. A first campaign on isolated laser spots using only one repetition loop aimed at showing the laser interaction effect on the DLC surface and identifying the ablation threshold. Then, in a futher campaign the effect of multiple loops and pulse overlap was investigated. An ON-OFF criterion was therefore established in order to select those configurations where the DLC coating was entirely removed. Within the selected modifications, full planar etching was finally shown.

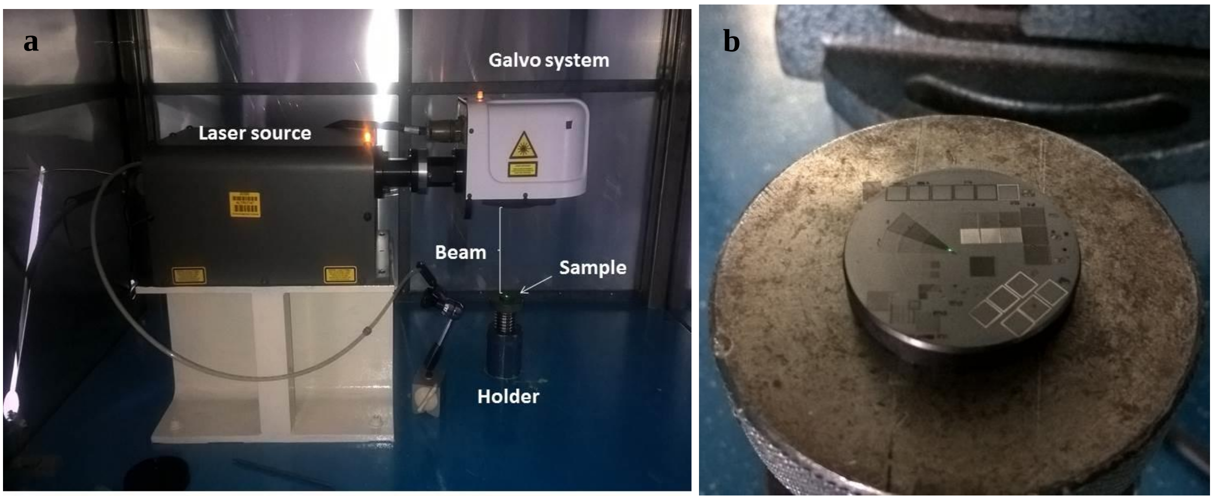


Fig. 1. Left: experimental setup. Right: DLC sample.

2. Experimental Tests

The laser setup employed in the present work is shown in Fig. 1. A LEP Lee Laser (Nd:YVO4, 8 W q-switched, λ = 532 nm) was used in pulsed mode. The outgoing laser beam is collimated in a galvo system to impose a remote control in the x and y directions. The DLC sample with a diameter of 30 mm was fixed on a holder at a distance equal to the focal distance (160 mm) from the galvo head. All laser parameters are reported in Table 1. Average laser power was measured with a power meter. Pulse overlap percentage in x and y (Fig. 2b) were indirectly controlled by marking speed (v), laser frequency (f) and filling line gap (flg) according to the formulas reported in table 1. The flg is defined as the distance between two parallel lines of the laser path.

Table 1. Material and laser setup parameters used in the present study.

Material	
Coating type	DLC+DLC:Cr on C40 Steel
Deposition technique	CAE-PVD + RF-PECVD
Thickness - z	6.6 µm
Lased sample area	3 x 3 mm^2
Laser	
Wavelength	532 nm
Spot diameter - D	0.1 mm
Focusing length	160mm
Frequency - f	20 kHz
Duty cycle - dc	20%
Pulse duration – dt	10 µs
Marking speed - v	200-2500 mm/s
Max power - P	8 W
Number of loops - N_{loop}	1-30
Filling line gap - flg	0.01 - 0.1mm
OLx = 1-flg/D	0-90%
OLy = 1 -v/fD	0-90%
Laser path	parallel lines
Atmosphere	air

DLC layers were deposited on EN 10083 C40 carbon steel via different deposition techniques. Cathodic Arc Evaporation Physical Vapour Deposition (CAE-PVD) with solid targets was used for the CrC/Cr interlayer while the DLC top layer was obtained through Radio Frequency Plasma Enhanced Chemical Vapour Deposition (RF-PECVD) from Nano Liquid Diamond (NLD) precursors. The doped DLC:Cr layer was obtained through a hybrid process of both mentioned techniques. The resulting multilayer structure is described in Fig. 2.
EDS as well as OM and R_a measurement were repeated on three different replicas of the same ablation spot. Surface roughness R_a after laser etching was estimated with a profilometer (Mitutoyo SJ301).

