ACS APPLIED MATERIALS & INTERFACES
Research Article
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Chemical Vapor Deposition of Highly Adherent Diamond Coatings onto Co-Cemented Tungsten Carbides Irradiated by High Power Diode Laser

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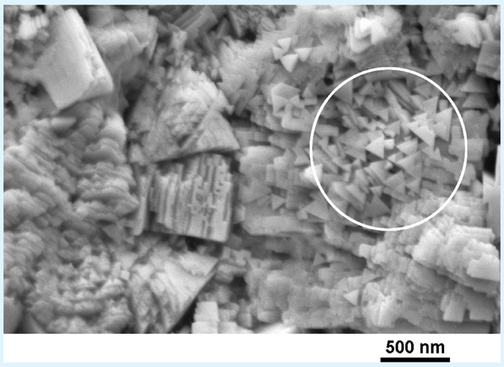

ABSTRACT: The present investigation deals with the definition of a new eco-friendly alternative to pretreat Co-cemented tungsten carbide (WC−Co) substrates before diamond deposition by hot filament chemical vapor deposition (HFCVD). In particular, WC-5.8 wt %Co substrates were submitted to a thermal treatment by a continuous wave-high power diode laser to reduce surface Co concentration and promote the reconstruction of the WC grains. Laser pretreatments were performed both in N_2 and Ar atmosphere to prevent substrate oxidation. Diamond coatings were deposited onto the laser pretreated substrates by HFCVD. For comparative purpose, diamond coatings were also deposited on WC-5.8 wt %Co substrates chemically etched by the well-known two-step pretreatment employing Murakami's reagent and Caro's acid. Surface morphology, microstructure, and chemical composition of the WC-5.8 wt %Co substrates after the different pretreatments and the deposition of diamond coatings were assessed by surface profiler, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction analyses. Wear performance of the diamond coatings was checked by dry sliding linear reciprocating tribological tests. The worn volume of the diamond coatings deposited on the laser pretreated substrates was always found lower than the one measured on the chemically etched substrates, with the N_2 atmosphere being particularly promising.

KEYWORDS: *CVD, diamond, hard metal, chemical etching, substrate pretreatment, diode laser*

1. INTRODUCTION

The structure of diamond and its very strong chemical bonding lead to unique mechanical and thermal properties, which explain why diamond is widely used as material for first-rate tools.[1] Diamond is the hardest of all natural materials: as steel is to butter, so is diamond to steel. The coefficient of friction for the diamond natural surface in air at room temperature is in the 0.05−0.15 range,[2] i.e., comparable to that of Teflon, although in the case of polycrystalline films grown by chemical vapor deposition (CVD) the friction coefficient is strongly influenced by the surface morphology.[3] Diamond has a large chemical inertness, and the onset of graphitization in an inert atmosphere or in vacuum begins around 1520 °C. With unmatched thermal conductivity, diamond appears to be the perfect heat exchange material. Therefore, diamond is widely used for tooling applications in the form of crystals within a metal matrix.

Since the discovery of chemical vapor deposition of diamond onto nondiamond substrates,[4,5] diamond film technology has attracted many research groups around the world to study new synthesis methods and applications. A great deal of interest was paid on the deposition of diamond coatings onto Co-cemented tungsten carbides (WC−Co). They belong to the class of hard metals, and they are widely used for the manufacturing of cutting tools, sliding bearings, drawing dies, and a large variety of wear-resistant components.[6] Coating hard metals with superhard materials like diamond is therefore of utmost interest as it can further extend their wear life beyond their nominal performance.[7−15] However, premature failure of CVD diamond coatings onto carbide inserts and worn parts caused by a combination of mechanical, chemical, and thermal factors remains a difficult challenge. In fact, the deposition of diamond coatings onto WC−Co can be extremely complicated as a result of poor adhesion. This can be essentially ascribed to: (i) the mismatch in thermal expansion coefficients between diamond and WC−Co, which leads to large thermal residual stresses at the interface; (ii) the role of Co inside WC−Co, whose presence at the substrate surface promotes carbon dissolution and diffusion during diamond CVD.[16−20] Therefore, the interfacial Co must be effectively removed from the WC−Co substrate for the deposition of highly adherent diamond coatings. Moreover, the resulting increase in the substrate

Received: September 22, 2011
Accepted: December 29, 2011
Published: December 29, 2011

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surface roughness prior to diamond deposition allows an increase in the surface area of contact at the coating/substrate interface and promotes their mechanical interlocking with consequent enhancement of film adhesion.[21]

There are different ways by which WC−Co substrates can be treated and have their surface Co removed, although the most widespread techniques can be summarized as follows: (i) Co etching, in which aqueous solutions of either strong oxyacids or hydrochloric acid, as well as more complex multistep etching procedures, etch the Co out of the outermost layers of WC−Co.[22−29] This, sometimes, also corrugates the WC grains;[29] (ii) use of intermediate layers of various materials (ranging from metallic Cr, Ti, Ta, etc. to CrN, TiC, TiN, β-SiC, and Si_3N_4) onto the WC−Co surface preventing Co and C diffusion.[30−34] In addition, interlayers can be designed to adjust the mismatch of thermal expansion coefficients between WC−Co and diamond, thus reducing thermal residual stresses which develop inside the coating when the diamond coated substrate is left to cool down to room temperature; (iii) mechanical treatments, in which mechanical interlocking between diamond and WC−Co is promoted by micro- or macro-corrugating WC−Co or the interlayer surface;[35−37] (iv) WC−Co thermal or thermochemical treatments, reducing interfacial Co concentration, inducing surface reconstruction of the WC−Co substrate and the consequent modification of surface morphology and microstructure.[38−41]

