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SLIDING WEAR RESISTANCE OF THERMAL SPRAYED WC-12Co COATINGS REINFORCED WITH CARBON NANOTUBES

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Abstract

Thermal sprayed coatings based on WC-Co are widely used for providing wear resistance to engineering components. The High Velocity Oxygen Fuel (HVOF) thermal spraying technique is one of the most commonly employed for depositing wear resistant coatings on steel substrates and constitutes one of the coating processes that have been technically validated for the replacement of electrolytic hard chrome (EHC) coatings, especially for extreme operating conditions. The present work aims at studying the tribological behavior, under sliding wear conditions, of a coating based on WC-12Co, with and without the reinforcement of carbon nanotubes (CNTs). The coating has been deposited by HVOF thermal spraying on a SAE 1045 substrate steel. Wear tests were carried out under the ball-on-disk configuration, at a constant sliding velocity of ~ 0.2 $m.s^{-1}$ and an applied load of 10 N, employing WC-6Co balls as static counterparts. The results for the CNTs reinforced coating have shown a decrease of ~ 58% and 86% in the values of the average friction coefficient and wear rate, respectively, as compared with the conventional coatings. The observed wear mechanism was mainly of an abrasive type.

Keywords: Thermal sprayed coatings, WC-Co, carbon nanotubes, sliding wear

1. Introduction

Although WC-based thermal sprayed coatings have been extensively studied, they are still widely investigated particularly in relation to the optimization of properties in applications that require good wear resistance for the replacement of EHC coatings [Bolelli et al., 2015; Nascimento et al. (2001); Koon et al. (1999); Hazra et al. (2012); Agüero et al. (2011)]. These researchers have evaluated different coatings based on the WC-Co and WC-Co-Cr systems under ball-on-disc sliding contact conditions and have found that their tribological performance is better than that of EHC coatings, whose wear coefficient is ~10^{-4} mm^3 /(Nm). Agüero et al. (2011), when testing the coatings based on WC-Co-Cr under a pin-on-disc configuration against static alumina counterparts, at a load of 10 N and 1000 m of sliding distance, could not observe any wear damage. On the other hand, Bolelli et al. (2015) studied similar coatings of WC-10Co-4Cr on a pin-on-disc tribometer, under

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a load of 10 N, 0.1 m/s of sliding speed and 5000 m distance against an alumina counterpart. They reported mild wear rates of < 10^{-7} $mm^3/(Nm)$ and friction coefficients of ≈ 0.5 and concluded that WC-10Co-4Cr coatings outperform the reference EHC coating under these testing conditions. The wear mechanisms found included extrusion and removal of the binder matrix, with the formation of a wavy surface morphology, as well as brittle cracking.

WC-12Co coatings have a lower hardness and higher toughness than WC-10Co-4Cr coatings [Santana et al. (2011)]. The latter have been extensively studied in sliding wear by different authors [Bolelli et al. (2015), Liu et al. (2016), Agüero et al. (2011)]. According to Kim et al. (1986) the contact severity in these coatings is inversely proportional to their fracture toughness. Therefore, if the fracture toughness of these thermal sprayed coatings increases, the wear resistance is also expected to increase. In this sense, Zhang et al. (2004) reported an increase of 17% in hardness and 35% in fracture toughness of WC-Co coatings doped with CNTs deposited by a spark plasma sintering technique. These results were explained by the bonding enhancement of CNTs to the matrix, which resulted in an increase of the metal-ceramic interface strength.

Additionally, Rodríguez et al. (2014) carried out dry sand rubber tests on WC-12Co coatings doped CNTs and studied the effect of the dispersion time on the microstructure and three body abrasive wear resistance. The doped coatings were obtained by mixing 0.35 wt.% CNTs with WC-12% Co micrometric powders. Mixing was carried out in a jar mill with an ethanol solution for four different times (24, 36, 48 and 72 h). Subsequently, the coatings were deposited by HVOF on steel substrates. The experimental results showed that a milling time of 36 hours was the most adequate to disperse the CNTs within the WC-Co powders, since it give rise to coatings with higher hardness values, less porosity and an increase in the abrasive wear resistance of approximately 80% as compared to conventional coatings obtained in the same conditions.

