Materials Research. 2025; 28(suppl. 1):e20250133
DOI: https://doi.org/10.1590/1980-5373-MR-2025-0133

Study of (12Co–4Cr WC) and (Cr3C2–25NiCr) coatings sprayed by the HVOF process and subsequently laser remelted

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Received: January 10, 2025; Revised: April 17, 2025; Accepted: April 21, 2025

The laser remelting technique on tungsten carbide (12Co–4Cr WC) and chromium carbide (Cr_3C_2–25NiCr) coatings deposited by HVOF provides improvements in surface properties, such as increased hardness and resistance to abrasive wear. This process uses a laser beam to selectively melt the coating, promoting a uniform and adherent layer. In the present work, tungsten carbide and chromium carbide alloy coatings were deposited on properly prepared SAE 1020 substrates using the high-speed oxy-fuel (HVOF) technique. After deposition, the coatings were remelted with a laser beam, varying the scanning speed and the laser beam power of the ytterbium fiber to obtain a pore- and crack-free coating and better metallurgical anchorage to the substrate. The samples were characterized by scanning electron microscopy (SEM), X-ray diffractogram, ASTM G132 Standard Test Method for Pin Abrasion Testing wear and microhardness. The results show that it was possible to obtain coatings with greater hardness after the laser remelting process, reducing pores or imperfections and metallurgically bonding to the substrate.

Keywords: *wear resistance increase, fiber laser, WC, remelting coating.*

1. Introduction

The HVOF spraying process was developed as an alternative to the D-Gun spraying process and is currently also emerging as an alternative to plasma spraying. This is because the initial installation cost is much lower and the quality of the sprayed coating has properties that are sometimes even superior to these two processes[1,2]. High-speed oxy-fuel spraying is a technique based on the design of a spray torch (gun) in which the fuel, usually propane, propylene, methyl-acetylene, or kerosene, is mixed with oxygen and burned in a combustion chamber where the flame is compressed. The combustion products are then released and expand through a nozzle where the gas velocities become supersonic. The coating powder is introduced into the nozzle, generally axially, and is heated and accelerated out of it. Due to the impact on the substrate, the sprayed particles are finely distributed, which produces a very dense coating with excellent adhesion to the substrate[2,3].

In this context, most of the sprayed powders are carbides, mainly tungsten and chromium (ASM, 2004). The main types of coating materials cited in the literature that have high hardness, including hot working conditions, wear resistance and corrosion resistance are: WC-Co, WC-Ni, WC-Co-Cr, WC-Cr-Ni and Cr_3C_2-NiCr. These materials have the characteristics of having high hardness carbides, immersed in a relatively tough and ductile matrix of Co, Ni, Co-Cr or NiCr, whose function is to promote particle union[4-7].

Chromium carbide is recommended for environments that need to resist wear at high temperatures and is highly resistant to abrasive and erosive wear. Tungsten carbide is highly resistant to abrasive and erosive wear, but should not be used in environments containing acidic materials. Its use is also not recommended in environments with working temperatures above 450 degrees Celsius. Tungsten carbide does not withstand impacts[7,8].

Erosive wear is found in components of industrial process machines in practically all segments of industry. Wear is the progressive loss of a material due to the relative movement between the surface and the substance with which it comes into contact. There are several types of wear, including fatigue (contact, thermal and S-N curve), friction, cavitation, adhesion, abrasion and also erosion, which is what we will discuss today. Understanding this wear mechanism is important for all professionals who specify materials for machine components because it is very similar to abrasive wear. Confusing these two concepts can lead professionals to make mistakes that can cause serious

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damage to the component and equipment, in addition to inducing the purchase of expensive materials that are not appropriate for these work environments[3].

The first step to preventing erosive wear is to understand and identify the fluid, the eroding agent and the base material of the part. The more the particle causing the wear is impacting the surface at low angles, the more likely it is to use hard materials, such as on the surfaces of hydroelectric turbine blades. In this case, the use of coatings applied by thermal spraying is a viable alternative. If the working temperature is below 400ºC, Tungsten Carbide is the most suitable material. For environments with temperatures above 400ºC, the use of Chromium Carbide is recommended. When erosion occurs due to the action of coarser particles, coatings applied by HVOF may peel off. One of the solutions that can be quite effective is remelting the coating onto the substrate. These processes create a metallurgical bond with the substrate/coating and will withstand the impact of a stone, for example, without detaching the surface material, in addition to providing a significant increase in the durability of the components