Singh et al. and, subsequently, Li et al. proposed the use of a pulsed laser, operated at very high irradiance (>80 MW/cm^2), to reduce the Co concentration at the WC−Co surface, induce its corrugation and, therefore, promote the adherent growth of CVD diamond coatings.[42−44] The laser treatments led to remelting of the irradiated material and gave rise to a sort of complete surface reconstruction rather than to the removal of Co from the WC−Co surface.[44] The final result was a macrocorrugated morphology with rather flat peaks, essentially composed of WC, and hollow valleys in which some residual Co was still present. In addition, some Co and W oxides could be easily generated at such a high processing temperature, if precautions to protect the WC−Co substrates from oxygen were not taken.[44] These results necessitated the combination of the pulsed laser source with further chemical treatments like etching with dilute acid solutions to remove the excess in Co and, eventually, most of the oxides, thus reducing the potentiality, safety, and industrial suitability of the technique.[42,44]

Veillère et al.[45] pretreated WC−Co substrates using a Ti sapphire femtosecond (fs) laser. The laser wavelength was centered at around 800 nm, with a maximum energy of 1 mJ, with a 50 fs pulse width at 1 kHz repetition rate. However, similarly to Singh et al.,[42] they had to perform an acid etching after the laser treatment in order to reduce the surface Co concentration.

Recently, some of the authors have used a continuous wave-high power diode laser source to modify the surface chemical composition and morphology of as-ground hard metals.[46] To prevent Co and WC oxidation, they performed the laser treatments in pure Ar atmosphere. They found that the proper adjustment of the laser processing parameters allowed the selective removal of Co from the outermost layer of WC−Co, the recrystallization and coarsening of WC surface grains with consequent surface roughening, and the relief of microstrains induced in WC−Co by the grinding process. Following this, the present investigation is aimed to (i) validate the laser treatment of hard metal substrates described in ref 46; (ii) study the hot filament chemical vapor deposition (HFCVD) of diamond coatings onto WC−Co substrates pretreated by continuous wave-high power diode laser; (iii) evaluate the effect of different inert gases (namely, Ar and N_2) on both the substrate surface morphology that develops upon laser irradiation and coating adhesion; (iv) compare the wear resistance of diamond coatings grown onto laser treated substrates and onto substrates subjected to a well-known two-step wet chemical etching pretreatment, employing Murakami's reagent and Caro's acid.[29]

2. EXPERIMENTAL SECTION

Ten × ten × three millimeter as-ground substrates of WC-5.8 wt %Co (supplied by Fabbrica Italiana Leghe Metalliche Sinterizzate SpA, Anzola d'Ossola (VB), Italy) with an average grain size of 0.7−0.8 μm, a hardness of 90.0 HRA, and 2900 MPa transverse rupture strength (TRS, according to ISO 3327) were subjected to three pretreatments, namely, two laser pretreatments (LP) in either Ar (ALP) or N_2 (NLP) atmosphere and a two-step wet chemical etching (Murakami's reagent and Caro's acid, MC). LP substrates were irradiated by a 940 nm continuous wave-high power diode laser (cw-HPDL, Rofin Sinar DL015). To prevent Co and W oxidation and to evaluate the effect of different atmospheres, the samples were placed in an aluminum chamber flushed with either pure Ar (99.999%) or pure N_2 (99.999%). A high transparent Perspex window at the top of the chamber allowed delivery of laser irradiation and visual inspection. Moreover, it minimized the amount of laser radiation absorbed prior to substrate irradiation. As a result, laser power was set at 650 W and scan speed was kept constant at 1 mm/s. Irradiation pretreatment tests were performed by focusing the laser beam through a 63 mm long focus lens, giving rise to an elliptical spot of 3.8 × 1.2 mm at the sample surface. The beam was moved back and forth along three linear and parallel patterns to uniformly cover the entire substrate surface with an overlap of 0.7 mm between two consecutive linear patterns. The total sample treatment lasted about 1 min. For comparative purposes, as-ground WC−Co substrates submitted to a two-step chemical etching (MC) were also investigated. MC is a well-known chemical pretreatment,[29] widely used for adhesion improvement of diamond films to WC−Co substrates. During MC, the WC−Co substrate was first etched for 15 min with Murakami's reagent (10 g of $K_3[Fe(CN)_6]$ + 10 g of KOH + 100 mL of H_2O) to corrugate the WC grains. Then, after rinsing in deionized water, the substrate was etched with Caro's acid (3 mL of 96 wt % H_2SO_4 + 88 mL of 30% (w/v) H_2O_2) for 10 s to wash surface Co out and rinsed again in H_2O.

After each pretreatment (ALP, NLP, or MC), the substrates were seeded in an ultrasonic bath with a slurry of diamond particles (1/4 μm in diameter) in ethanol for 15 min. The deposition of diamond films was performed in a stainless steel HFCVD reactor. The gas phase, a mixture of hydrogen and methane with a 1% CH_4/H_2 volume ratio, was activated by a set of linear tungsten filaments (0.79 mm in diameter), whose temperature was kept at about 2500 K and monitored by a two-color pyrometer (by IRCON). Total flow rate was 4000 standard cm^3 min^{-1} (sccm), and pressure was 10 kPa. Several samples were positioned on the substrate holder (a Mo grid) just below the filaments, with the distance between the filament and the center of their top surface being 12 mm (see Figure 1). These substrates will be referred to as UF (under filament) samples.

