

WC-Co COATED CARBIDE SUBSTRATE SURFACE TEXTURING WITH A PULSED CuHBr LASER

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Abstract. *Alternatively to the commonly used mechanical micro-blasting, this work deals with a substrate surface pre-processing of MT-CVD TiCN+Al₂O₃+TiN coated carbide cutting tools using a laser texturing technique. The equipment used was a pulsed 510 nm, 30 ns, CuHBr laser. The influence of the laser pulses quantity and laser intensity on the surface morphology, surface structure and coating's adhesion was investigated. The experimental results showed that a large variety of carbide surface textures are possible depending on the laser intensity and number of applied laser pulses. At low intensities, the laser beam only cleaned the surface and the surface roughness increment was small compared with the grinded unlasered surfaces. High intensities and/or many laser pulses induced a violent material ablation generating complex surfaces with elevated roughness and non stoichiometric carbide phases like β -WC_{1-x} and α -W₂C. Laser texturized substrates were coated and Rockwell C indentation test was used to compare coating's adhesion quality. Results showed that it is possible to improve coating's adhesion resistance with the laser texturizing process, but more work must be done in order to find the appropriated laser intensity and the number of laser pulses for enhanced adhesion.*

Keywords: *Lasers, Laser texturization, Coating adhesion, Tungsten carbide hardmetal.*

1. INTRODUCTION

Tungsten carbide hardmetal is a material with a broad range of application fields, especially for metal machining cutting tools. Through laser processing, by adjusting the laser beam intensity, hardmetal can be treated to obtain since surface properties changes or accurate material removal or even substantial material removal (Dumitru *et al.*, 2005). The laser surface treatment of materials is used in a broad set of applications that include thermal treatment, engraving and cleaning among others (Zhang, 2004). This process has demonstrated to be a very advantageous alternative to replace some steps in surface preparation like water cleaning and sand blasting. Those techniques, regardless be widely used and efficient, show ambient and operator health disadvantages (Verdier, 2003). Additionally, laser processing is suitable to operation automation, selective treatment and three dimensional processing (Neves *et al.*, 2006). The most of hardmetal cutting tools are coated in order to improve their longevity. The adhesion's quality between the coat and the substrate influences directly the tool's performance (Bouzakis *et al.*, 2000). The coating process includes substrate surface preparation in order to obtain good adhesion. Usually this surface preparation consists of surface micro-blasting and surface ultrasound washing (Bouzakis *et al.*, 2005). The effects of this treatment are just creating an appropriated surface roughness, remove the surface cobalt binder and promote compressive surface residual stresses (Taher, 1999). Neves *et al.* (2006) used the substrate laser texturing technique to improve de adhesion of a PVD-TiN coating applied on HSS twist drills; it also resulted in a considerable machining performance increase. For coated hardmetal tools fabrication, it is established that the excess of cobalt binder in the substrate surface produces poor coating adhesion. Li *et al.* (2002) reported the use of an ultraviolet industrial excimer laser in order to selectively remove the surface cobalt binder of hardmetal substrates. They used 125 MW/cm² intensity and with 300 laser pulses they find the least surface cobalt content and the best adhesion of the later applied CVD diamond coating. Substrate surface laser processing to improve CVD deposited diamond adhesion over hardmetal substrates was tried too by Cappelli *et al.* (1999) and Lee (1998) with courageous results.

In this work, the laser texturing technique was used to prepare the substrate surface of MT-CVD TiCN+Al₂O₃+TiN coated hardmetal inserts in order to establish if it could be a suitable substrate surface preparation method to enhance the adhesion of this kind of coating. The laser produced substrate surface topography and structural modifications were examined by using Scanning Electron Microscopy (SEM), roughness-meter and X-ray diffraction analysis. Different surfaces fabricated with various laser intensity values and laser pulses quantity were considered. The coating adhesion for each surface, including a grinded not laser treated one, was qualitatively compared through the Rockwell-C indentation test. Finally, it is discussed the coating adhesion performance.

2. EXPERIMENTAL DETAILS

Grinded surfaces of hardmetal commercial inserts for rough-finishing milling machining (ISO equivalent P25, M15 and K30) were used as specimens for the laser surface texturing. They are composed of 9% cobalt binder, 90% tungsten carbide and 1% other carbides (TiC, TaC, NbC). The carbides grain size is 3-5 μm . Both lasered and unlasered inserts were MT-CVD coated with TiCN+Al₂O₃+TiN.