According to Ronzani et al.[9], the remelting of tungsten carbide using laser remelting demonstrated significant improvements in cavitation resistance. The erosion wear process of a component begins imperceptibly. As the damage becomes more pronounced, it increases. Rotating parts end up losing balance, generating vibration, and the damage can spread to other parts of the equipment, such as damaging bearings. In hydroelectric rotors, erosion wear can become cavitation wear. The turbine loses efficiency in generating energy and will necessarily have to be stopped for maintenance to repair or replace components. These events are expensive, pose a high safety risk, and compromise the financial results of companies.

The effect of sulfide on the erosion-corrosion behavior via ultrasonic cavitation of the WC-Cr_3C_2-Ni coating sprayed by the HVOF method under alkaline conditions, showed that the erosion resistance by ultrasonic cavitation of the coating decreases as the concentrations of sulfides increase[10].

The mechanical resistance of a sprayed coating basically depends on the adhesion between it and the substrate, and the cohesion between its particles[10,11]. In many practical applications, some coatings cannot be used because they have low and insufficient adhesion strength.

Due to the characteristics of the deposition process, the coating formed normally contains imperfections such as pores, oxides and cracks, whose sizes and distributions decisively influence its performance in service[12].

In this context, the main objective of this work is to evaluate the improvement of the surface properties of the WC-CoCr and Cr_3C_2-25NiCr /HVOF coating by laser remelting, aiming at reducing the friction coefficient and sliding wear, and ultimately optimize the energy consumed by the hydraulic equipment. The coating was deposited on a surface of SAE 1020 steel. Then the laser remelting was carried out, changing the scanning speed and the power of the laser beam. The coatings' microstructure, phase composition and microhardness were used in their evaluation.

2. Materials and Methods

2.1. Materials preparation

The material used as substrate in this study was SAE 1020 carbon steel. The samples were subjected to an aluminum oxide abrasive blast pre-treatment (Al_2O_3), with particle size between 0.7 and 1 mm, to remove contaminants, oil residues, surface degreasing and promote an average surface roughness (Ra) of 6 µm for a good mechanical anchorage of the coating on the substrate.

For the application of the WC–10Co–4Cr and Cr_3C_2-25NiCr coating, a robotic arm powered SULZER METCO DJ 2700 equipment was used and propane combustion (C3H8). The powder used was WOKA 3653 (WC–10Co–4Cr) containing remaining wt% W, 5.2% wt% C, 10% wt% and 4% wt% Cr, sold by Harris Brastak Soldas Especiais SA.

Conventional commercial Cr_3C_2-25NiCr spray powder (PRAXAIR Surface Technologies) containing 75 wt% Cr_3C_2, 20% Ni, and 5% Cr was used in the present study

For the application of the tungsten carbide coating by HVOF thermal spraying at the Rijeza company, a Praxair-TAFA JP-5000 HP/HVOF spraying apparatus was used and moved by a Praxair Model 1270 robotic arm, together with a hopper and the combustion was carried out with kerosene. Tables 1 and 2 shows the parameters of the HVOF thermal spraying, already determined by the company.

2.2. Laser remelting

Figure 1 shows the alumina blasting, HVOF thermal spraying and laser beam remelting processes.

Table 1. Parameters of HVOF spray process coating (12Co–4Cr WC) Rijeza company[9].

HVOF PROCESS	
Parameter	Condition
Oxygen flow	253 l/min
Propane flow	77 l/min
Air flow	376 l/min
Nitrogen flow	12.5 l/min
Spray distance	230 mm
Power Feed rate	38 g/min

Table 2. Parameters of HVOF spray process coating (Cr_3C_2-25NiCr) Rijeza company[13].