Other samples (referred to as BF samples from here on) were positioned on the Mo grid in such a way that the center of their top surface was between two parallel filaments. The substrate temperature was ~600 °C, as measured by placing a thermocouple in the bulk of a WC−Co substrate located under the filament (UF). The different position of the samples with respect to the filaments implied a slightly different substrate temperature and/or composition of active species impinging the substrate surface during CVD, thus leading to a slightly different thickness of the deposited diamond films. In particular, in the case of BF samples, the substrate temperature and/or gas phase

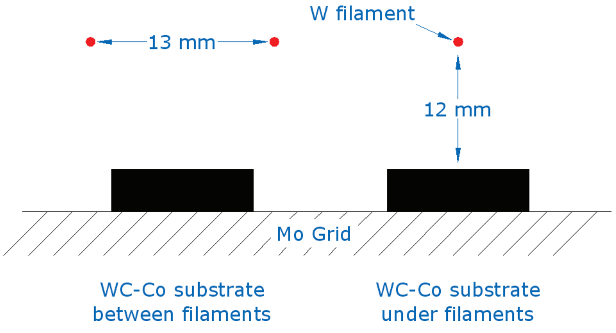

Figure 1. Sketch of the experimental setup.

composition were slightly different, with the deposition rate slightly smaller, namely, 0.57 μm/h instead of 0.63 μm/h. Deposition duration was 14 h. Therefore, the thickness of diamond films deposited on UF and BF samples was about 9 and 8 μm, respectively. The average roughness of diamond films was always ~0.3 μm whatever the substrate pretreatments. Table 1 summarizes the six different scenarios which were investigated.

Table 1. Experimental Schedule

scenario	sample	pretreatment	laser power (W)	scan speed (mm/s)	position in the CVD reactor
1	ALP-UF	cw-HPDL in Ar	650	1	under filament
2	ALP-BF		650	1	between filaments
3	NLP-UF	cw-HPDL in N_2	650	1	under filament
4	NLP-BF		650	1	between filaments
5	MC-UF	Murakami's reagent + Caro's acid			under filament
6	MC-BF				between filaments

Sample roughness was measured by a contact gauge surface profiler (Taylor Hobson Surface Topography System Taly-Surf LI 2000). A hundred surface profiles with a lateral spacing of 10 μm and with a resolution of 0.5 μm were recorded. A very low scan speed of 50 μm/s was adjusted during the measurements in order to minimize the sliding speed of the stylus tip onto the WC−Co substrate and ensure measurement accuracy. TalyMap software Release 3.1 was used for data analysis and image processing.

WC−Co substrates before and after laser treatments were characterized by X-ray diffraction (XRD) with a Philips X'Pert Pro diffractometer, equipped with a plane monochromator using Cu Kα radiation (λ = 1.5418 Å). Field emission gun scanning electron microscopy (FEG-SEM, LEO model Supra 35) and energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Ltd., model Inca 300) were used to characterize the surface morphology of the pretreated substrates, of the CVD diamond films, and of the worn tracks, as well as to perform chemical analyses of the WC−Co substrates before and after each pretreatment. Diamond films were also characterized by Raman spectroscopy. Raman spectra were recorded with a DILOR XY triple spectrometer (in macro-Raman configuration) equipped with a liquid nitrogen cooled CCD detector and an adapted Olympus microscope. The 514.5 nm line of an Ar-ion laser was used as the exciting source. The laser spot on the sample was 0.4 mm in diameter. The polarization of the scattered radiation was not analyzed. The spectral resolution was 1 cm^{-1}. Lines of a Ne lamp were used for frequency scale calibration.

Dry "linear reciprocating" tribological tests (Optimol SRV Tribometer) were performed in order to check wear resistance and film adhesion to differently pretreated WC−Co substrates. The samples were tested at different loads (20, 40, 50, and 60 N) and back-and-forth sliding (stroke length: 2 mm; frequency: 50 Hz; duration: 10 min) of the upper WC-5.8%Co ball (10 mm diameter). Wear resistance of the coatings was assessed using the above-mentioned contact gauge profiler. Volume, dimension, and average depth of the wear tracks were obtained using the features of the TalyMap software.

3. RESULTS AND DISCUSSION

3.1. Morphology of the WC−Co Substrates after the Pretreatments.

Figure 2 shows the surface morphology of as-ground WC−Co and of substrates pretreated by two-step wet chemical etching (MC), by continuous wave-high power diode laser (cw-HPDL, 940 nm, 650 W) in flowing Ar (ALP), and by cw-HPDL in flowing N_2 (NLP).

The surface morphology of as-ground WC−Co shows the formation of a deformed surface layer of approximately 1.5 μm consisting of fragmented, pulverized, and plastic deformed WC grains bonded by smeared out cobalt.[47] This surface is wholly unsuitable for the deposition of adherent diamond coatings.[48] MC pretreatment is able to modify significantly both morphology and chemical composition of the substrate surface. A sufficiently long etching time with Murakami's reagent removes the deformed surface layer formed by grinding[48] and corrugates the WC grains underneath, thus increasing the roughness of the hard metal surface. The subsequent etching with Caro's acid oxides the binder to soluble Co^{2+} compounds, thus reducing the binder content in the outermost layers below the detection limit of EDS.[29,41]

Also, the cw-HPDL treatments allowed one to alter significantly the surface morphology and composition of the WC−Co samples. In fact, after laser processing, the damaged surface layer underwent a deep reconstruction; WC grains protruded from the surface, completely deprived of Co (Figure 3).

