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# Wear Resistance of Thermal Spray WC-Co-VC Nanostructured Coatings

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Additional information is available at the end of the chapter

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## Abstract

Thermally sprayed WC-Co-VC coatings are widely used based on their resistance to abrasive wear. This chapter shows the fabrication procedure of bimodal WC-Co-VC coatings applied by a high-velocity oxy-fuel (HVOF) thermal spray process. We analyzed the effects of the mixture content of the nanostructure and microstructure phase on the mechanical properties and wear resistance of the coating. Additionally, VC was added to the bimodal mixture and it presented the best characteristics. The combination of VC additions and a bimodal WC particle size distribution in the WC-Co coatings proved successful in increasing their mechanical properties, which permitted the coatings processed in this work to show better mechanical properties than those reported in the literature for coatings having exclusively a bimodal WC particles size distribution or those only doped with VC additions. The effects of nanostructured phase contents on the microstructure and wear resistance of the coating are included.

**Keywords:** wear, thermal spray, nanostructured, coatings

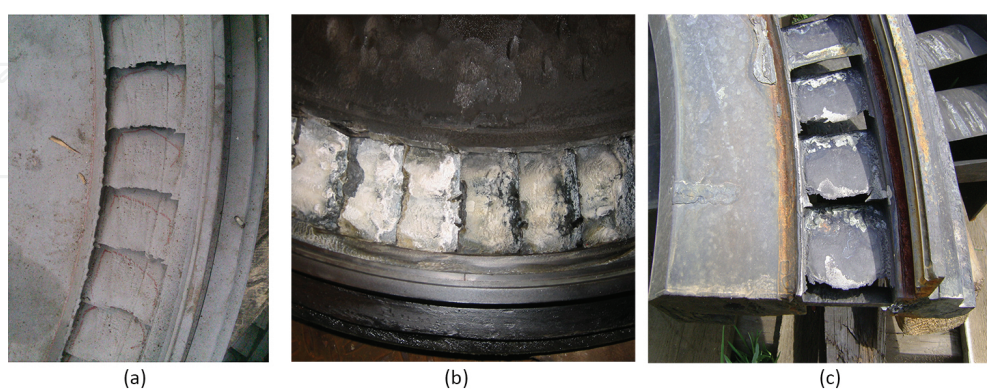
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## 1. Introduction

In industrial processes, the materials are exposed to corrosive and erosive environments that lead lifetime reduction for certain components and trigger, furthermore, high maintenance costs. In the different wear mechanisms, there is an intersection of phenomena and by this means a severe damage, for example, in a suction system can be found: cavitation and erosion; or heat (thermal fatigue) and erosion of a steam turbine blades or abrasion and corrosion, in

a screw pulp pump by the presence of  $\text{Cl}^-$  ions. Once the wear mechanisms present on an equipment or component have been determined, there is a need for search for the alloy or coating, metallic, polymeric, ceramic or a mixture thereof that can prolong its service. The most critical area of structural and nonstructural components is usually the surface where the maximum loads are reached (e.g., mechanical and thermal stresses, corrosion, wear and their combinations thereof).

A material that works at high temperature normally is not operating in protective atmospheres. Usually the working environment is air and, in this case, the oxidizing agent is oxygen, but it is also likely that the atmosphere is composed of aggressive gases that damage the material. Carburization is the formation of metal carbides in a material as a result of exposure to a carbon containing atmosphere. In service, it can result in loss of mechanical properties over time in addition to wastage of the material. Sulfidation is a chemical reaction of a metal or an alloy, with sulfur in some form in its working environment. This produces compounds of sulfur that usually form on the solid surface or under the surface of the metal or alloy. Sulfidation most often causes serious deterioration of the solid surface and the vital functional properties of the affected substance. Nitridation is a process that results in the formation of nitrides in a material. It results from exposure to reducing, high temperature environments with high nitrogen activity. Since nitrides are inherently hard, brittle phases, nitridation can produce local or widespread loss of material strength and possible metal wastage or chemical attack in presence of salt deposits or ashes [1, 2]. In all environments that trigger corrosion in the above-mentioned problems, the oxygen activity is high enough to promote oxidative processes. Furthermore, the operating conditions of the materials forming part of the steam turbines or part of thermal plant components suffer corrosion processes at elevated temperature where the atmosphere contains a lot of water vapor, with this being more aggressive atmosphere than the air [3]. In reducing environments, the degradation of the material is controlled by the activity of species such as  $\text{CO}/\text{CO}_2$  and  $\text{H}_2/\text{H}_2\text{O}$ , and they are usually more aggressive than oxidants, because the driving force for forming a protective oxide is less favorable [4].