HVOF PROCESS	
Parameter	Condition
Oxygen press	150 PSI
Oxygen flow	560 ft^3/h
Pressure Propane	100 PSI
Propane flow	160 ft^3/h
Air pressure	100 PSI
Fluxo do ar	850 ft^3/h
Feed rate	35 g/min
Spray distance	230 mm
Spray angle	90º

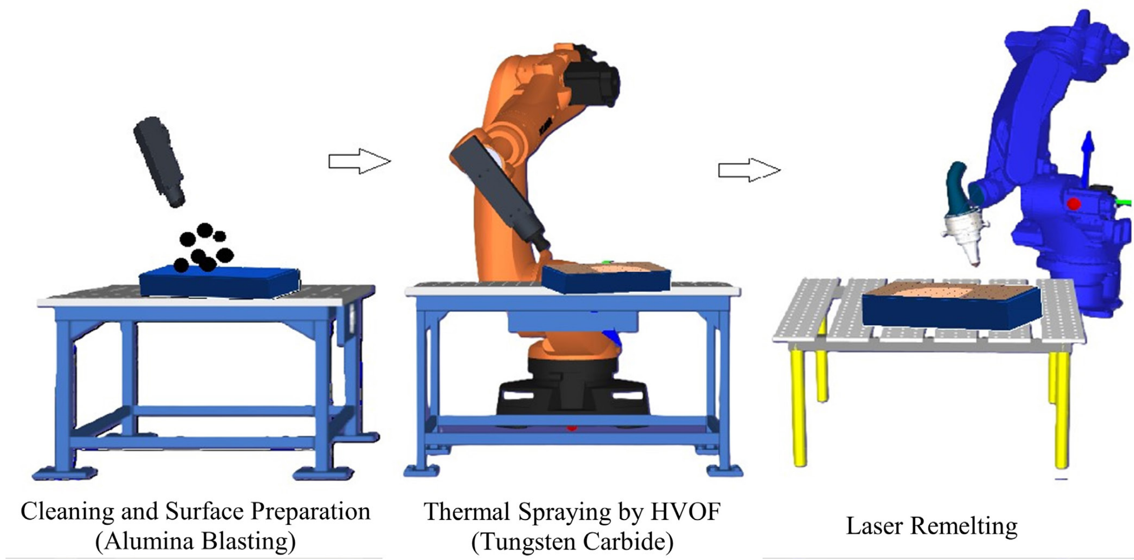

Figure 1. HVOF process after laser remelting under coatings (12Co–4Cr WC) and (Cr_3C_2-25NiCr).

The procedure for preparing the substrate aims to leave the surface active, allowing the propelled particles to have, at the moment of impact, maximum adhesion potential.

Before coatings are applied, the substrates undergo the following steps: 1 - Pre-machining: The coating area must not have sharp corners. They must be machined in a chamfer (minimum of 1 mm) or radius. 2 - Cleaning: The coated area must be clean. All oxide, grease and oil residues must be removed. 3 - Sandblasting: The surface to be coated must be sandblasted with aluminum oxide to generate the roughness necessary for anchoring the coating.

For the HVOF process, a rough surface is very important, as it has more surface area than a polished surface. This means that the particles will have more contact area, an active zone, to adhere to the substrate, as it will have more mechanical anchoring points. It will also eliminate the preferential shear planes that exist in the deposited layers due to their typical lamellar structure. Large tensions develop in these layers parallel to the base, which are responsible for their low tensile strength, and this can be verified when adhesion tests are performed.

In some cases, mechanical anchoring is not enough to protect the part where wear is most severe; the coating/substrate must have a metallurgical bond. Bonding materials are those that have an affinity to form a strong interatomic, physical or diffusion bond with the substrate material[1].

The remelting of the coating was performed with an ytterbium fiber laser and cladding head (IPG YLR-1500). The laser has λ = 1.07µm and a maximum power "P" of 1500W. The head has an optic that produces a Top-Hat beam, with an incidence diameter "bd" of 6mm. It is "operated" by a Yaskawa GP25 robot; with a payload of 25kg and precision of 100µm, through routines in Python language through the RoboDk interface. Figure 2 shows Laboratory set-up equipment. This system is also equipped with an STC-HD203DV camera; which records (with 10X magnification) the laser action. Table 3 shows the parameters of the laser process.

The samples was embedded in Bakelite, sanded in the grit sequence of: 120, 220, 320, 400, 800 and 1200. After that, polished in the alumina grit sequence: 0.5 and 1um. And finally, chemically attacked by Nital 5%; with application for 10s, followed by alcohol rinsing and drying.

Next, for the analysis were used: a Zeiss optical microscope, Tecsan Vega SEM coupled to energy dispersive X-ray spectroscopy (EDS) detector, Vickers microhardness and wear test.