This modification was similar, although not identical, to what can be observed after suitable heat treatments of hard metal substrates in HFCVD reactors. R. Polini[48] and S. Ullram et al.[50] reported that in situ thermal treatment of as-ground WC−Co substrates may lead to recrystallization of the damaged surface layer and evaporation of the binder, with a significant decrease of its surface concentration. They found that surface modification of WC−Co was induced by heating the sample at around 1000 °C (according to thermocouple reading) and, at the same time, exposing it to a monohydrogen rich atmosphere in the HFCVD reactor. Under these process conditions, the actual surface temperature should exceed substantially the "nominal" substrate temperature due to the exothermic recombination of H atoms. If the surface temperature approaches the eutectic temperature of the W−C−Co system, a liquid phase forms with concurrent Ostwald ripening, and consequent growth, of WC grains in the surface damaged layer. As a result, that layer undergoes recrystallization and stress relaxation.

The large surface temperatures developed under our novel diode laser treatment induce a similar effect. WC grains at the substrate surface acquired a polygonal shape when the treatment was carried out in Ar atmosphere, although a slight increase in the WC grain size could be observed. According to SEM micrographs (Figure 2), the size of the outermost grains was in the range of 1−2 μm, with the average grain size of bulk WC being 0.8 μm. Moreover, differently from pulsed lasers operating from 80 MW/cm^2 onward with a wavelength of 308 nm and causing ablation,[42] using the diode laser at lower energy

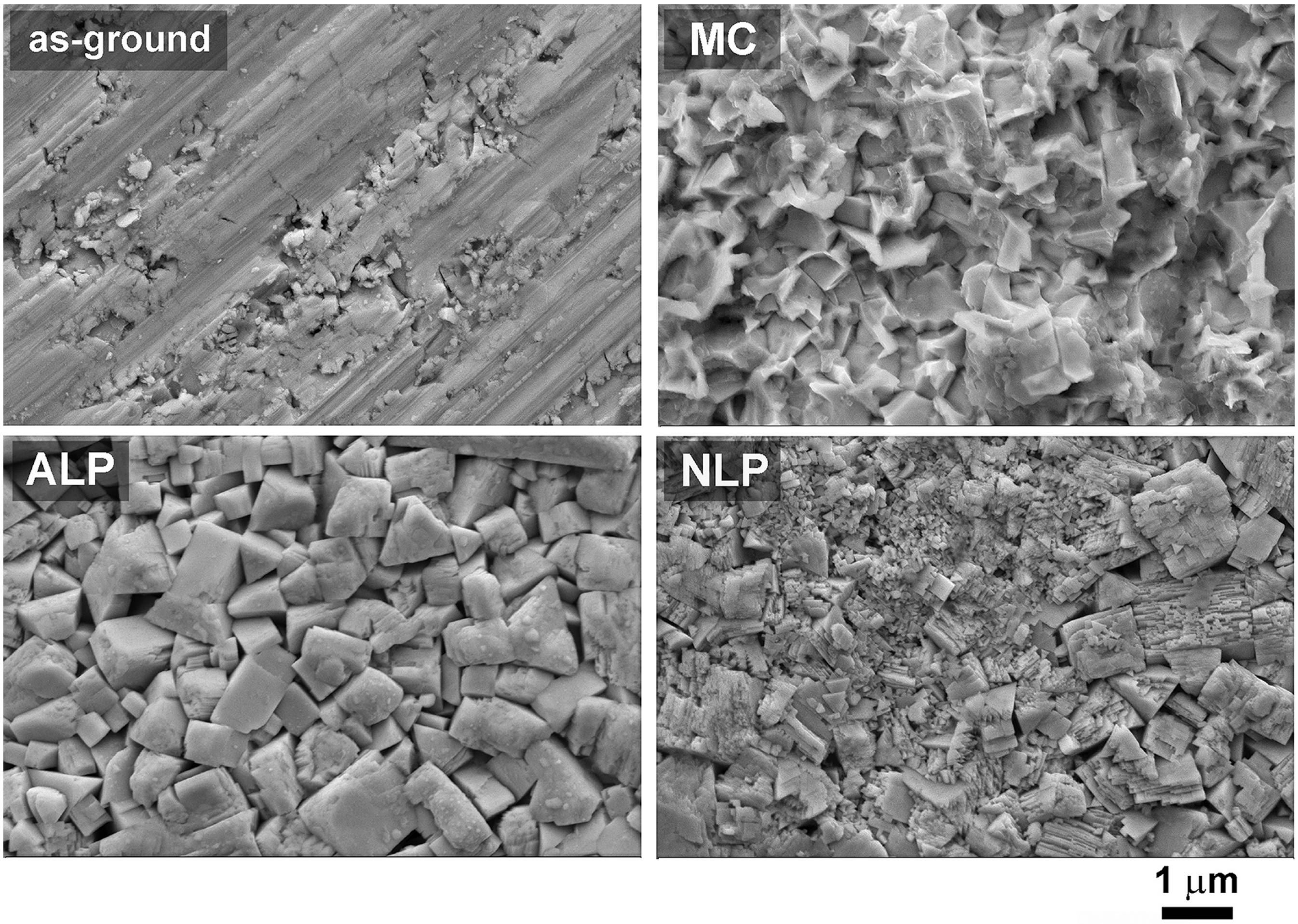

Figure 2. SEM micrographs of the hard metal substrates before (as-ground) and after different pretreatments (MC: two-step chemical etching with Murakami's reagent and Caro's acid; ALP: diode laser treatment in Ar atmosphere; NLP: diode laser treatment in N_2 atmosphere).