For laser texturing was used a pulsed CuHBr laser with wavelength $\lambda = 510 \text{ nm}$, pulse duration $\tau = 30 \text{ ns}$, circular beam with 30 μm focal diameter and 13.8 kHz pulsing frequency. The beam movement over the work surface was controlled by a scanning head unit. The transverse beam speed and path superposition was programmed based on the number of pulses planned for irradiate each point of the work surface. After preliminary tests to evaluate the CuHBr laser-hardmetal interaction and ablation threshold, several substrate surfaces were laser processed using intensities of 137, 239, 273, 308 and 410 MW/cm^2 with fixed 32 pulses. Other group of substrates was processed using 16, 32, 64, 128, and 256 pulses with fixed intensity of 273 MW/cm^2 . The texturing was made in open atmosphere. After the laser process, the substrates were ultrasound washed and MT-CVD coated with a $\sim 5\mu\text{m}$ TiCN+Al₂O₃+TiN coating. A substrate without laser texturing was also processed in this way. The morphology of the fabricated surfaces was verified with Scanning Electron Microscopy (SEM) using the JEOL-JXA-840A microscope and its R_{z-ISO} surface roughness was measured with the Mitutoyo SJ-201P roughness-meter. For phase structural change analysis the X-ray diffraction (XRD) equipment Rigaku Dmax 2200 was used, and for the indentation adhesion Rockwell-C test, a Pantec durometer was used.

3. RESULTS AND DISCUSSION

3.1. Morphology of the lasered surfaces

The WC-Co ternary eutectic temperature is 1553 K (Dumitru *et al.*, 2005); at 1768 K, Co melts; with 3143 K there is WC fusion; over 3200 K, Co evaporates and 6273 K is the WC evaporation temperature (Li *et al.*, 2001). Lee (1998) and Li *et al.* (2001) calculated for the laser process conditions they used that with 32 MW/cm^2 laser intensity Co melts, with 80 MW/cm^2 WC melts and Co evaporates and with 200 MW/cm^2 WC evaporates. For the laser facility used in this work the ablation threshold experimentally found was 137 MW/cm^2 .

First with 32 fixed laser pulses, texturized hardmetal surfaces were fabricated with laser beam intensities of 137, 239, 273, 308 and 410 MW/cm^2 . After other texturized hardmetal surfaces were fabricated with 16, 32, 64, 128 and 256 laser pulses and 273 MW/cm^2 fixed laser intensity. Figure 1-A shows the effect of the laser intensity on the surface roughness (R_{z-ISO}) of texturized surfaces. Surface roughness had small increase between 137 and 273 MW/cm^2 intensities. At high intensities, there was a sharp rise in surface roughness. It is evident the influence of laser beam intensity on the surface roughness. Figure 1-B shows the influence of laser pulse quantity on surface roughness. After a sharp increase with pulse quantity between 0 and 32, the slope of the curve decreased between 32 and 256 pulses. Those surface roughness effects are better understood seeing the scanning electronic microscope images of the laser textured surfaces showed in Fig. 2 and Fig. 3.

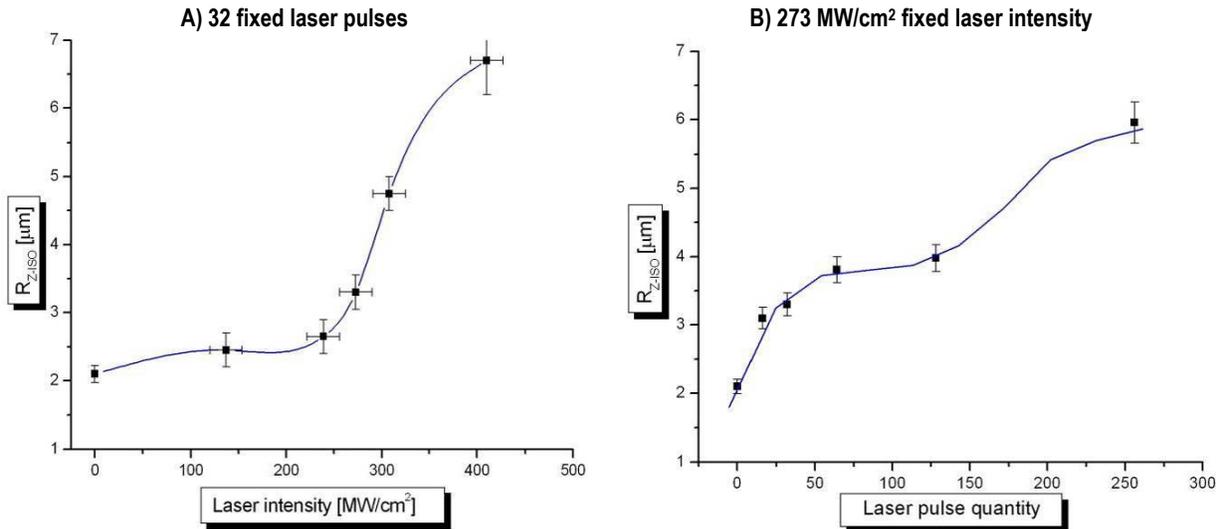


Figure 1. Laser pulses quantity and laser intensity influence on surface roughness.