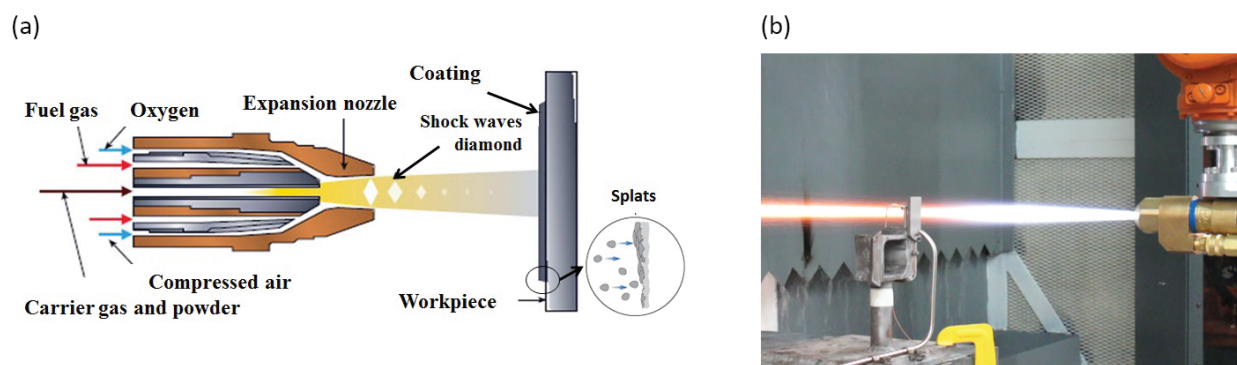


**Figure 1.** Steam turbine blades showing corrosion wear.

The protection of the metal components can be done with hard coatings to improve wear resistance. They are applied with different techniques, with the thermal spraying techniques

being the most developed in recent years, where its increasing applications is to reduce the wear in industrial processes. In steam turbine, components like blades, body rotor, nozzle and auxiliary devices for cooling and lubrication must be developed to work properly under the required steam conditions for pressure and temperature. The most common vanes failures are associated with erosion, stress corrosion, corrosion fatigue and fatigue [5]. Some of these failures are shown in **Figure 1**.

The thermal spraying is one of the most versatile techniques ever used for coating materials application to protect components from wear by abrasion, adhesion, erosion, corrosion and fatigue [6]. This technique tends to extend the lifetime of the components, with the aim of obtaining high yields for longer and reducing the number of failures. The advanced technology of thermal spraying provides all types of techniques to the industries, being one of the most effective resources ever developed to combat premature wear by getting ahead of the failure or even when the equipment or item stops working in optimal conditions. Hence, it optimizes equipment availability, the maintenance costs are reduced and the lifetime of the equipment and machinery is maximized, increasing the reliability of critical systems. Through processes of high-velocity thermal spraying (HVOF), it is possible to obtain coatings with low porosity structures, low oxidation and high adhesion, thereby minimizing problems caused by the degradation processes on the components of steam turbines used for the electric power generation [7–10]. In this technique, oxygen and fuel gas at high pressures and flow rates are combined to produce a combustion which produces very high-speed particles and temperatures of about 2000°C, which can be considered low compared to other thermal spraying processes, such as vacuum or air plasma [11]. These flame characteristics are suitable for the application of corrosion- and wear-resistant coatings. **Figure 2** shows a schematic of high-velocity oxy-fuel (HVOF).



**Figure 2.** Schematic of an HVOF torch.

The materials that are often selected for applications at elevated temperatures must have the fundamental requirements to resist the corrosion and atmosphere deterioration where they are set. Usually, they are the austenitic stainless steels, nickel-, cobalt- and titanium-based alloys and besides the intermetallic materials [12, 13]. The selection of suitable material will depend on the operating temperature, the atmosphere and lifetime required for the working component in the equipment.



It is well known that Ni-based coatings show good corrosion resistance at high temperature and besides have good wear resistance after addition of W and Mo as alloying elements [15]. These alloys exhibit improved properties due to the formation of an amorphous phase that came from a rapid solidification and a suitable alloy composition [16, 17]. Some researchers have found that spraying the alloys Ni-Mo-Cr-B to make coatings using atmospheric plasma exhibited improved wear and corrosion resistance due to the formation of an amorphous phase coming from the rapid solidification and a suitable alloy composition [18]. An amorphous alloy phase in the protective coating is achieved by adding some appropriate refractory materials such as Mo and W and metalloids such as B and C in the base powder [19]. Those additions result in better resistance to abrasion and wear, while providing resistance to corrosion in aqueous and alkaline media [20, 21].