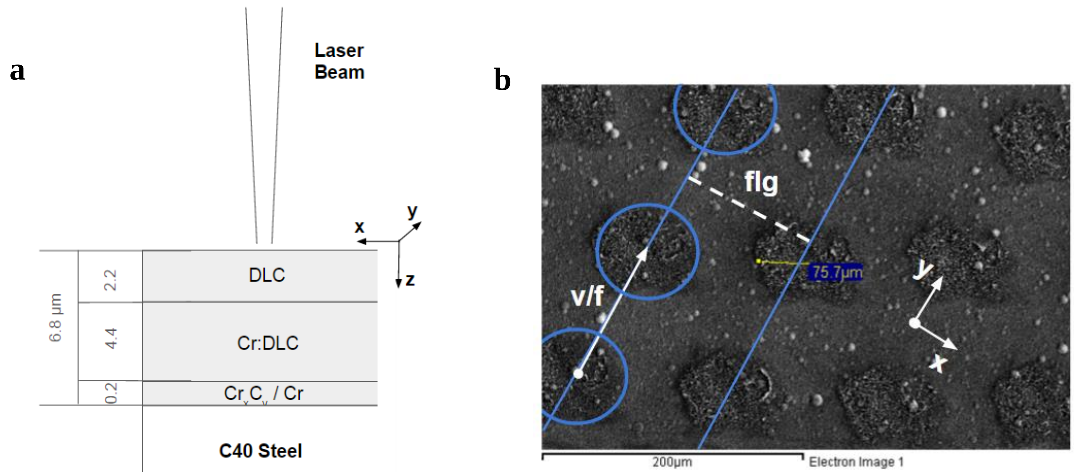


Fig. 2. (a) Multilayer structure from calotest; (b) Laser path (blue lines) and overlapping parameters v/f and flg on the DLC surface.

2.2 On-off criterion for complete DLC etching

An ON-OFF criterion was set to determine the conditions of full removal along z of the bilayered DLC coating. First, EDS + SEM inspection were carried out to verify the lased surface composition and to obtain a proof of complete DLC removal. In fact, withstanding the difficulty in the quantitative evaluation from EDS, for the present case a large reduction of the percentage of Carbon (>70 wt.%) was considered a proof of the DLC + DLC:Cr removal and set as the required criterion. To confirm this, reference thicknesses of the multilayer were independently obtained through a calotest (CSM Instruments) and compared with depth measurements from OM on one reference lased configuration (#10).

2.2 Laser process parameters

Directly and indirectly controlled laser parameters are listed in table 2. Three levels of fluence (0.006, 0.1, 1 J/cm²) and four levels of loops N_{loop} (1, 10, 20 and 30) were firstly changed while maintaining the geometrical configuration of well separated spots (configurations ID #1-12). This approach allowed to determine the full decoating conditions without the biasing effect of geometrical overlapping. The most effective laser fluence and the minimum number of loops satisfying the ON-OFF criterion were herewith identified. Finally, conditions for planar decoating were investigated varying the overlapping parameters OLx and OLy.

Table 2. Varied laser parameters and related configurations . Directly controlled parameters are marked with *. The ON/OFF output variable refers to complete DLC removal along z.

ID	*P_{avg} [W]	*flg [mm]	*v [mm/s]	*N_{loop}	F [J/cm2]	OLx	OLy	ON/OFF DLC removal
#1	0.2	0.1	2500	1	0.006	0.00%	0.00%	OFF
#2	0.2	0.1	2500	10	0.006	0.00%	0.00%	OFF
#3	0.2	0.1	2500	20	0.006	0.00%	0.00%	OFF
#4	0.2	0.1	2500	30	0.006	0.00%	0.00%	OFF
#5	0.65	0.1	2500	1	0.1	0.00%	0.00%	OFF
#6	0.65	0.1	2500	10	0.1	0.00%	0.00%	OFF
#7	0.65	0.1	2500	20	0.1	0.00%	0.00%	OFF
#8	0.65	0.1	2500	30	0.1	0.00%	0.00%	OFF
#9	2.09	0.1	2500	1	1	0.00%	0.00%	OFF
#10	2.09	0.1	2500	10	1	0.00%	0.00%	ON
#11	2.09	0.1	2500	20	1	0.00%	0.00%	ON
#12	2.09	0.1	2500	30	1	0.00%	0.00%	ON
#13	2.09	0.01	2500	10	1	0.00%	90.00%	ON
#14	2.09	0.01	600	10	1	70.00%	90.00%	ON
#15	2.09	0.01	200	10	1	90.00%	90.00%	ON