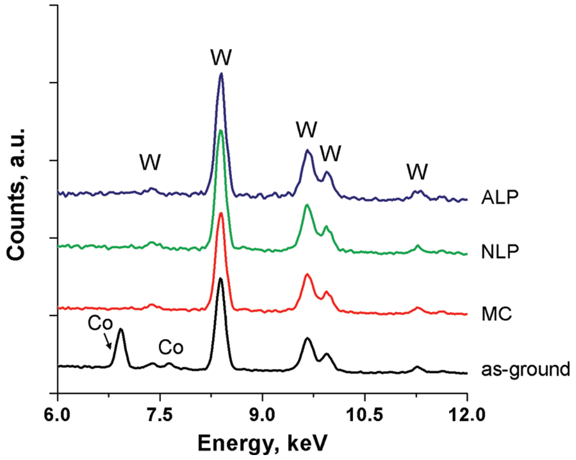

Figure 3. EDS spectra on as-ground, MC-treated and laser treated (in Ar atmosphere, ALP, or in N_2 atmosphere, NLP) WC−Co substrates.

density (~18 MW/cm^2) allowed one to selectively evaporate the Co binder, without affecting largely the grain size of the hard metal grade.

It is worth noting that the gas atmosphere employed to "protect" the sample from oxidation had a strong influence on the reconstruction process. Although the average surface roughness of the samples treated in Ar atmosphere (ALP samples) was slightly larger (Figure 4), NLP samples showed a significantly different morphology of WC grain facets. Figure 5 shows the high magnification SEM micrograph of a NLP sample. The picture suggests that the recrystallization process of WC was in an early stage and did not reach completion. In fact, many small WC crystallites can be detected. Most likely, these crystallites nucleated from the strained, defect-rich layer formed by grinding.[47] Only a fraction of these small crystallites grew during the duration of the laser pretreatment in N_2, thus suggesting that the nitrogen atmosphere did slow down in some way the growth and coalescence of WC nuclei during the recrystallization process induced by the laser treatment.

It has been found recently that a pronounced grain refinement effect can be obtained by introduction of nitrogen, at a pressure of more than about 0.5 atm, in the sintering hard metal furnace after dewaxing but before pore closure, preferably before 1000 °C.[51] This finding indicates that the nitrogen atmosphere inhibits WC grain growth, also in the presence of grain growth inhibitors (Cr_3C_2, VC, TaC, TiC, etc.),[51] which are added intentionally to fine-grained hard metal powders. Therefore, the different surface morphology of NLP samples might be ascribed to dissolution of N-atoms in the liquid W−C−Co phase during resintering of the outmost layer of as-ground hard metal and to consequently slower grain growth kinetics. As a net result, the surface morphology of NLP

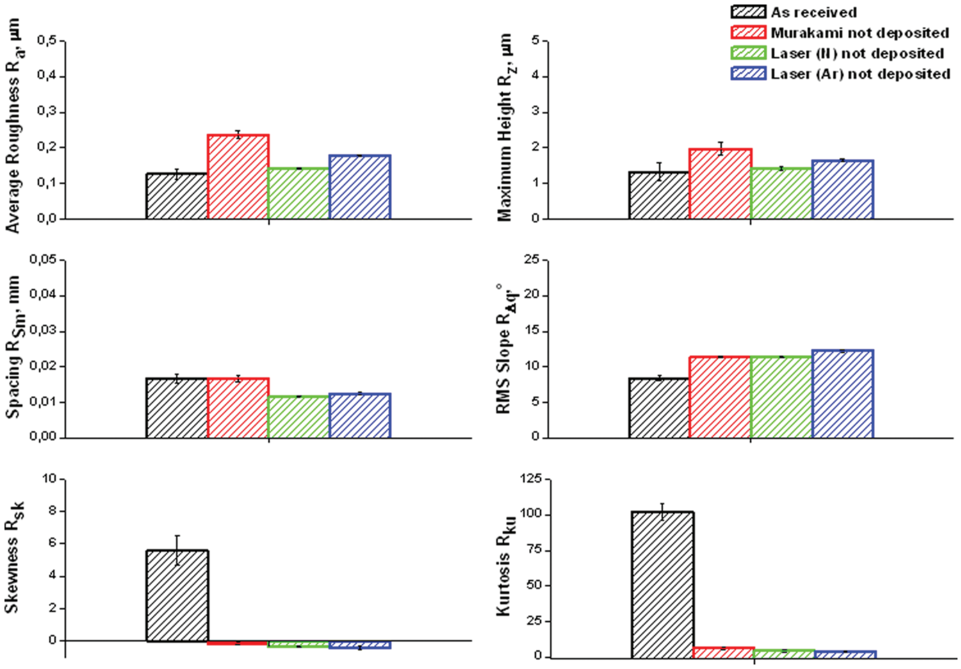

Figure 4. Roughness parameters of as-ground, MC-treated, and laser treated (in Ar atmosphere, ALP, or in N_2 atmosphere, NLP) WC−Co substrates.

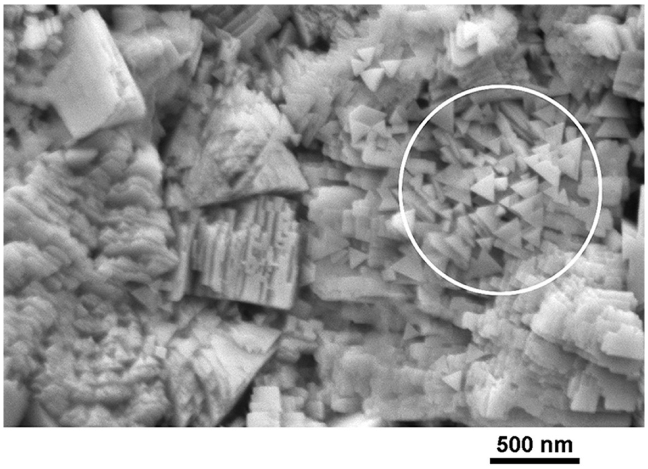

Figure 5. Large magnification SEM micrograph of the WC crystallites formed after high power diode laser pretreatment of WC−Co substrates in N_2 atmosphere (NLP substrate).

samples was characterized by finer corrugation with respect to ALP samples.