Figure 2 shows the hardmetal surface morphology as it evolved with 32 fixed laser pulses and laser beam intensity increase. Figure 2-A shows the hardmetal grinded surface without any laser process. With 137 MW/cm^2 (Fig. 2-B), surface change was little with almost imperceptible material ablation. Part of Co in the surface was melted and evaporated and WC was melted. There was a re-solidified thin layer with some small blowholes. Probably this layer was composed of new WC grown grains. For intensity of 239 MW/cm^2 (Fig. 2-C) the surface presented a uniform valley-hills topography probably originated by the vapors expansion and the differentiate ablation threshold for Co and WC. Many $\sim 0.5 \mu\text{m}$ blowholes were observed which suggests exiting vapors and/or gases from the surface. With 273 MW/cm^2 intensity (Fig. 2-D), the valley-hills with blowholes structure appeared more interlaced and also evidenced the laser beam processing movement orientation. Using a laser intensity of 308 MW/cm^2 , a channel oriented in the same laser beam path direction was formed over the surface (Fig. 2-E). There was still the valley-hills topography, but with parallel mountain ranges apparently formed by melted materials displaced by the laser beam momentum. Also, for a Gaussian laser beam, the laser intensity is usually highest at the center, which could also explain more material ablation at beam's center path. For the laser beam intensity of 410 MW/cm^2 (Fig. 2-F), the irradiated surface morphology was very irregular. Apparently, there was massive evaporation-sublimation of both CW and Co. The melted material flux was evident and the surface showed violent ablation with irregular channels patterns and re-solidified material drops.