3. Results

3.1 Non-overlapping pulses (single spot)

Firstly, non-overlapping laser spots were studied at different fluence values. In this case N_{loop} was set equal to 1 (only one repetition) to isolate the effect of single laser pulses. A damage threshold of approximately 0.1 J/cm2 was found as evident in Fig. 3 where different laser spot fingerprints for increasing fluence values are shown.

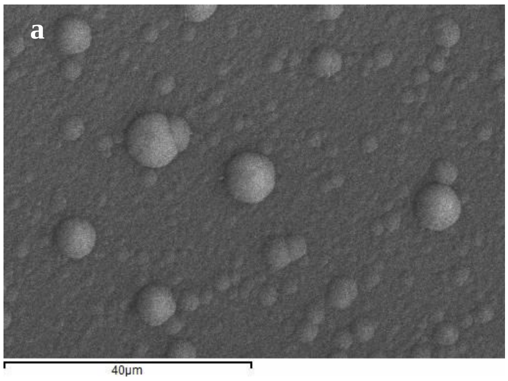
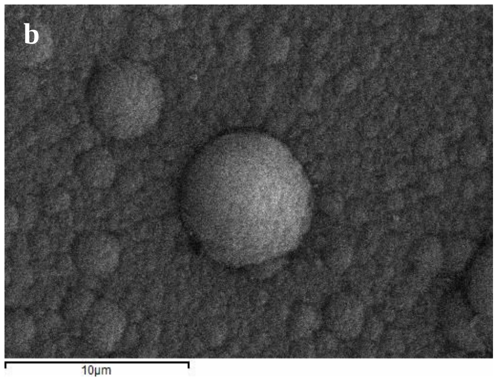
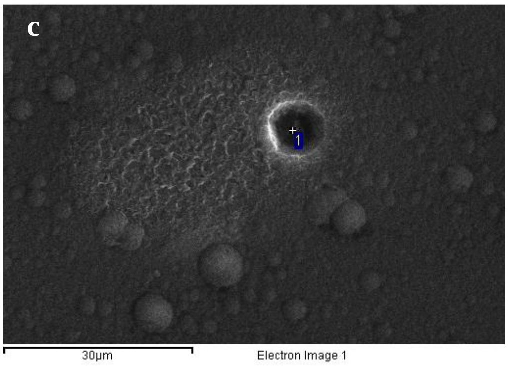
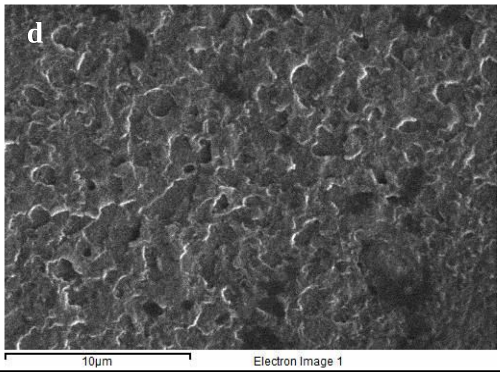
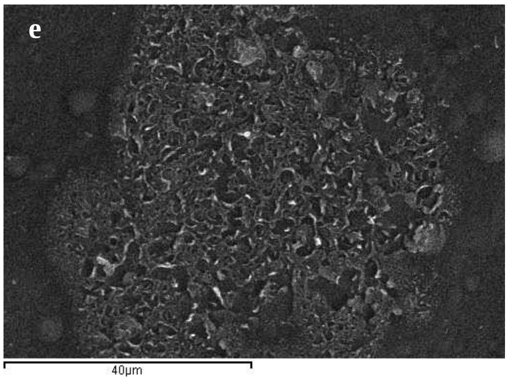
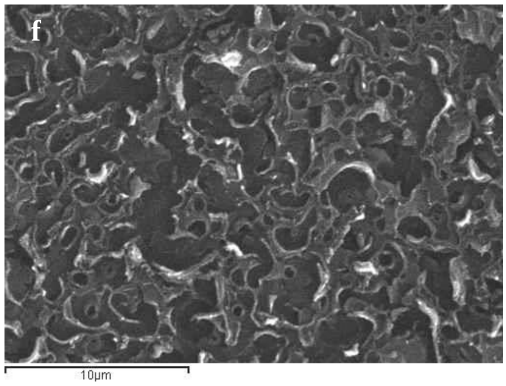
	5000 X	20000 X
#1 **F=0.006 J/cm^2**		
#5 **F=0.1 J/cm^2**		
#9 **F=1 J/cm^2**		