Figure 4 shows the roughness parameters obtained by contact profilometry on the WC−Co substrates after the different pretreatments and their comparison with the as-ground substrate. MC treatments were found to cause an increase in the amplitude parameters R_a and R_z. The increase can be ascribed to the removal of the outermost layer of WC−Co damaged by the grinding process and the subsequent etching with Caro's acid, which removed surface Co. Laser treatments (ALP and NLP) did not significantly change the amplitude parameters. Only ALP treatments were found to produce a certain increase in R_a and R_z, more likely ascribable to the slight enlargement of the WC grain size and to the removal of surface Co. Conversely, NLP treatment did not take to any significant increase in amplitude parameters, despite the effective removal of surface Co and WC−Co surface reconstruction,. Probably, the formation of many WC crystallites (Figure 5) tended to fill the gaps among the WC grains and, thus, to leave the amplitude parameters nearly unchanged. As far as concerns spacing parameters, both the laser treatments were found to decrease R_{Sm}. This result can be attributed to the surface reconstruction promoted by the laser processing. In fact, Co removal in ALP treatments and the onset of the new geometrical features (WC crystallites) in NLP treatments reduced the distance between subsequent peaks and valleys in the surface profiles of the laser treated WC−Co substrates. Accordingly, reduced spacing R_{Sm} were measured. The same effect is probably very difficult to measure on the MC treated substrate whose R_{Sm} was nearly unchanged if compared with the one of the untreated substrates. Indeed, the two-step chemical etching is able to both remove Co and attack the individual WC grains, thus modifying significantly their morphology. Yet, the scale of the new geometrical features is so small, which could not be appreciated by inductive gauge contact profilometry. Co removal and the reconstruction of the WC grain geometries took also to an increase in the average slope of the surface profile after any treatment (MC or LP). This way, the slope $R_{\Delta q}$ was found to be significantly increased.

The hybrid parameters, Skewness and Kurtosis, of the as-ground substrate were very large, with R_{Sk} positive and $R_{Ku} > 3$. Positive values for R_{Sk} mean the starting surface profile of the as-ground WC−Co substrate are antisymmetrical with a flat bottom and some occasional sharp peaks. Large R_{Ku} means the starting surface profile is distributed iper-normal, with all the surface profiles concentrated very close to the average line. After any pretreatment (MC or LP), the hybrid parameters Skewness and Kurtosis are close to nil. This means all the roughness profiles became nearly symmetric around the average line and normally distributed around it. Such result can be ascribed to the peculiarity of the MC and cw-HPDL treatments, which acted to remove the surface Co and emphasized the presence of the individual WC grains protruding out from the substrate surface.

3.2. XRD Characterization of the WC−Co Substrates after the Pretreatments. It is worth recalling that, due the large absorption coefficient of WC−Co, the penetration depth of Cu Kα radiation in hard metal is limited to a couple of micrometers.[47] Therefore, $\theta/2\theta$ XRD patterns are representative of the outermost layers of the materials here investigated.

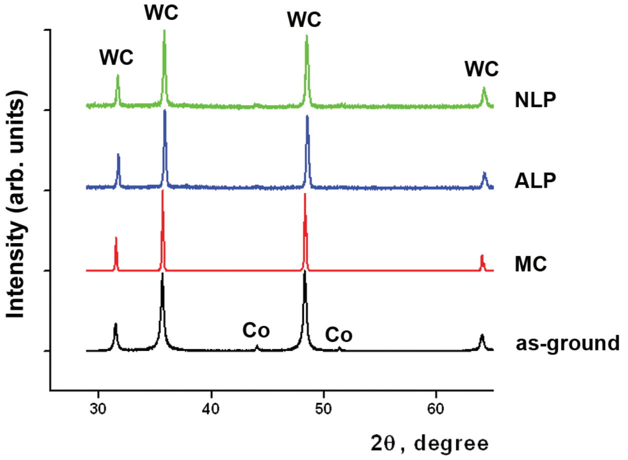

Figure 6. $\theta/2\theta$ XRD patterns of as-ground, MC-treated, and laser treated (in Ar atmosphere, ALP or in N_2 atmosphere, NLP) WC−Co substrates.

Figure 6 shows the XRD pattern of the different WC−Co samples. As-ground WC−Co sample showed only the presence of WC and small Co peaks. WC peaks were not as sharp as WC peaks detected in pretreated samples, where the deformed surface layer was either etched away or subjected to a laser treatment that induced surface recrystallization. As a matter of fact, the full widths at half-maximum (fwhm) of WC(100) peak for as-ground, MC, ALP, and NLP samples were ∼0.29, ∼0.15, ∼0.20, and ∼0.22°, respectively. The intensity of Co peaks decreased significantly after the laser pretreatments, confirming the reduction of the Co content at the substrate surface.