The experimental results of wear carried out in the UNIVAP tribology laboratory were analyzed using the Archad or Rabinowicz equation15, which evaluates the wear ratio and the wear coefficient, relating the accumulated lost volume per sliding unit with the wear resistance using the linear equation[14,15].

$$Q = \frac{V}{S} = K\frac{FN}{H}\left(mm^3/m\right) \quad (1)$$

where Q is the parameter that measures the wear ratio or "wear rate" (accumulated lost volume V or mass lost per unit of sliding S), FN is the applied normal load, H is the hardness of the softest material and K is the wear coefficient: it is dimensionless and less than 1. In general, wear resistance is defined as being 1/K. Therefore, the wear coefficient is given by V=m/ρ (m= mass; ρ = density).

With the Archard model it is observed that the wear rate has an inverse relationship to hardness and thus the great efforts to increase the hardness of materials to avoid wear can be understood.

The tribological test to characterize friction and wear was performed on a tribometer using the sphere-on-disc technique, using a Universal Tribometer brand tribometer, to determine the coefficient of friction during sliding according to the ASTM G132 Standard Test Method for Pin Abrasion Testing technical standard. This test used an alumina sphere, 5N loads and a speed of 200mm/s for 10 min RPM.

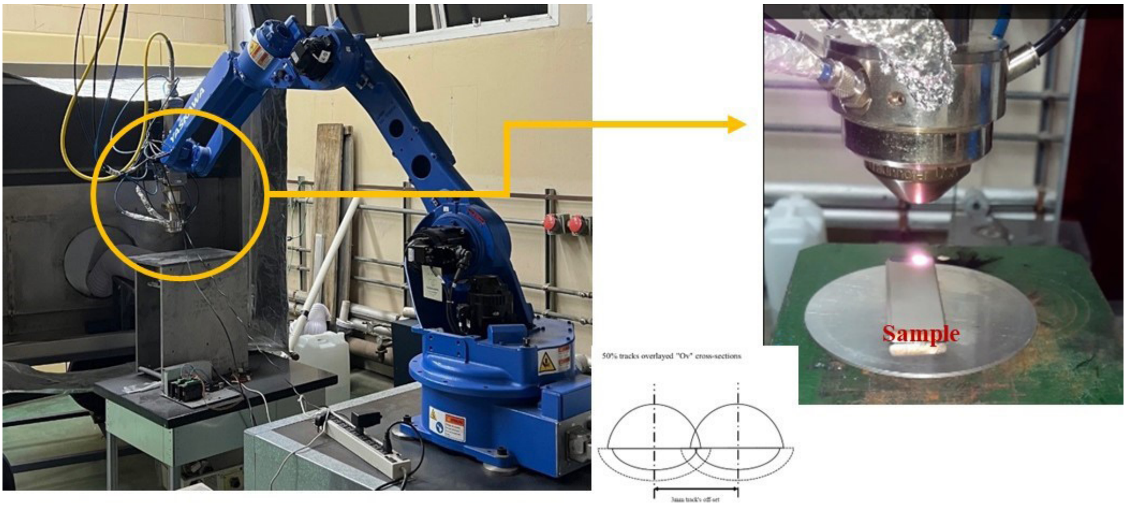

Figure 2. Laboratory set-up equipment.

Table 3. Parameters of laser remelting process.

Parameters	Symbol	Sample WC	Sample CCr
Laser Power	P	80	60
Scanning Velocity	v	6	12
Overlapping tracks	"O_v" (%)	50	50

The groove area was used to calculate the wear rate. The area left by the alumina sphere after the tribological test was analyzed. A profilometry was performed, that is, a scan of the part with a diamond tip. The software used to measure the area was Vision.

3. Results and Discussion

The microstructure and crystalline phases properties of WC–10Co–4Cr and Cr_3C_2-25NiCr coating were evaluated regarding the alloy characteristics before and after remelting with laser. Likewise, microstructural, chemical and mechanical properties were compared between initial and cladded substrates, in the spectrum of wear resistance gains; also, being evaluated through dilution level and quality of cladding at the parameters.

The coating is homogeneous, with no surface cracks, about 110 µm thickness, pore presence and good mechanical adhesion to the steel substrate, with no crack between the coating/substrate interface as expected from an optimized HVOF process. However, the presence of pores and oxides in the coating is visible.

Figure 3 shows the cross sections of the sprayed sample as well as the laser remelted samples under the parameter (Table 3). Figure 3a shows the microstructure before the remelting process; a well-defined interface can be observed.