Fig. 3 SEM image serie of single laser pulses on the DLC surface at different fluencies.

3.1 Non-overlapping pulses (single spot)

No surface modification was found at 0.006 J/cm² where the droplets (typical of the PECVD deposition process) are the same of the untreated sample. At 0.1 J/cm² the lased surface shows a change of topography characterized by a total removal of the surface droplet and the presence of a partial melting of the coating. Finally, in the transition from intermediate to high fluence (0.1 to 1 J/cm²), a clear increase of the ablated spot area was observed. Hence the effect of multiple laser pulse repetitions on the isolated spots was investigated by varying the number of loops (N_{loops}). To roughly quantify this effect the percentage of the elements Carbon (C) was monitored via SEM-EDS analysis for increasing values of N_{loops} and F. At a fluence value of 1 J/cm^2, a dramatic drop of the %C is observed when increasing N_{loop} from 1 to 10 (Fig. 4a). This variation - from about 80% to 10% - can be considered as a first clue of complete DLC + DLC:Cr removal in the z direction. This observation is further supported by SEM analyses, where the transition from DLC to the CrC interlayer is clearly visible (Fig. 4b). Moreover, etching depth estimations (Δz) with optical microscope finally confirmed a total removed coating thickness larger than 7 µm (±0.5µm due to instrumental accuracy limit). However, neither EDS nor OM can determine which of the sub-layers left between the CrC, the metallic Cr and the steel substrate due to uncertainty in the electron beam penetration depth and many other factors affecting the accuracy of EDS. Nonetheless, a clear saturation effect on the %C is observed for N_{loops} > 10 and F = 1 J/cm^2 (Fig 4c) once the DLC layers are completely removed and further pulses impinge on the CrC/Cr interlayer. This saturation effect is certainly related to an increase in ablation threshold once the ablated surface reached the CrC/Cr interlayer. Concerning the transition depth from DLC:Cr to non-DLC layers, results are in good agreement with calotest. This can be stated in view of uncertainty from calotest and optical measurement (±0.5μm) as well as of layer thickness irregularity caused during deposition.