Protective coatings are widely used in the aircraft industry because they provide better surface properties of the structures where they are deposited. Besides, the characteristic that they must possess is the high structural performance due to the conditions of service that are subjected. Innovation in this area has focused on nanotechnology and gives special relevance in the world of materials. Regarding coatings, the extreme mechanical conditions that they must resist must be taken into account. Many components of an aircraft are subject to wear conditions; to address this problem, the pieces are coated with materials having good tribological properties. The components that are subject to wear and corrosion are generally those found in the undercarriage. The landing gear systems must withstand thousands of cycles of fatigue and shear stresses during the service life of the aircraft, whereby the material that forms the protective coating must have a high resistance to fatigue. Many components of the landing gear are coated with hard chrome and the inner surface of the cylinder sliding as well. However, environmental regulations require the replacement of those coatings where the use of hexavalent chromium [14] is required. Given this requirement, the coatings obtained by HVOF thermal spraying today are a viable alternative, enhancing the benefits obtained with traditional hard chromium coatings, both wear resistance and corrosion resistance.

The thermal spraying of WC-Co, WC-CoCr or  $\text{Cr}_3\text{C}_2$ -NiCr by HVOF, that is, applying a consistent coating made of metal matrix reinforced with high hardness ceramic inclusions [22] plus the addition of nanocrystalline WC particles, provides to the coatings an improvement in the hardness and tribological properties [23, 24]. The WC-Co coatings applied by HVOF are useful for operating temperatures up to  $900^\circ\text{C}$ , while the maximum pressure is up to 1200 MPa, its friction coefficient is only 0.01 (80 times lower than steel). The WC-Co coatings applied by HVOF containing nanoparticle sizes have better mechanical and tribological properties by providing an effective control of processing variables during thermal spraying application [25]. The wide applications as protective coatings permit to be an excellent choice on steam turbines in the industrial power generation sector and at the same time useful in the aeronautical industry.

This means that the corrosion behavior depends on the phases and microstructure of the applied coating.

Regarding the opposite corrosive behavior of the two main components of the alloy, Co and W, in respect to the influence of the medium [26], it is described that the cobalt shows stable

passivity in alkaline solutions, while W is readily soluble; the situation observed in acid electrolytes is completely reverse. Therefore, these hard metals typically fail by corrosion of the less resistant phase, which is triggered by the testing environment [27]. On the other hand, it has to be taken into consideration the galvanic interactions between the existing phases, where typically the WC is nobler than Co [28].

It has been found, according to the literature reports, that VC effectively retards thickening of tungsten carbide grains after prolonged heat treatment, [29] and furthermore, promotes the formation of compounds (W, V) C, inhibiting, beside, the formation of brittle species [30]. The corrosion resistance of WC-Co alloys can be improved with the addition, in small quantities, of transition carbides. An example of this is the addition of  $\text{Cr}_3\text{C}_2$ , in amounts of only 0.5%, improving significantly the corrosion resistance [31]. However, the influence of the additions of VC was not so easy to assess as the case of  $\text{Cr}_3\text{C}_2$ .

Some studies have found that small additions of VC in WC-Co had a neutral effect on the corrosion resistance [31]. On the other hand, the tungsten carbide alloys reinforced with cobalt and chromium (cermets) and thermally sprayed by HVOF are currently good substitutes for hard chrome, typically present in some components such as aircraft landing gears, hydraulic rods, ball valves, printing rollers, etc. [14]. The use of nanocrystalline particles of WC is expected to improve properties in terms of hardness and tribological coatings [23, 24, 32, 33]; however, due to their high surface area-to-volume ratio, these suffer grain size growth and oxidation during their passage through the flame, which is detrimental to the coatings in good final properties such as hardness and wear resistance [34]. However, it has been reported, in different works [35, 25], a better mechanical and tribological properties using WC-Co coatings enriched with nanoparticles and deposited under HVOF technique, provided that an effective control of the processing variables was carried out during thermal spraying. The resistance against wear and erosion depends on the thickness of the coatings [36] and also on its hardness [37].

The processing and characterization of tungsten carbide coatings with a bimodal particle size distribution, that is, nanostructured and microstructured particle sizes of WC-Co, have been reported by several authors [35, 25]. The use of nano-sized particles in the compounds of cermet has resulted in a greater hardness than that found in their counterparts containing micron size particles. Furthermore, their combination, as bimodal particle size distribution, the under HVOF thermally applied WC-Co coating results in improved wear resistance, compared to those coatings produced solely from nano-sized powders. Excessive decarburization of nanoparticles by the torch flame and the formation of  $\text{W}_2\text{C}$  in the coating are considered to be responsible for the decrease in wear resistance of the mentioned coatings. Exposure to high temperature of WC nanoparticles in the torch flame during the HVOF process results in an undesirable increment of such particles. As a result, a decrease in hardness and wear resistance is observed. On the other hand, one effect of the mixed matrix hardening, done together by nanoparticles plus the strong arrangement of micrometer WC size grains, was proposed as possible reasons for the improved wear resistance of the bimodal coatings.