The treated zone was shown to be homogeneous in the observation in Figure 3b, it can be seen that in some cases circular holes were observed at the edges of the zone affected by radiation. This would be due to gas occlusions. The debonding of the coating did not appear, but in some specimens, other parameters, transverse cracks were created. Since the diameter of the beam did not allow to remelt the entire coating in a single pass, it was necessary to make several passes. The overlap was established to obtain a homogeneous treated zone, although it was observed that at the edges of the tracks the porosity did not disappear completely, probably due to the fact that in this zone there is a lower concentration of energy. Finally, an overlap of 50% was adopted.

According to Chagas[16], the presence of pores occurs due to the trapping of gases from the decomposition of the WC and rapid solidification of the matrix. Cracks, on the other hand, occur in a manner analogous to surface defects[17].

The WC–10Co–4Cr powder XRD patterns used as a spray coating are shown in Figure 3 together with the respective coating and remelting. It is verifed that the powder used has other phases besides WC–10Co–4Cr, as can be observed by the indexation of the peaks. After HVOF spraying, the only change observed is the disappearance of the contribution relative to the metallic W phase, predominating the polycrystalline phase of WC.

The EDX analysis of metallic elements and show the presence of Fe in the zone of the coating close to the interface something that does not occur in the specimen without laser treatment. It seems to indicate that the remelting gave way a process of dilution of the material of the substrate in the coating, which should improve the adherence.

In Figure 4a it is possible to observe the Cr_3C_2-25 NiCr coating after the HVOF process and the defined interface and

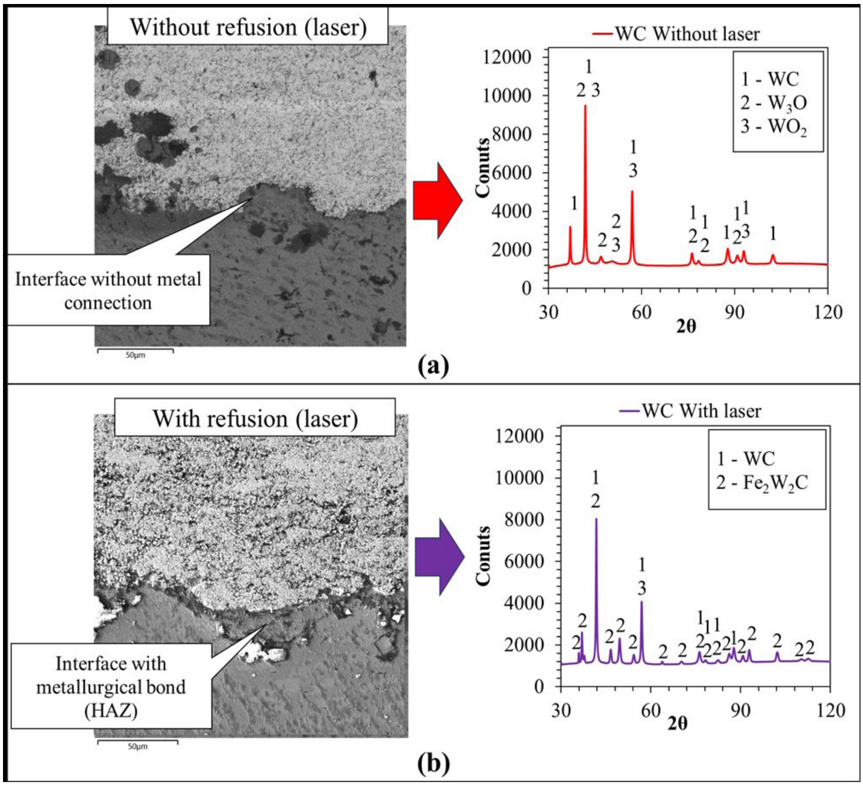

Figure 3. SEM micrograph substrate/WC–10Co–4Cr: (a) sprayed coating (b) laser remelted coating.