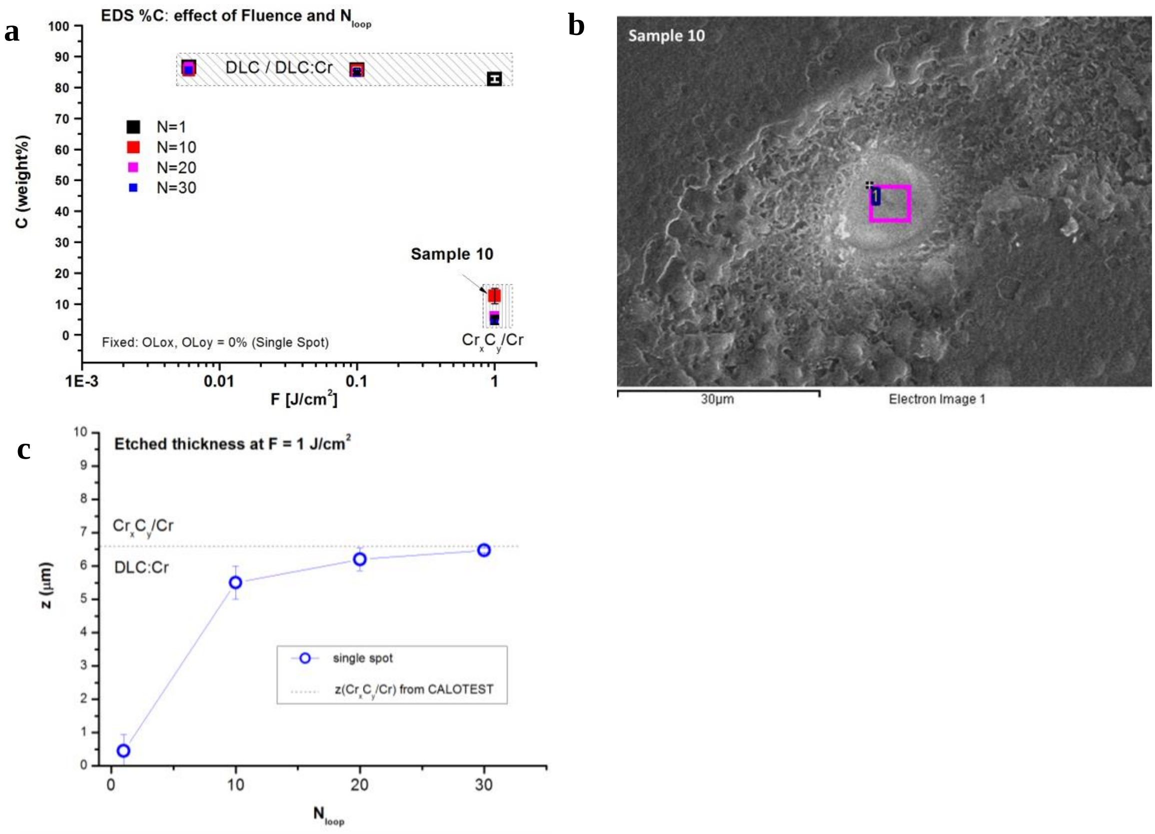


Fig. 4. (a) %C from EDS analysis on the ablated surface at different values of N_{loops} and F; (b) SEM image of the reference lased surface #10 showing full DLC removal at the ablation spot center; (c) Removed thickness estimated with optical microscope compared to results from calotest.

3.2 Overlapping pulses

Among the different configurations which satisfied the condition of complete DLC removal along the z-axis, the parameters of marking speed (v) and filling line gap (flg) were further varied to obtain different overlapping conditions in the in-plane directions (x and y of Fig. 2b). These configurations are the #13-15 in table 1. In Fig. 5 three of the resulting textures are shown while fixing N_{loop} = 10 and flg = 0.01 mm. Parallel vertical lines were obtained at v = 2500 mm/s and 600 mm/s (Fig. 5a,b). The resulting decoating channels have a width of about 70 µm in the first case with pronounced residual roughness of the engraved CrC/Cr layers. At 600 mm/s thinner channels (ca. 30 µm width) are observed as an effect of increased overlapping of the laser spot along x. Although the theoretical overlap was 70% (config. #14 in Tab.1), residual borders of partially ablated DLC:Cr are still evident due to non-uniform energy distribution of the laser spot. Moreover, some debris are evident on the channel surface. Finally, planar uniform etching was obtained at v = 200 mm/s and flg = 0.01 mm (Fig. 5e,f). In this case the lased surface appears very clean with a measured residual roughness of about 0.2 µm. EDS analysis on this surface (Fig. 6) also confirmed a very low value of Oxygen (~3 wt.%) upon which one envisages the possibility of DLC redeposition after proper surface handling. However, future investigations are needed including the evaluation of mechanical properties of the redeposited coating.