Different studies have reported the influence of VC additions in the kinetics of grain coarsening of WC-Co cermets [37, 38]. However, there is little information on the influence by additions

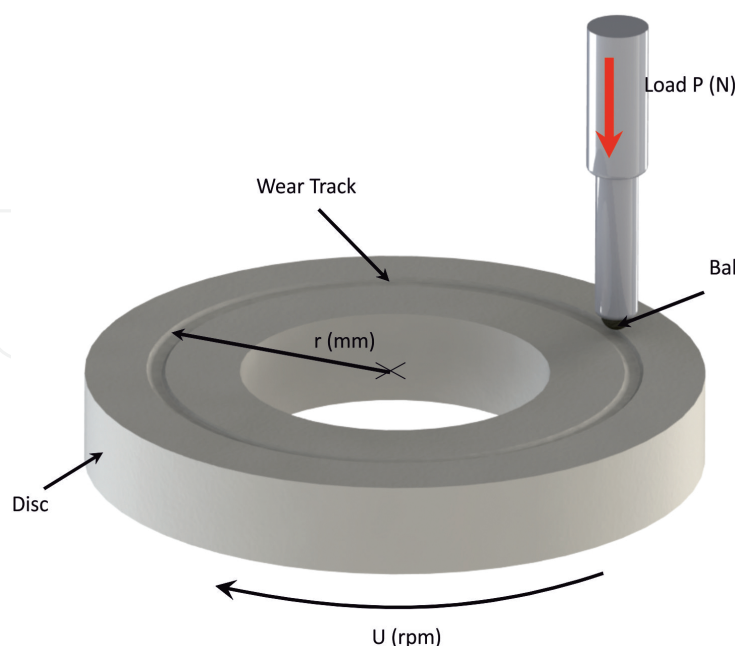
of VC in the properties of WC-Co coatings applied with HVOF technique. Some authors [39, 40] have reported an increase in abrasion resistance of WC-Co-VC coatings compared to their commercial counterparts WC-Co coatings.

This research explored the influence by additions of VC powders in bimodal WC-Co coatings manufactured with HVOF thermal spraying, their mechanical properties and compared with those said properties, found in commercial counterparts.

## 2. Coatings fabrication

The nanostructured WC-Co powder was processed by mechanical milling in a Simoloyer CM01 high-energy ball mill for 20 h at 600 rpm under an argon atmosphere. The powder was then agglomerated employing a 2% methyl cellulose solution to form slurry which in turn was baked in a muffle at 80°C for 24 h under an inert nitrogen atmosphere. A solid block of material was then obtained and crushed into powder. The resulting powder was sieved through 450 and 635 meshes, +32 and +20  $\mu\text{m}$ , respectively. Three powders were employed as feedstock in the present work. A commercial WC-12 Wt%Co powder, a bimodal mixture of commercial and nanostructured WC-Co powder having the same chemical composition (75 wt% commercial-25 wt% nanostructured), and a bimodal mixture doped with additions of 2 wt% vanadium carbide. The bimodal and bimodal doped with VC mixture were mixed mechanically in a double cone blender for 30 min at 20 rpm before being thermally deposited by HVOF.

All powder mixtures were sprayed on AISI 3014 stainless steel substrates employing a Sulzer Metco DJH 2700 hybrid HVOF gun, with propane being the fuel gas. A KUKA KRC robot arm



**Figure 3.** Schematically Pin-on-Disk test to ASTM G 99 [41].

was employed in order to control the gun transversal speed, at 1.5 m/s for all the experiments. Also, constant spray distance and powder feed rate (229 mm and 38 g/min), respectively, were employed.

The microstructure of the coatings was evaluated in the transversal section using a Philips XL 30 ESEM. Coating thickness, interface contamination, oxide contents and porosity percentage were determined from Backscattered electrons micrographs employing SigmaScan image analysis software. The Pin-on-Disk test is a model test for friction and wear determination of two solid surfaces being in sliding contact (pin or ball against coated disk). The test method and procedure are described in ASTM G99-94A [41] and shown in **Figure 3**. The normal loads applied to the ball are typically in the range of 1–10 N. As a result of rotational speed and radius of the sliding path, the relative velocity between ball and surface varies between  $v = 0.19$  and 0.73 m/s. The relative humidity can be adjusted between 5 and 95% using different salt solutions.

Sliding wear measurements were performed in a CSM Instruments Pin-on-Disk 18-280 Tribometer employing a 10 N load. Samples were tested at ambient temperature using 6-mm-diameter 440C stainless steel balls as the counterpart. Testing time was 2000 min and the linear speed was 5 cm/s. Vickers microhardness of all coatings was measured transversally in an LECO M440H1 microhardness tester, using a 500-gf load and a 15-s dwell time.