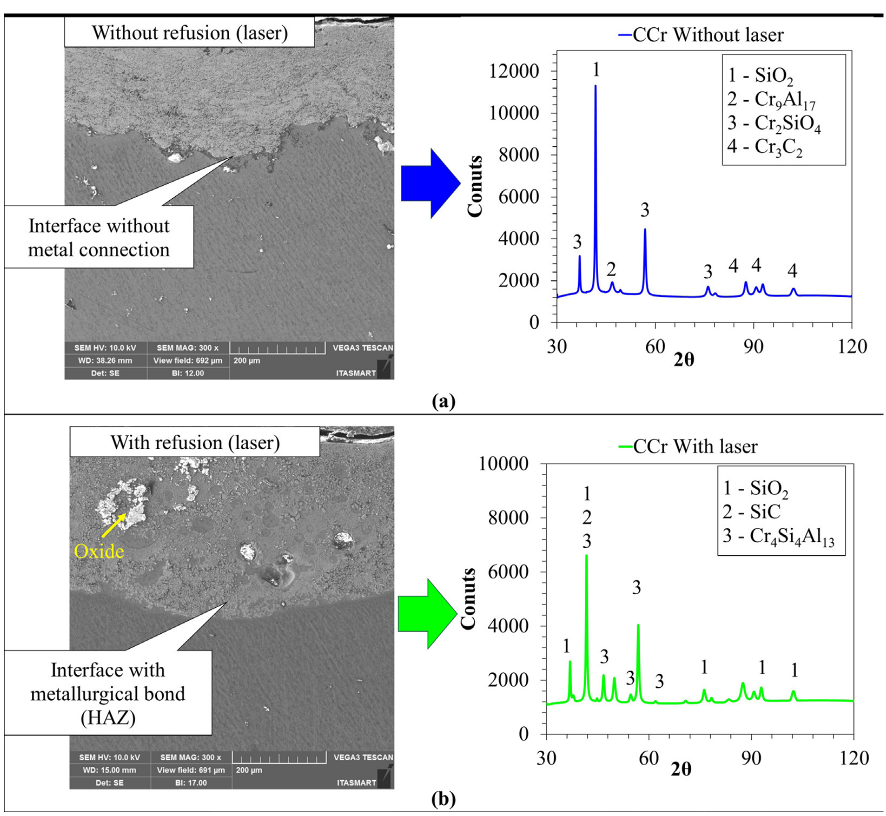

Figure 4. SEM micrograph substrate/Cr_3C_2-25NiCr: (a) sprayed coating (b) laser remelted coating.

Table 4. Hardness 50gf for 10s for coating WC-10Co-4Cr (WC) and Cr_3C_2-25NiCr (Cr).

Coating	Point (distance)	P1	P2	P3	P4	P5	P6	P7
WC	No refusion	1697.8	1422.0	4325.3	1082.5	269.5	287.4	255.6
	Refusion	4188.5	2579.9	21013.0	2288.6	519.5	408.8	340.2
Cr	No refusion	1328.3	1240.6	2065.5	1336.2	320.5	282.9	232.5
	Refusion	2988.6	1679.6	1914.1	1754.3	1661.6	410.7	260.3

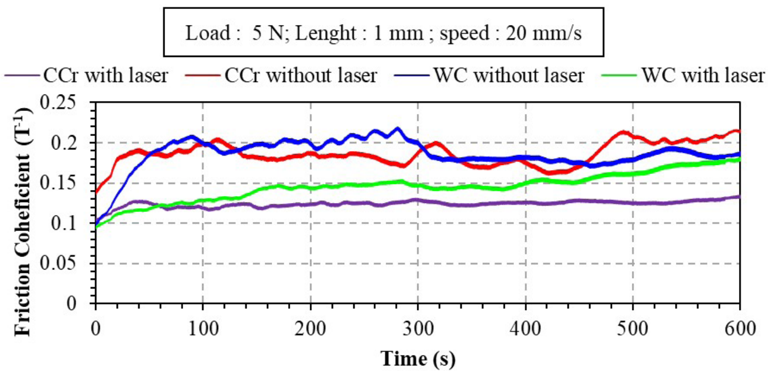

Figure 5. Wear test of coatings (12Co–4Cr WC) e (Cr_3C_2-25NiCr).