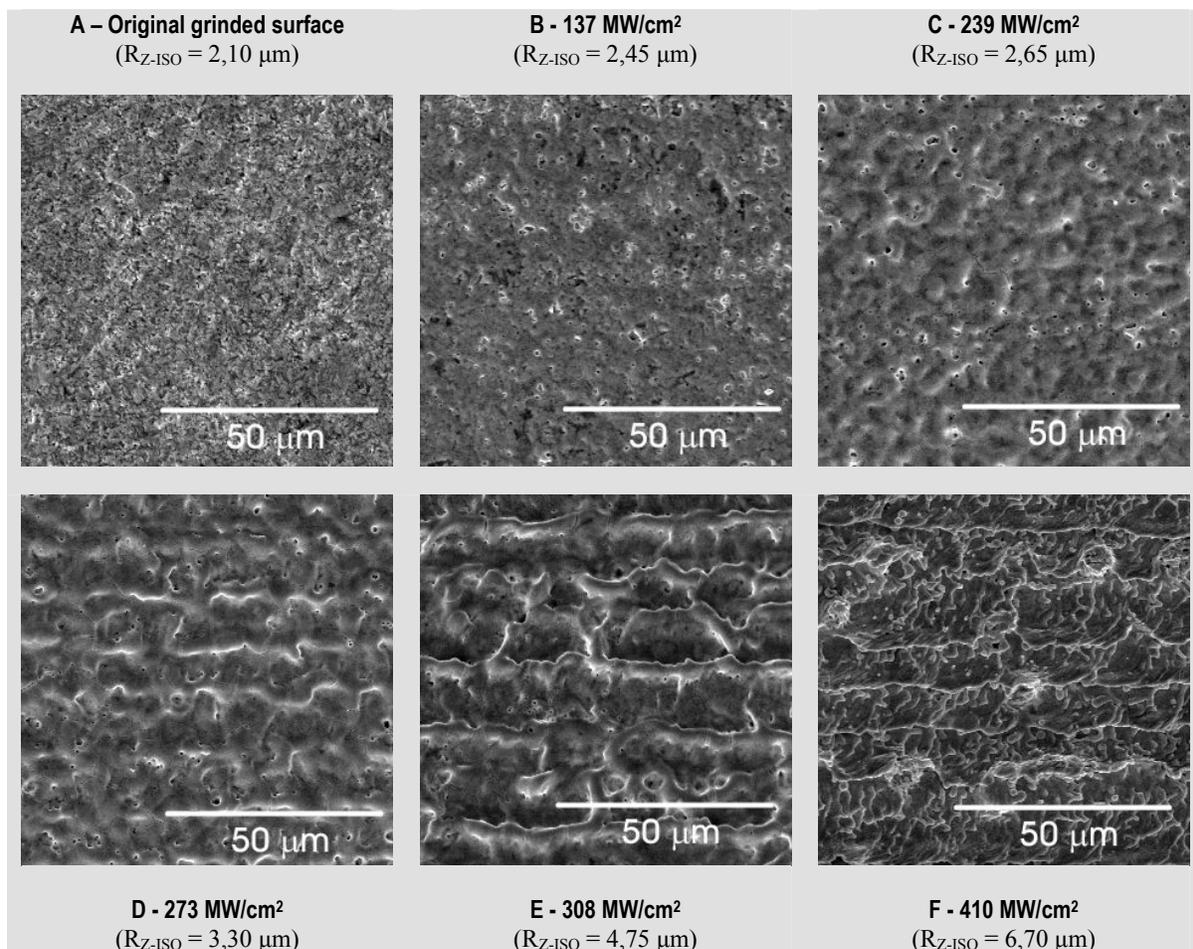


Figure 2. SEM images of the fabricated hardmetal surfaces with different laser intensities and 32 pulses.

Figure 3 shows the pulses quantity effect over the surface morphology with a laser beam intensity of 273 MW/cm^2 . With 16 laser pulses (Fig. 3-B) there was a clear channel topography oriented in the same direction of the laser beam path over the surface. Parallel channel mountain ranges were formed by displaced melted material and there were numerous blowholes. For 32 laser pulses (Fig. 3-C) an interlaced valley-hills with blowholes structure appeared and the mountain range appeared much less evident. It could be because the accumulated laser pulses had produced more evaporation. With 64 and 128 pulses (Fig. 3-D and Fig. 3-E) there were interlaced valleys with hills morphology evidencing the laser beam path orientation. The mountain range frontier previously observed (Fig. 3-B) was not present and there was not evidence of melted material flow. The main ablation mechanism seems to be evaporation-sublimation. The surface processed with 256 pulses (Fig. 3-F) showed a spontaneous structure of drilled holes of $\sim 6 \mu\text{m}$

mean diameter and $\sim 14 \mu\text{m}$ periodicity. The great quantity of laser pulses; probably explain the holes formation by intensive accumulated reflection of laser energy at the bottom of the initially created valleys producing localized vaporization. It is also possible that some bubbles coming from the layer just below the melted layer produced such volcanic aspect.