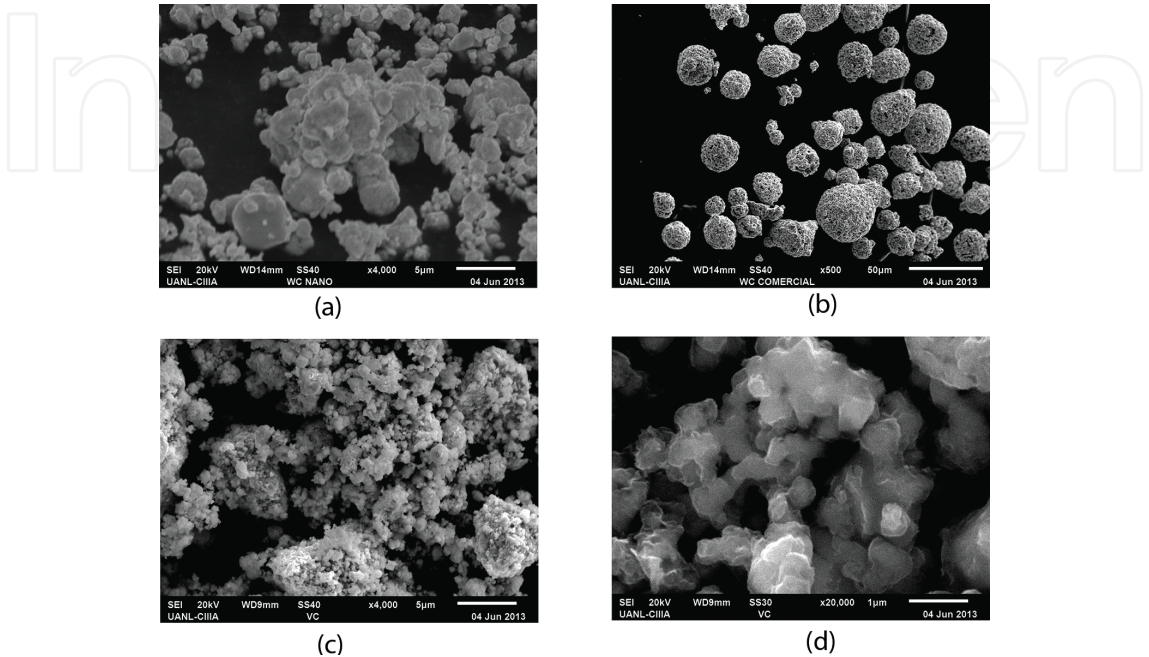
### 3. Microstructured of the powders and coatings

The morphology of the initial powders used in coatings in this investigation is shown in **Figure 4**. The powders of WC-Co nanostructured show long and irregular conglomerates small particles of WC and Co, while the commercial powder consists of spherical shape particles, which is a typical characteristic of the sintered agglomerate powder mixtures. Furthermore, bimodal mixtures showed a combination of fine powder agglomerates of nanostructured WC-Co and spherical particles, near in shape to commercial powder. VC powder shows a smaller particle size in relation to the commercial and nanostructured powders.

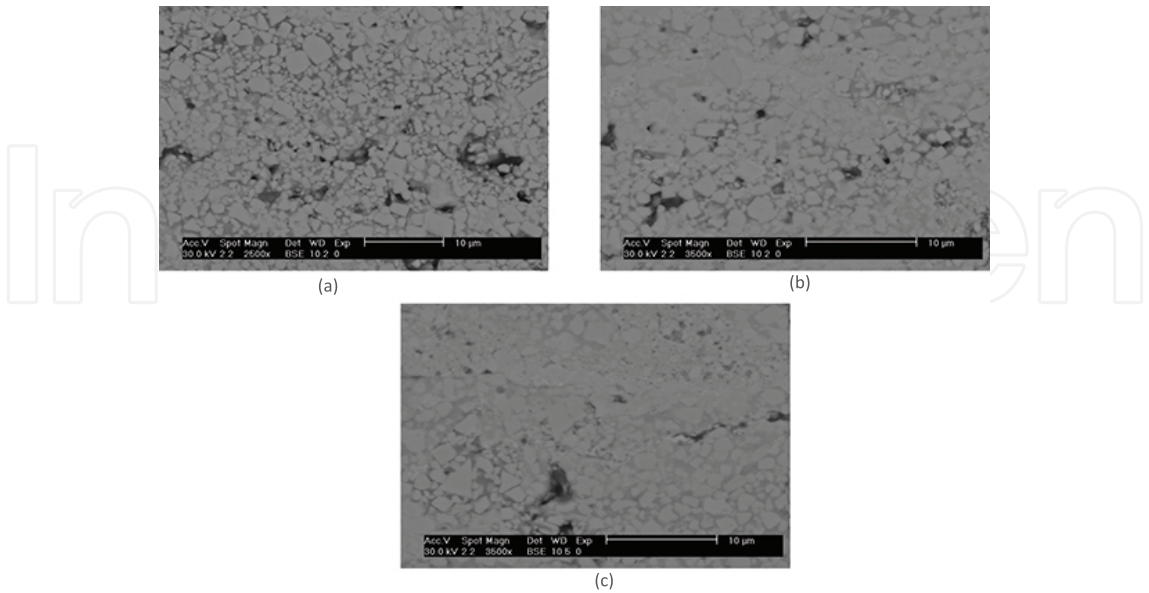
The microstructure of the three-alloy powder obtained by thermal spraying coatings is shown in **Figure 5**. From the BSE micrographs, it can be observed that the microstructure of the three coatings are typical of WC-Co coatings with WC islands, having different size distribution are embedded in a cobalt matrix. As can be seen from **Figure 6**, the WC particles size distribution was similar to the three studied coatings. The characteristic feature of the observed coatings is the strong refinement of their microstructures. The coatings contained different phases, which can be distinguish by the diversification of the microstructure contrast. A good coatings adherence was observed. There are discontinuities between the substrate and coatings. The roughness of the substrate contributes to the better adhesion of deposited coatings and as it is necessary in the thermal coatings technologies. This result indicated that the deposited coatings have nanometric microstructure. Nanometric coatings were deposited by thermal spraying HVOF method, which confirms the possibility to apply nanostructured coatings by this technique [42]. The statistical analysis showed a slight influence of VC