3.3. Characterization of Diamond Coatings. Figure 7 shows typical morphologies of diamond films deposited onto substrates placed between filaments (BF) and under filament (UF; see Figure 1). The films deposited onto UF samples showed a slightly better crystallinity, namely, smoother crystal faces, ascribable to different substrate temperature and/or to larger concentration of atomic hydrogen and other active species at the substrate surface.[52]

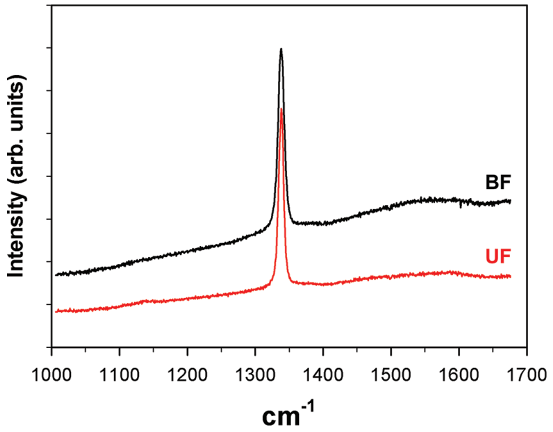

Figure 8. Raman spectra (λ = 514.5 nm) of diamond films grown on BF and UF substrates.

Figure 8 shows the typical Raman spectra of diamond films grown on samples UF and BF. An intense diamond band at 1338 cm^{-1} was present in both spectra. The 6 cm^{-1} blue-shift in the Raman diamond band compared to pure diamond (1332 cm^{-1}) corresponds to ∼3.4 GPa residual compressive stress in the diamond film[53,54] partly due to the large thermal expansion coefficient of WC-5.8 wt %Co (CTE = 5.0 · 10^{-6} K^{-1}) when compared to diamond (CTE$_{\text{diamond}}$ = 3.2 · 10^{-6} K^{-1}, the value integrated over the 298−1023 K temperature range).[55]

The full widths at half-maximum (fwhm) of the diamond Raman bands of UF and BF films were 9 and 11 cm^{-1}, respectively. Moreover, the BF spectrum showed a slightly more visible sp^2 amorphous carbon band centered at around

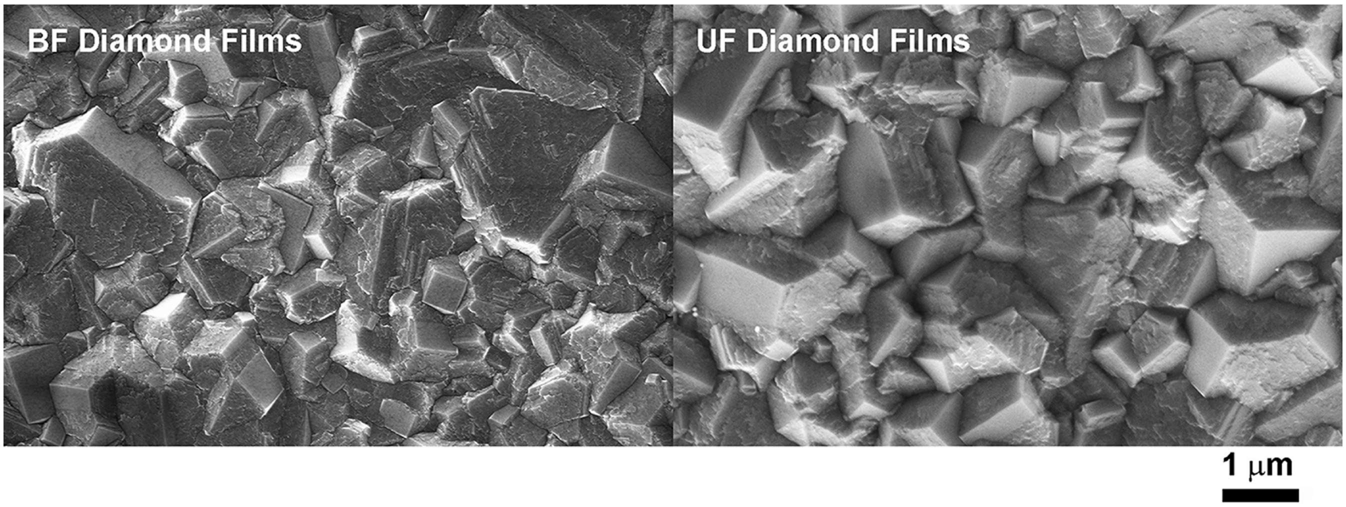

Figure 7. Typical morphologies of diamond films deposited on ALP WC−Co samples positioned in the HFCVD reactor between filaments (BF, upper panel) or under the filament (UF, lower panel), as shown in Figure 1. The different pretreatments do not change the morphology of the diamond coatings.

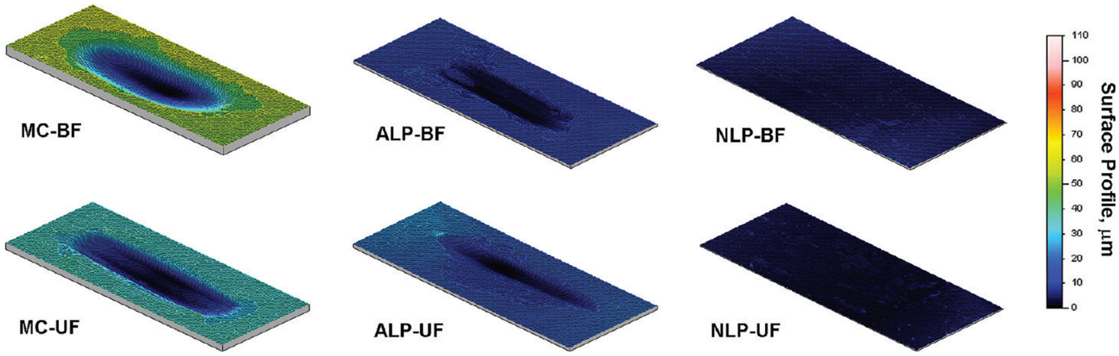

Figure 9. Tribological test results at 60 N load of the diamond coatings grown onto differently pretreated WC−Co substrates. The labels of the six different scenarios are listed in Table 1. Wear volumes of samples MC-BF, MC-UF, ALP-BF, ALP-UF, NLP-BF, and NLP-UF were 0.0124, 0.0078, 0.0019, 0.0029, 0.0000, and 0.0000 mm^3, respectively.