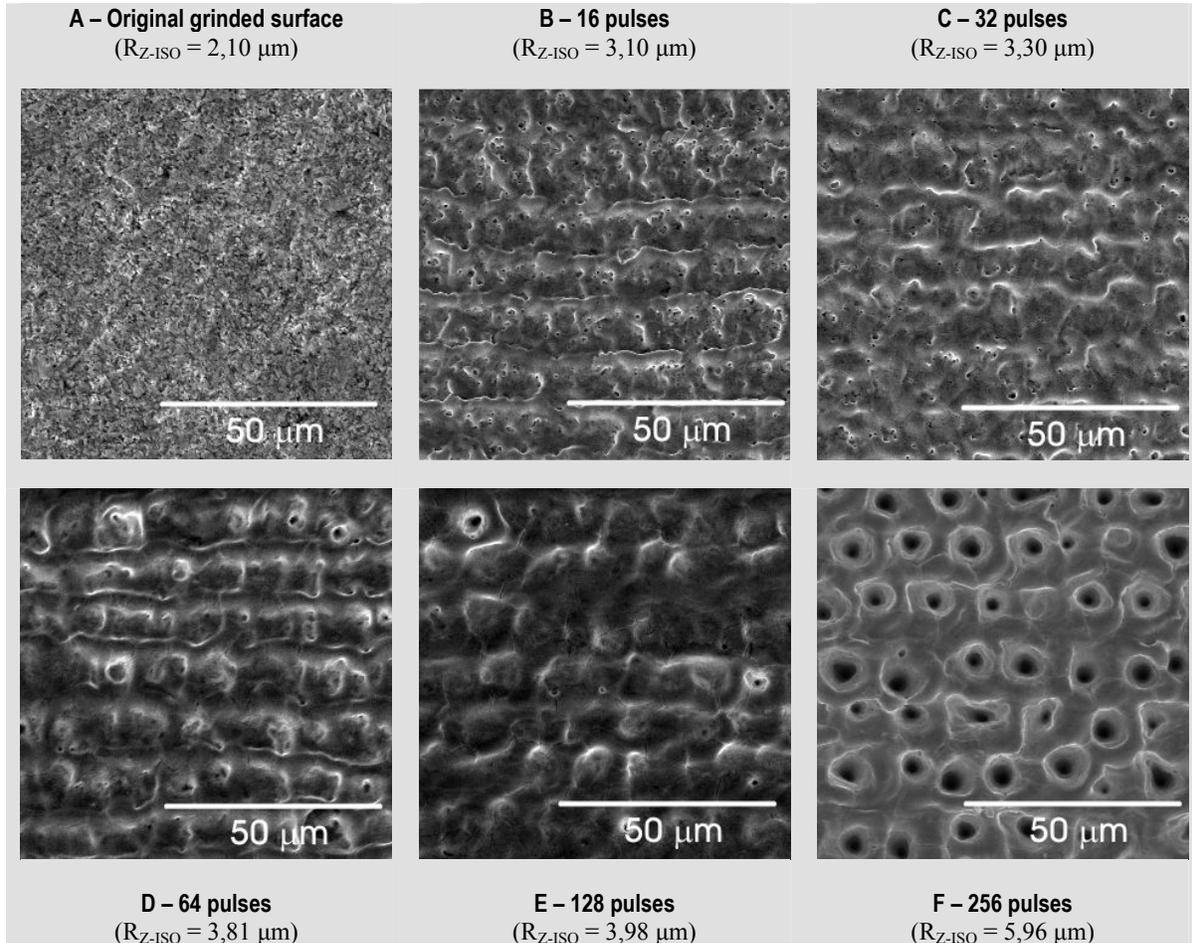


Figure 3. SEM images of the fabricated hardmetal surfaces with 273 MW/cm^2 and different pulses quantity.

3.2. Laser surface texturing induced structural changes

For XRD analyses were used the JCPDS (*Joint Committee for Powder Diffraction Studies*) cards 15_0806, 42_0853, 35_0776, 31_1408, 25_1047, 20_1316, 32_1383, 35_0801 and 38_1364.

Figure 4 shows the diffractograms of the processed surfaces with 32 fixed laser pulses and beam intensities of 0, 137, 239, 273, 308 and 410 MW/cm^2 . The unlasered original grinded surface (0 MW/cm^2) presented typical sharp CW peaks and tenuous peaks of Co. Because of grinding condition, the surface had probably the same composition of the bulk substrate, without superficial segregated cobalt from the sinterization process. The surface processed with 137 MW/cm^2 presented incipient peaks of $\beta\text{-WC}_{1-x}$. With 239 MW/cm^2 , there was a rise in $\beta\text{-WC}_{1-x}$ peaks and appeared a tenuous $\alpha\text{-W}_2\text{C}$ peak. For the surfaces processed with further higher intensities the dominant peaks were still of WC but with consecutive less height; the $\beta\text{-WC}_{1-x}$ and $\alpha\text{-W}_2\text{C}$ peaks increased and there was tenuous presence of other less carbon content non stoichiometric tungsten carbide phases like $\text{W}_6\text{C}_{2,54}$ and W_3C . This decrease on the surface carbon was probably produced by the formation of CO_x gases by reaction with ambient air under high temperatures.

Figure 5 shows the diffractograms of the processed surfaces with 0, 16, 32, 64, 128 and 256 laser pulses and 273 MW/cm^2 fixed laser intensity. In a similar way to the structural changes produced by increasing laser intensities, with the pulses quantity increase there were a $\beta\text{-WC}_{1-x}$ and $\alpha\text{-W}_2\text{C}$ peaks rising and some negligible $\text{W}_6\text{C}_{2,54}$ and W_3C evidences. The WC phase was the dominant one at all process conditions and the superficial Co presence was negligible. Probably the pulses accumulation produced a temperature rise that benefited the CO_x gases formation in a similar way of that with high intensities and less laser pulses.