additions on the final size of WC grains within the coatings, as a lower mean WC size was measured in VC-doped coatings compared to that found in the bimodal WC-Co coating. On the other hand, the calculated mean WC particle size for bimodal mixture was slightly higher than that of the commercial coating.

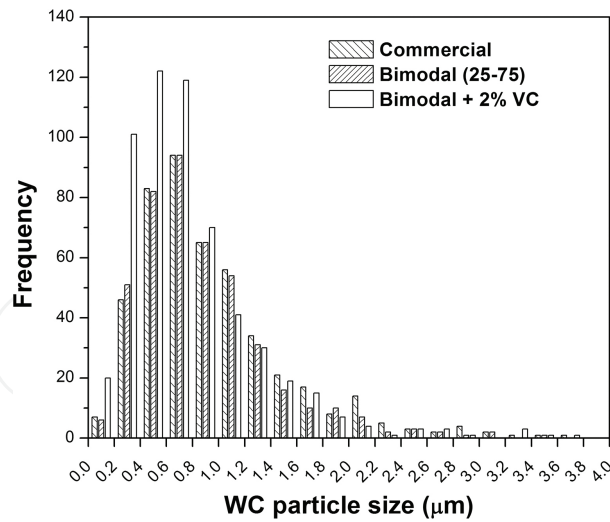


**Figure 4.** Micrographs of the starting powders, (a) nanostructured WC-Co after agglomeration, (b) WC-Co commercial, (c) bimodal mixture and (d) VC powder.



**Figure 5.** Backscattered electron micrographs in coatings WC-12Co, (a) commercial, (b) bimodal and (c) bimodal mixture + 2wt% VC.





**Figure 6.** Particle size distribution of WC-Co coatings applied by HVOF.

The average porosity, oxide content, mean WC particle size, thickness and microhardness of the coatings are included in **Table 1**. The VC-doped and commercial coatings showed the highest levels of porosity, whereas the commercial alloy contained higher interface contamination and oxide contents than those found in bimodal mixture. Average microhardness levels of bimodal and VC-doped coatings were comparably higher than the microhardness measured in commercial samples. The thicknesses of all WC-Co coatings fell within allowable limits commonly accepted in the industry for the processing of OEM (Original Equipment Manufacturer) components and/or reconstruction of worn parts [43].

	Commercial alloy	Bimodal WC-12Co	Bimodal WC-12Co-(2% VC)
Thickness (μm)	154 ± 8	133 ± 6	99 ± 4
WC mean particle size (μm)*	1.1	1.5	1.2
Porosity (%)	4.4 ± 0.1	3.9 ± 0.1	4.6 ± 0.2
Oxide content (%)	0.27 ± 0.02	0.16 ± 0.02	0.19 ± 0.02
Interface contamination (%)	32.3 ± 1	21.1 ± 1	25.1 ± 4

All average values with standard error from 10 measurements.

\* From statistical analysis shown in **Figure 5**.