1520−1540 cm^{-1}.[56] These findings confirm that the quality of diamond deposited on UF samples was slightly larger. Nevertheless, both SEM and Raman data confirmed that good-quality microcrystalline diamond grew also on substrates positioned between filaments (BF samples) in the HFCVD reactor.

3.4. Wear Tests. To measure the wear resistance of the diamond films, several tests were performed at increasing loads of 20, 40, and 50 N. All the tests did not lead to any perceptible wear volume on all the checked diamond films. For such reason, the tests were rescheduled at 60 N, where some damage to the diamond coated samples could be induced.

Figure 9 reports the 3D maps of the wear tracks after fretting tests at 60 N load. Tribological tests showed that the diamond coated samples obtained by laser pretreatments of WC−Co substrates performed significantly better than samples pretreated by two-step chemical etching. This finding holds for diamond films grown under filament and between filaments as well. Therefore, given the difference in deposition conditions and growth rate of the two arrangements (UF and BF), the wear results were clearly ascribable to the quality of the diamond/substrate interface. In fact, the measured wear volumes of coated samples MC-BF, MC-UF, ALP-BF, ALP-UF, NLP-BF, and NLP-UF were 0.0124, 0.0078, 0.0019, 0.0029, 0.0000, and 0.0000 mm^3, respectively. This is quite a remarkable result, as MC pretreatment is known to be very effective in enhancing the adhesion strength of diamond coatings on WC−Co tools and wear parts. It is also very important to underline that the wear resistance of diamond films deposited onto WC−Co substrates pretreated by cw-HPDL in nitrogen atmosphere was the largest one. This could be due to a better adhesion of diamond that can be in turn ascribed to the effective microroughening the cw-HPDL pretreatment was able to induce onto the WC−Co substrates (Figures 2 and 5). In particular, the growth of the small WC crystallites that the NLP treatment was able to promote on the WC−Co substrate (see Section 3.1) is very promising to increase locally the specific contact surface at the interface between the diamond film and the underlying substrate, thus increasing their adhesion by mechanical interlocking.

Indeed, the presence of tiny WC crystallites at the interface between diamond films and NLP treated WC−Co substrate could play another crucial role, too. As said before (Figure 5), they could fill the gaps between diamond films and underlying substrates and/or leave smaller voids at the interface. Smaller gaps at the diamond/substrate interface imply a larger adhesive toughness, i.e., a smaller critical load value to start interfacial crack propagation. Such aspect is a really crucial one, with such geometrical configuration being able to assist the WC−Co substrate to sustain the overlying diamond film in withstanding the action of the counterpart during the tribological tests. The resultant diamond films show superior tribological properties with high load-bearing capacity and excellent wear resistance.

4. CONCLUSIONS

The present investigation concerned the use of a continuous wave-high power diode laser (cw-HPDL) to thermally treating WC−Co substrates and making them prone to depositing highly adherent diamond coatings. The following conclusions can be drawn: (1) cw-HPDL allows one to selectively heat treat the outermost layer of the WC−Co; (2) the surface heat treatment led to the recrystallization of the surface damaged layer of as-ground WC−Co and the concomitant selective removal of Co from the substrate surface; (3) the use of the “inert” gas employed to protect the sample from oxidation during laser irradiation did affect the recrystallization process; (4) when N_2 was used in the cw-HPDL treatment, the microstructure of the thermally treated material showed many small WC crystallites, with size around 100 nm, which indicated a significantly slower kinetics of WC grain growth and ripening; (5) the diamond coated samples obtained by laser pretreatments of WC−Co substrates performed significantly better in tribological tests than samples pretreated by a well established two-step chemical etching, (6) diamond coated samples obtained by laser pretreatments in N_2 atmosphere showed the best wear endurance, thus suggesting a larger film adhesion, most likely due to the peculiar surface morphology and microstructure developed during the reconstruction process of the hard metal substrate surface. In conclusion, diode laser is able to selectively remove Co without any further chemical pretreatment. A proper choice of laser treatment parameters allows one to thermally alter the surface damage layer and to relieve the microstrains induced in the WC−Co substrate by the previous grinding process. The same laser processing allows one to roughen the hard metal substrate surface, although the use of the protecting atmosphere during the laser pretreatment influences the resulting surface morphology significantly. These deep modifications make the WC−Co suitable for diamond coating by CVD and allow one to avoid the use of hazardous etchants. The one-step processing here presented for the first time is also expected to be very competitive as reduced cost operations and quick setup time of the laser system can be inferred.

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ACKNOWLEDGMENTS

Dr. V. Valentini (CNR−IMIP, Istituto Metodologie Inorganiche e dei Plasmi, Rome, Italy) is kindly acknowledged for acquisition and treatment of Raman spectra. Dr. G. Marcheselli (Fabbrica Italiana Leghe Metalliche Sinterizzate, F.I.L.M.S. S.p.A., Anzola d'Ossola, VB, Italy) is gratefully acknowledged for the supply of WC−Co samples.

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