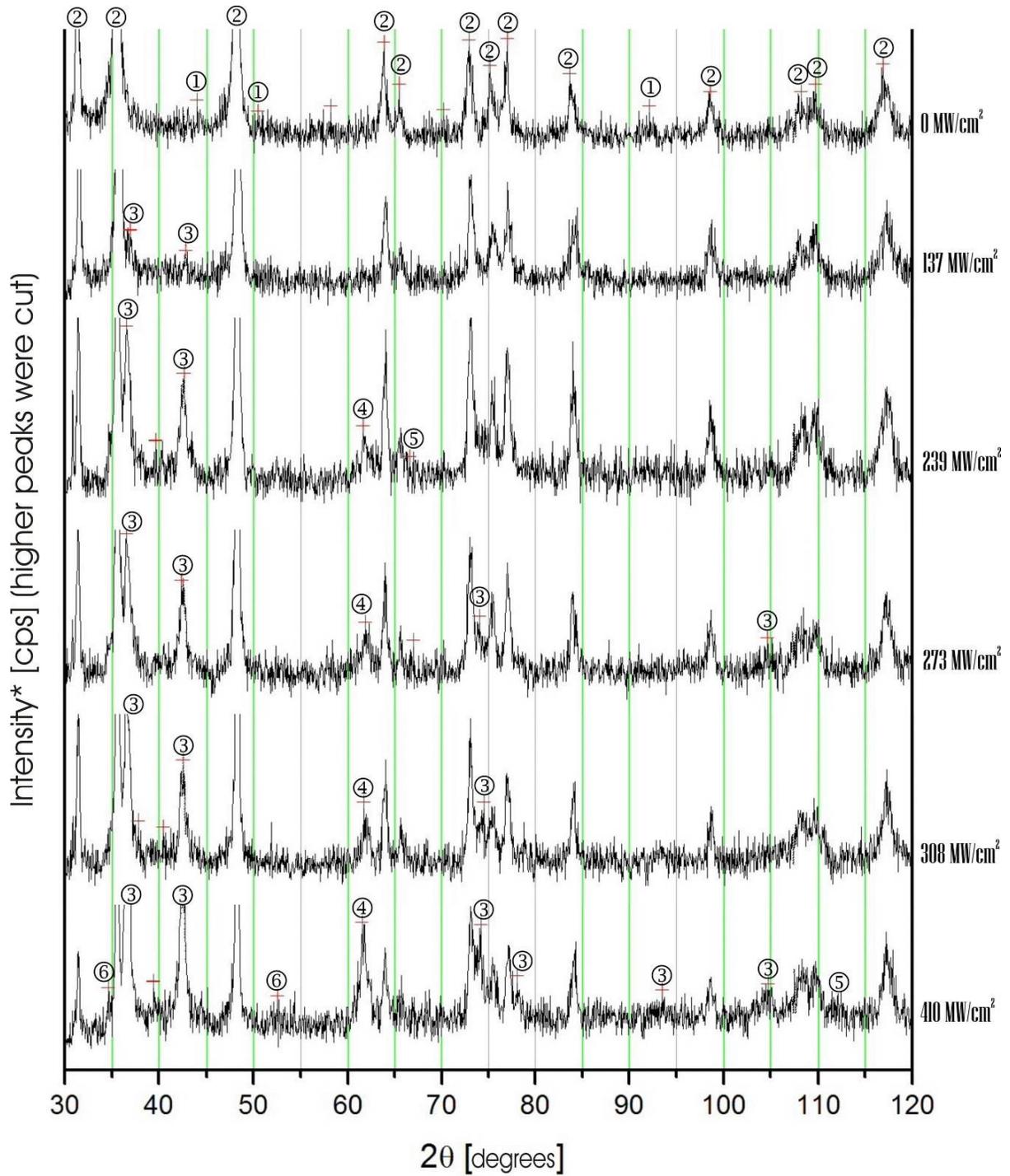


Figure 4. X-ray diffractograms of 32 pulses lasered surfaces with several intensity values: ①:Co, ②:WC, ③:β-WC_{1-x}, ④:α-W₂C, ⑤:W₃C, ⑥:W₆C_{2,54}.