Based on the study carried out by Rodríguez et al. (2014) and following their evaluation of the behavior of CNTs reinforced WC-12Co coatings, in this work, the characterization of the wear performance of these materials, employing a more severe wear test, is proposed. For this purpose, a ball-on-disc tribometer is employed for testing CNTs doped WC-12Co coatings milled during 36 h. The results are then compared with the performance of coatings obtained both by using WC-12Co powders without CNTs, subjected to the same milling time, as well as coatings produced by conventional HVOF process.

2. Experimental procedure

The WC-12Co-based coatings were industrially deposited by Plasmatec C. A., Venezuela, on SAE 1045 steel substrates by means of HVOF. The deposition procedure has been described elsewhere [Rodríguez et al. (2014)]. In the present research, only three types of specimens were employed: a) WC-12Co powders mixed with 0.35 wt% of multiwall CNTs and 36 hours of milling time, referred to in the forthcoming as the c-CNTs-36h condition. b) WC-12Co powders subjected to 36 hours of milling time, referred to as the c-36h condition and c) the original powder without CNTs and milling time, referred to as the WC-12Co condition. The original powder has a nominal particle size of 45 ± 15 µm, whereas the multiwall CNTs, with 95% purity, have a nominal diameter in the range of 20-40 nm.

Prior to the wear tests and their microstructural characterization, the samples were prepared metallographically following the sequence established by the Struers (2008). The porosity of the coatings was determined by means of image analysis of 20 fields for each coating, employing an optical microscope. The coatings were subsequently characterized using scanning electron microscopy (SEM) and optical microscopy (OM) in order to evaluate their thickness, as well as the distribution and morphology of the different phases and pores.

Instrumented indentation tests were conducted on a CSM microhardness tester by applying a maximum load varying between 100 to 3000 mN, during 15 s of dwell time and using a Berkovich indenter. The results were analyzed by employing the Oliver and Pharr´s method [Oliver and Pharr (2004)]. Additionally, the Vickers hardness of the coatings was also determined employing a load of 300 g.

The maximum contact pressure ($P_{\max}$) was determined using the approach proposed by Hertz (1882) as

$$p_{\max} = \left\{ \frac{6WE^{*2}}{R^2 \pi^3} \right\}^{1/3} \quad (1)$$

Where W is the normal load, R is the contact radius of the ball, and E^* is the reduced contact modulus given by

$$\frac{1}{E^*} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \quad (2)$$

In equation (2), the values for E_1 and ν_1 represent to coating elastic modulus and Poisson’s ratio, respectively. Similarly, E_2 and ν_2 represent the elastic properties of the static counterpart. In the present work, it has been assumed that $\nu_1 = \nu_2 = 0.25$. E_1 was determined by means of instrumented indentation and $E_2 = 575$ GPa.

The tribological study of the coatings was performed using sliding wear tests under a ball-on-disc configuration according to the ASTM G 99-05 standard [ASTM (2005)]. The tests on the coated samples were run at ~ 25°C and ~ 70% relative humidity. The normal load applied was of 10 N for a sliding distance of 5000 m, at a linear sliding speed of ~ 0.2 $m.s^{-1}$. The static counterparts used were WC-6%Co balls 6 mm in diameter. The wear volumes of the coated samples were determined by means of a Veeco Wyko NT9300 optical profilometer. On the other hand, the wear volume of the static counterparts was also determined according to ASTM G 99-05 standard [ASTM (2005)]. The wear constant (k) was obtained by means of the Archard equation [Rong (2001)] and the wear mechanisms were evaluated by employing SEM techniques.

3. Results and Discussion

The coatings thickness were of 453 ± 5, 556 ± 35 and 652 ± 28 μm for the WC-12Co, c-36h and c-CNTs-36h, respectively. In Figures 1a through c it can be clearly observed that the incorporation of the CNTs gives rise to a decrease in the coating porosity. The apparent porosity values of the different coatings under investigation are presented in Table 1. The c-CNTs-36h coating has a porosity of ~0.5%, which is 55% less than that of the conventional coating and 19% less than the c-36h coating. Although milling decreases the porosity by 19%, it can be stated that doping of the powders with CNTs is a more effective way to decrease the porosity of the coating due to the stronger bonds that are established between the WC particles. Similar results have also been reported by Zhang et al. (2004).