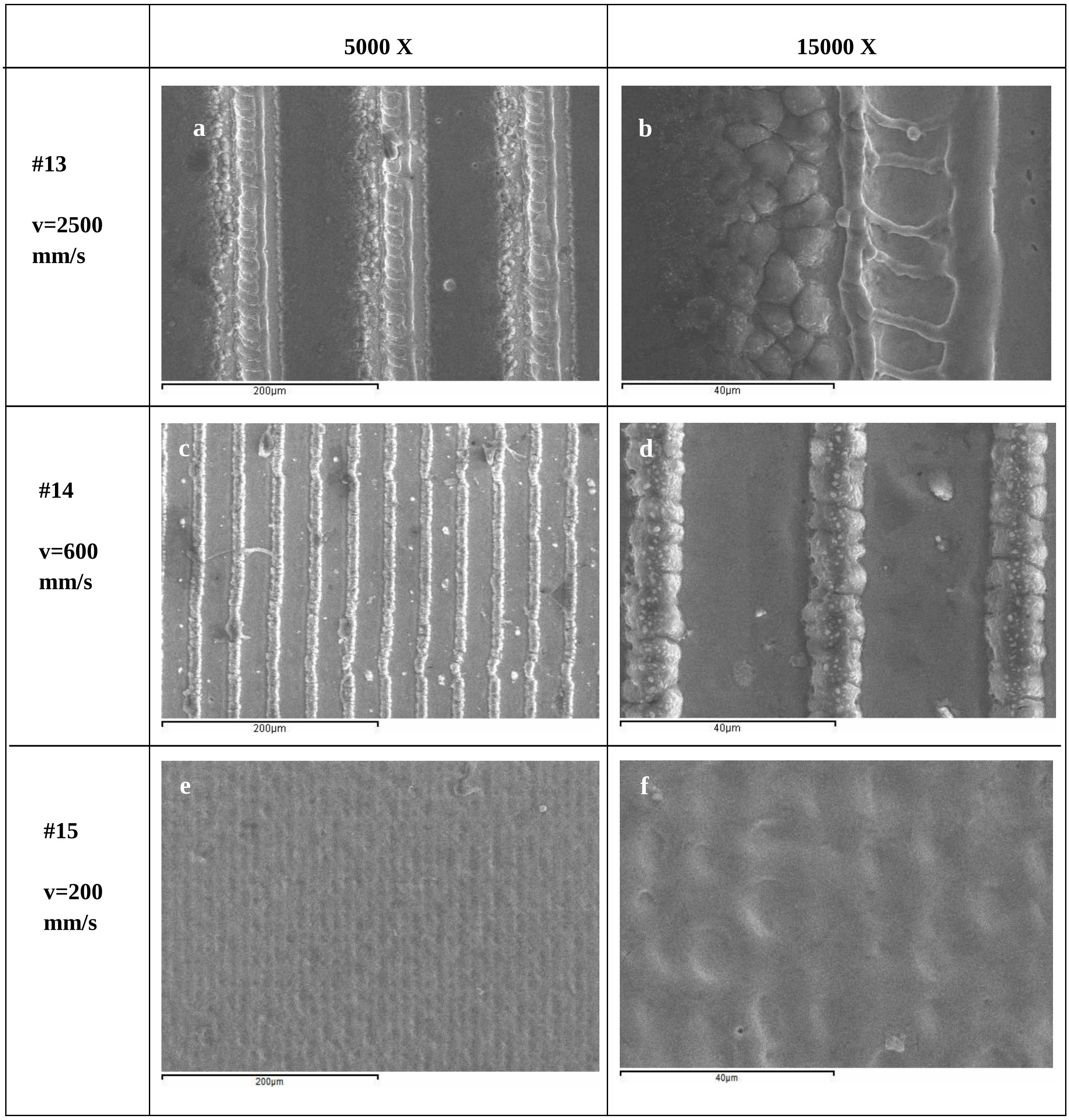


Fig. 5 Different surface textures showing full laser etching of DLC + DLC:Cr along z.

Table 3. EDS spectrum of configuration #15 .Scanned area 60 * 50 µm (Fig. 5f).

Spectrum	wt.%	C	O	Cr	Fe	Total
Spectrum 1		2.44	3.61	8.80	85.16	100.00
Spectrum 2		3.17	2.74	10.2	83.88	100.00
Mean		2.80	3.17	9.5	84.52	100.00
Std. Dev.		0.52	0.30	0.98	0.91	

4. Conclusions

In the present paper controlled laser ablation of a multilayer DLC coating has been studied. This technique is able to efficiently and selectively etch micrometric DLC layers giving rise to different surface textures. The present campaign aimed at showing the influence of laser fluence, loops number, and overlapping parameters on the final texture. A Nd:YVO4 laser source, with wavelength equal to 532 nm and average pulse power up to 2 W was employed in the experiments. Results highlight that uniform decoating of DLC with good surface quality of the rest surface can be achieved. This was shown at a conveniently high fluence (fairly above the ablation threshold) and at a conveniently low marking speed.

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