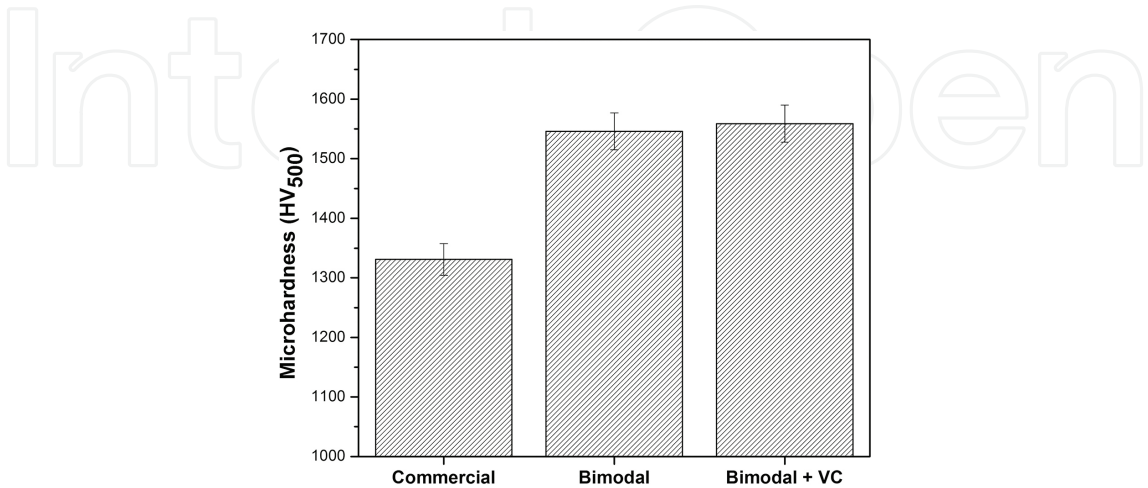
**Table 1.** Summary of properties from microstructure evaluation of coatings.

The morphology of the WC grains in all HVOF coatings processed in this work is less angular than that found in sintered WC-Co cermet, as already mentioned by different authors [39–44]. Although the coatings were processed from powders having different particle size distributions, the average particle size of WC in the final coating was similar. The effects of processing conditions of thermal spraying on the final microstructure of the coatings were the initial microstructure and size of the precursor particles of the WC-Co powders as key factors. This

can be attributed to the deposition conditions, which were the same for all processed samples. In all cases, a relationship 4.8 oxygen/propane was used in order to reach a temperature slightly lower than the maximum attainable ( $T_{\max}$ ), namely 2828°C, for a certain gas mixture using the relationship of 4.5  $O_2/C_3H_8$  [45]. Lower flame temperature than  $T_{\max}$  is preferred when nanostructured materials are processed, in order to preserve a fraction of the nanostructures in the coating; however, very low flame temperatures should be avoided since they result in coatings that contain high porosity. The oxygen/fuel used here resulted in samples with levels of porosity within the range reported for WC-Co coatings applied by HVOF [35, 46]. Coatings with addition of 2% of VC showed higher porosity compared to commercial coatings; this same behavior has been reported by Luyckx and Machio [39] when processed WC-Co coatings with VC additions. The commercial WC-Co coating contains the highest amount of oxides; this kind of contamination appears to have an important effect on the hardness and wear performance as shown by the commercial coating with lower hardness and higher wear rate than the whole coatings studied here. An optimization of the oxygen/fuel ratio, distance and transverse velocity spray gun has to be performed in order to find the conditions that may lead to reduced content of oxides.

4. Microhardness

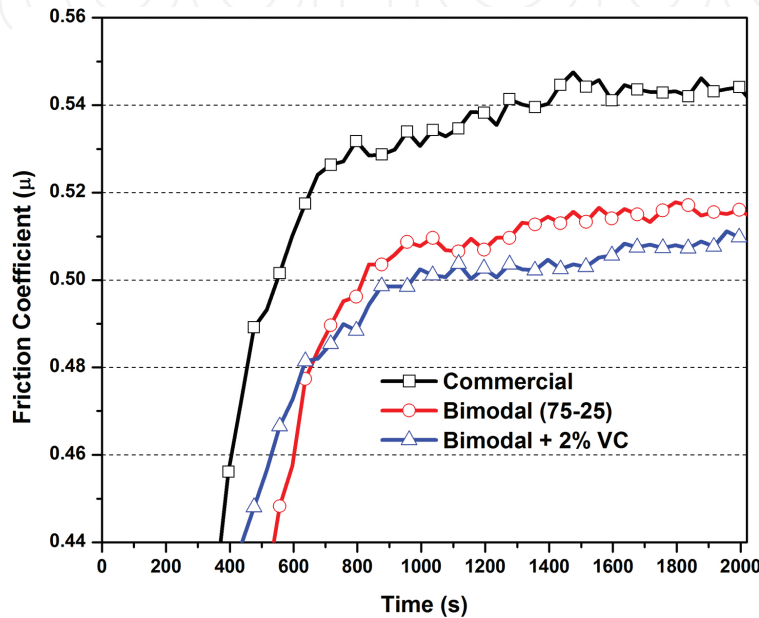
The microhardness of the three coatings obtained by thermal spraying is shown in **Figure 7**. The coating hardness is a key factor to optimize screening conditions and parameters, as well as comparisons between different deposited coatings. Bimodal WC-Co coatings and bimodal + 2% VC doped showed the highest hardness. These superior mechanical properties can be attributed to the bimodal structure of the tungsten carbides WC which provides a balanced amount of particles between micrometer sizes of WC and nano-sized particles of WC, where the latter being more prone to decarburization in the torch flame due to its high surface-to-volume ratio.