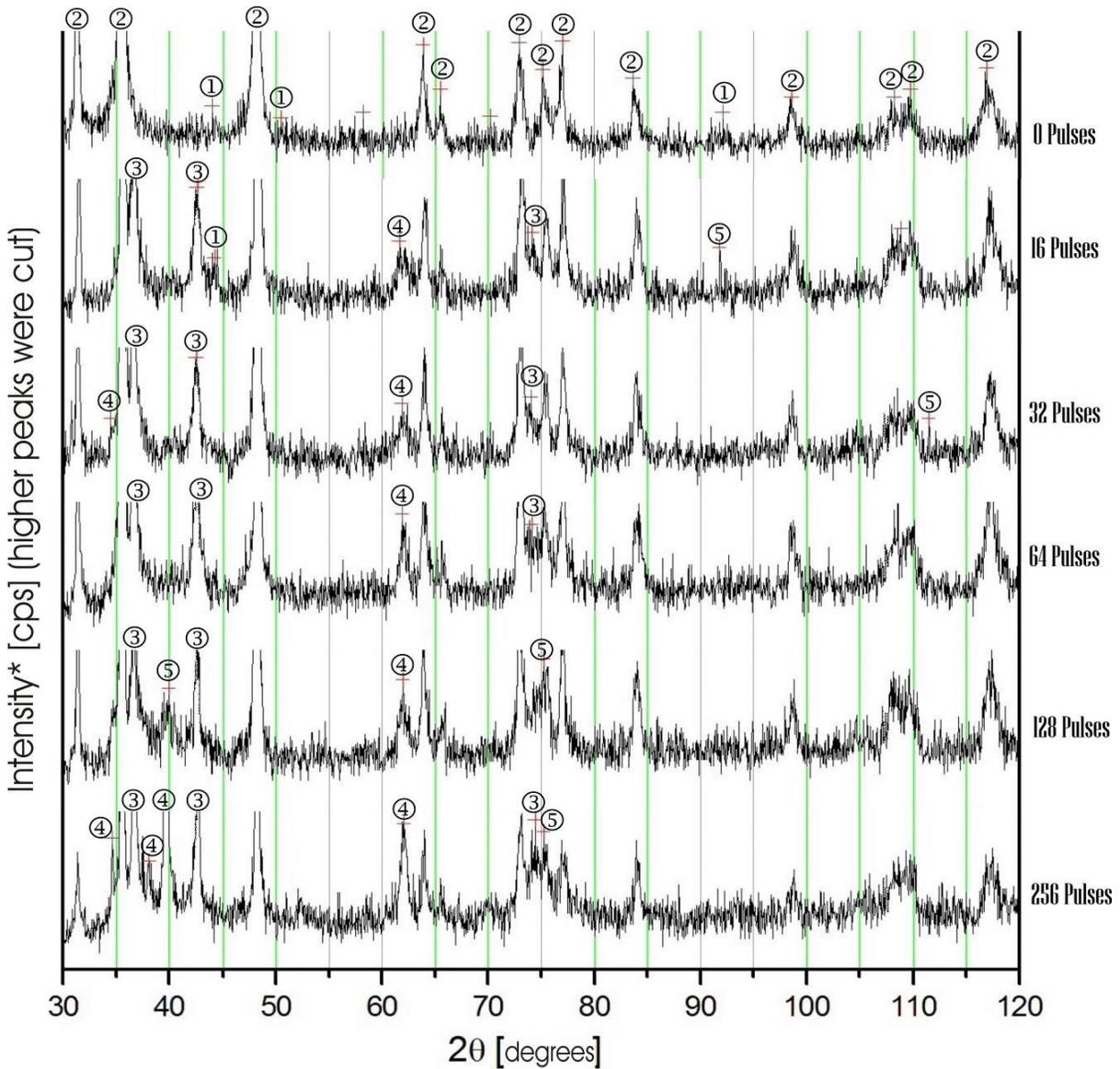


Figure 5. X-ray diffractograms of 273 MW/cm² intensity lasered surfaces with several pulses quantity: ①:Co, ②:WC, ③:β-WC_{1-x}, ④:α-W₂C, ⑤:W₃C.

3.3. Qualitative adhesion evaluation of laser processed coated substrates

After laser texturizing, substrates were cleaned by ultrasound bath and were MT-CVD (~800 °C) coated with a ~5µm TiCN+Al₂O₃+TiN coating. A substrate without laser surface texturization was processed in this way too.

Qualitative coating adhesion assessment was conducted by applying the Rockwell C indentation test. A standard diamond 120° tip with 10 Kgf pre-load and 150 Kgf load was used. In the HF adhesion classification system (*Verein Deutscher Ingenieure, VDI guidelines 3198*) the cracked and delaminated area around the indentation mark is compared with six standard drawings where the level HF1 corresponds to the best adhesion and the level HF6 to the worst one. Figure 6 shows the indentation images over the studied surfaces. The 410 MW/cm², 32 pulses laser textured surface (Fig. 6-E) exhibited the less coating de-lamination (HF3). The 273 MW/cm², 16 pulses laser textured surface (Fig 6-F) de-lamination was not so severe and could be HF4 classified. All other lasered surfaces and the unlasered one (Fig 6-A) had a poor HF5 coating adhesion classification.

Figure 7 shows a SEM typical image of the delaminated frontier in a lasered-coated substrate after Rockwell C indentation. The delaminated area shows the bulk substrate and does not exhibit the substrate laser textured surface demonstrating a cohesion fault. The interface between the created laser textured layer and the bulk substrate should be strong enough to avoid cohesive damage. The fast heating-cooling laser texturizing process produces thermal stresses; it

seems to be possible to find appropriated process parameters (i.e. intensity and pulses quantity) to minimize thermal stresses and consequent micro-cracks that lead to cohesive coating delamination.