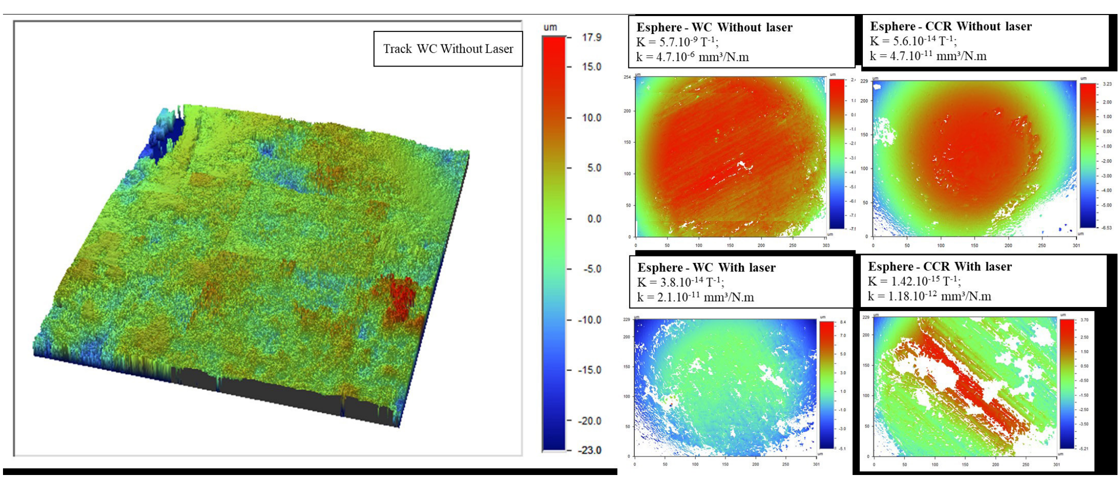

Figure 6. Wear of the aluminum sphere.

Figure 4b shows the microstructure after remelting where the mixture between the coating and the substrate can be seen

Figure 5 shows the coefficient of friction as a function of test time for all coating process conditions. The coefficient of friction reached the lowest value for the coated (Cr_3C_2-25NiCr) and remelted sample when compared to the other coatings.

The results showed that remelting reduced the friction coefficient from 0.19 to 0.12 chromium carbide and tungsten carbide from 0.21–0.15**.**

According to the prediction of the Archad equation, the wear on the sphere will be greater for a lower hardness and the same load. Therefore, the sphere that wore the coating (12Co–4Cr WC) after laser obtained a higher hardness. This is confirmed in Table 4 the coating by the HVOF process has a hardness of 1697.8 HV and the one remelted with laser has a hardness of 4188.5 HV.

The behavior of the average friction coefficient was similar, as seen in Figure 6. All tests with the same type of pin (alumina) and all resulted in moderate wear regime. K=4.7 10^{-6} mm^3/N.m for wear on the coating (12Co–4Cr WC) via HVOF and K=4.7 10^{-11} mm3/N.m, after remelting. For wear on the coating (Cr_3C_2-25NiCr) via HVOF is K=2.1 10^{-11} mm3/N.m and with remelting K=1.18 10^{-12} mm^3/N.m.

According to the work carried out by Casteletti et al.[18], the surface finish of the samples sprayed with HVOF influences their abrasion resistance.

The Vickers microhardness (HV0.5) for the laser sprayed and remelted samples is shown in Table 4 as a function of the depth in the cross section of the samples. The microhardness of the sample without laser treatment has an average coating value of 1697.8 HV, and after remelting this hardness is increased to 4188.5 HV.

4. Conclusion

In this paper, physical, chemical and tribological properties of steel starting samples and coated with (12Co–4Cr WC) and (Cr_3C_2-25NiCr) depositado por HVOF and after remelting by laser.

Laser remelting eliminates porosity and homogenizes tungsten carbide and chromium carbide coatings, although holes may form at the edges of the treatment zone due to gas retention. The hardness of the coating increases considerably with the treatment, resulting in uniformity throughout the coating. This increase is independent of the depth. The wear resistance is superior for both types of laser-treated coating.

5. Future scope

In view of the conclusions presented, some research opportunities were highlighted, expanding this research theme. To complement these studies, the following were suggested in the present work:

- Perform cold deposition together with the laser irradiation process, aiming to reduce oxidation, since the shielding gas flow would not be limited to avoiding powder dispersion;
- Investigate other laser scanning speed ranges, reducing coating temperatures to minimize the effect of gas entrapment;
- Perform deposition with laser cladding and compare it with reflow.

6. Acknowledgments

The authors would like the support form Rijeza Company, Instituto de Estudos Avançados IEAv and Universidade do Vale do Paraíba UNIVAP.

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