**Figure 7.** Microhardness of different coatings produced by HVOF.

## 5. Wear resistance

The variation of friction coefficient as a function of testing time from the Pin-on-Disc (POD) tests is included in **Figure 8**. When the steady state of wear conditions was reached by sliding in the POD testing set-up, the commercial coating showed greatest value ( $\mu \approx 0.54$ ), while the bimodal mixture added with 2% of VC coatings showed comparable levels of wear slightly lower ( $\mu \approx 0.48$ ) but still the lowest compared to the whole samples.



**Figure 8.** Friction coefficient as a function of testing time from POD test.

As final conclusion, the friction coefficient of bimodal WC-Co + 2% VC coatings was less than the commercial coatings. The addition of VC in bimodal coatings resulted in a slight increase in the mechanical and wear resistance properties. The same behavior is described by Guilemany et al. [25] for bimodal WC-Co coatings, who showed lower values of friction coefficient ( $\mu$ ) in nanostructured systems and in commercial, both with the same chemical composition. The wear resistance of WC-Co coatings can be explained by the limited amount of debris removed during the sliding wear tests, the nanostructured WC-Co coatings contain a lower volume fraction of cobalt than commercial coatings. Therefore, it has been shown in various studies that a bimodal particle size distribution of WC improves response to wear on WC-Co coatings use conditions without lubrication (Luyckx and Machio [39]). Therefore, this work shows that a combination of micro- and nanostructures is beneficial to improve the wear resistance of WC-Co coatings.

The major wear mechanism of the HVOF hard metal coating is connected with the gradual primary loss of the metal matrix from the areas between coatings hard particles, followed by the weakening of their particles and pulling them out of the coating surface. The design of the CSM Tribometer does not allow the wear debris to naturally fall off; they are trapped in the

wear track and serve as an abrasive medium. Then the mechanism of wear changes from sliding to abrasive wear [47, 48].

The wear mechanism of the cermet coatings is described as the contact between the pin and coatings-carbides, which are slightly protruding from the matrix due to grinding. Such conditions lead only to a very slight wear [49].

The wear resistance strongly depends on the smoothness of the coating surface [50, 51], which becomes better if the size of grains becomes smaller. From this point of view, the refinement of microstructure coating by thermal spraying has strong influence on their wear properties.

The dependence of wear resistant to the microhardness level implicates for searching other reasons of resistance against the wear of the deposited coatings. Some data suggest that the wear mechanisms depend on the roughness of the coating face [50, 51].

These results indirectly indicate that the wear resistance is a complicated mechanism and depends not only on the hardness but also on the state of the coating surface and its internal microstructure. Specifically it was found that the refinement of microstructure to a nanometric dimensions favorably influences the wear resistance.

## 6. Conclusion

As general conclusion, it can say to that the vanadium carbide additions to bimodal WC-Co deposited by HVOF make coatings that slightly increase the mechanical properties of microhardness with 15% and tribological properties decrease in friction coefficient to 0.48. Then, the obtained hardness in bimodal WC-Co coatings is primarily influenced by the reinforcing WC particles.

Other conclusions are as follows:

- There is slight influence of the VC additions on the final WC grain size present in coating. Nevertheless, the mean WC grain size doped with VC was shorter than the grain size in bimodal WC-Co coatings. On the other hand, the WC particle size in the bimodal mixture was slightly larger than that in commercial alloy coatings.
- The commercial WC-Co coating contains the highest amount of oxides; this kind of contamination appears to have an important effect on the reduction of hardness and wear performance.
- In microhardness, the bimodal WC-Co coatings and bimodal + 2% VC doped showed the highest hardness. These superior mechanical properties can be attributed to the bimodal structure of the tungsten carbides WC which provides a balanced amount of particles between micrometer sizes of WC and nano-sized particles of WC
- In steady state, the friction coefficient for commercial coatings is larger ( $\mu \approx 0.54$ ) than the bimodal mixtures + 2% of VC coating ( $\mu \approx 0.48$ ), being slightly lower the wear in the last one.

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