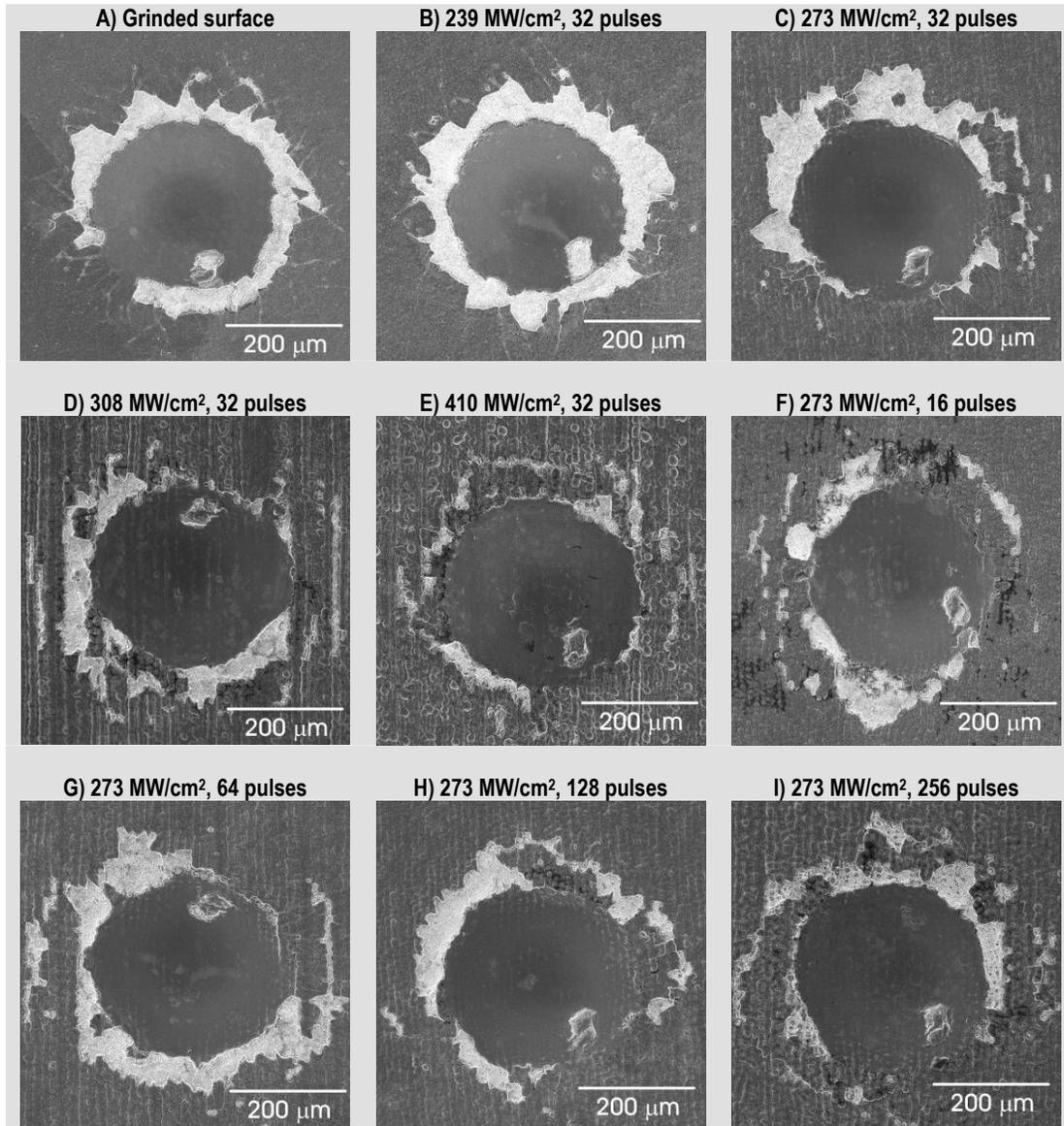


Figure 6. Rockwell C indentations over the coated surfaces

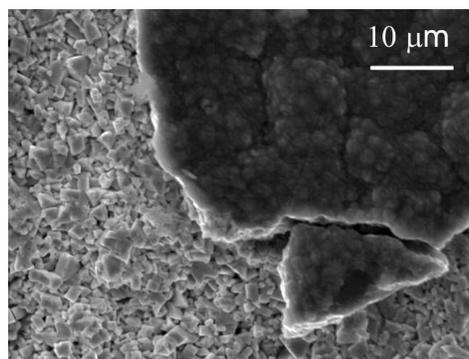


Figure 7. Cohesive de-lamination produced by the Rockwell C indentation test.

4. CONCLUSION

A wide variety of hardmetal surface morphologies can be produced with the CuHBr laser texturizing technique used in this work. The surface roughness of fabricated surfaces can be controlled with the laser intensity or with the laser applied pulses quantity. The adhesion of the MT-CVD TiCN+Al₂O₃+TiN coating applied over the laser texturized hard metal surfaces had a discrete improvement if compared with the as received grinded surface. The laser texturizing process can produce better coating adhesion but the cohesive de-laminations observed in the Rockwell C indentation tests, suggest further search on appropriated laser intensity and pulses quantity to produce a resistant interface between the thermally modified layer and the bulk hard metal substrate. That work is ongoing and will be published elsewhere once finished.

5. ACKNOWLEDGEMENTS

The authors wish to thank the support of National University of Colombia (UNCB), Campinas State University (UNICAMP), Institute for Advanced Studies (IEAv) and Sandvik-Coromant Brazil (Specially Mrs. Flavia Silva and Mr. Aldeci Santos).

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