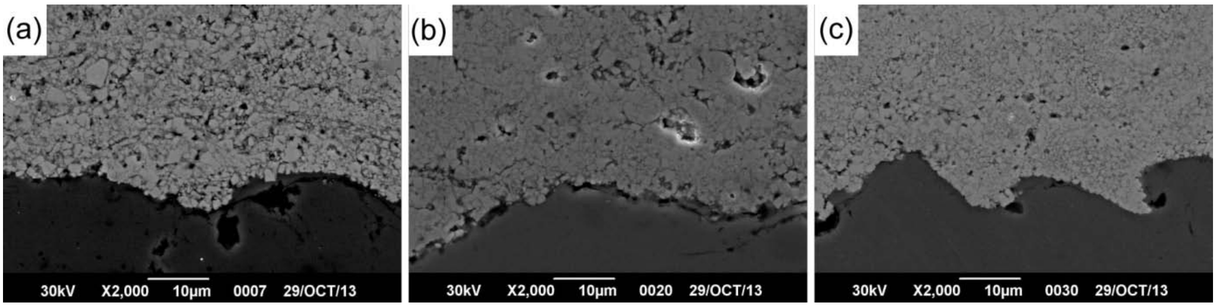


Figure 1. SEM photomicrographs of transversal section of the coatings: a) c-CNTs-36h; b) c-36h and c) WC-12Co.

The variation of the friction coefficient (μ) as a function of the sliding distance during the wear tests for the different coatings is presented in Figure 2. It can be observed that both the milling operation and the incorporation of CNTs gives rise to a considerable decrease in the average friction coefficient value, to ~0.25, as compared to the WC-12Co coating condition, whose average friction coefficient is of ~0.6. Nevertheless, milling was also observed to have a considerable influence in the friction behavior, since a drop in the average friction coefficient of to a magnitude of ~0.31 was achieved.

The fluctuations observed for all the friction coefficients curves are due to the formation of debris particles (mainly carbides) in the contact and their subsequent evacuation. In general, steady state is more rapidly achieved for the samples which contain CNTs and / or have been processed by milling.

Figures 3 through 5 illustrate the wear tracks morphologies corresponding to the different coatings. It can be observed that all tracks exhibit visible parallel scratches in the sliding direction, which suggest the abrasive effect of the WC-6Co counterpart. Also, the debris produced during the sliding contact remains in the wear track and therefore, these contribute to an increase in the coating damage due to a three body abrasion mechanism [Bonache et al. (2011)]. As shown in Figures 4 and 5, this phenomenon is more accentuated for the c-36h and WC-12Co coatings, respectively. However, it can also be noticed that the amount of carbide particles that have been detached and that are found in the wear track of the WC-Co sample is much greater than that corresponding to c-36h coating sample. As expected, the largest wear track is found for the static counterpart that was in contact with the WC-12Co coating sample, as can be observed by comparing Figures 3d, 4d and 5d.

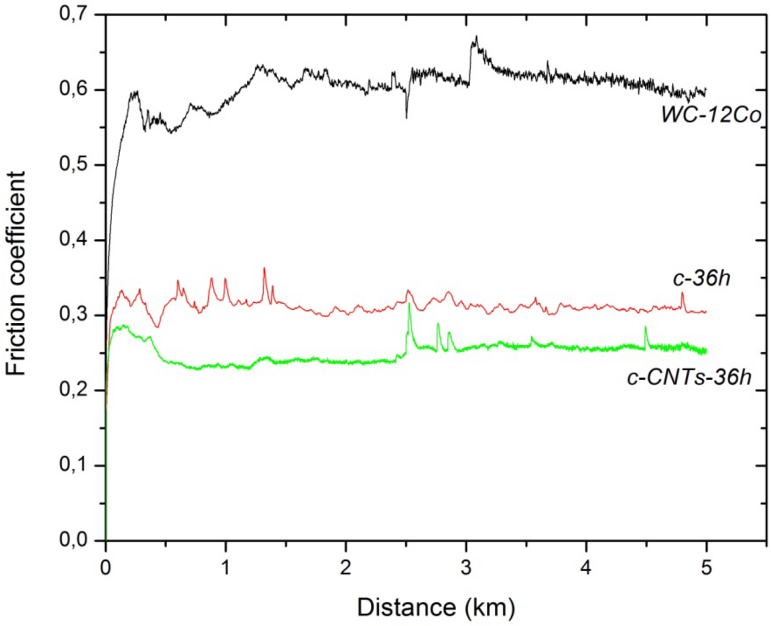


Figure 2. Variation of the friction coefficient with sliding distance for the different samples under study.

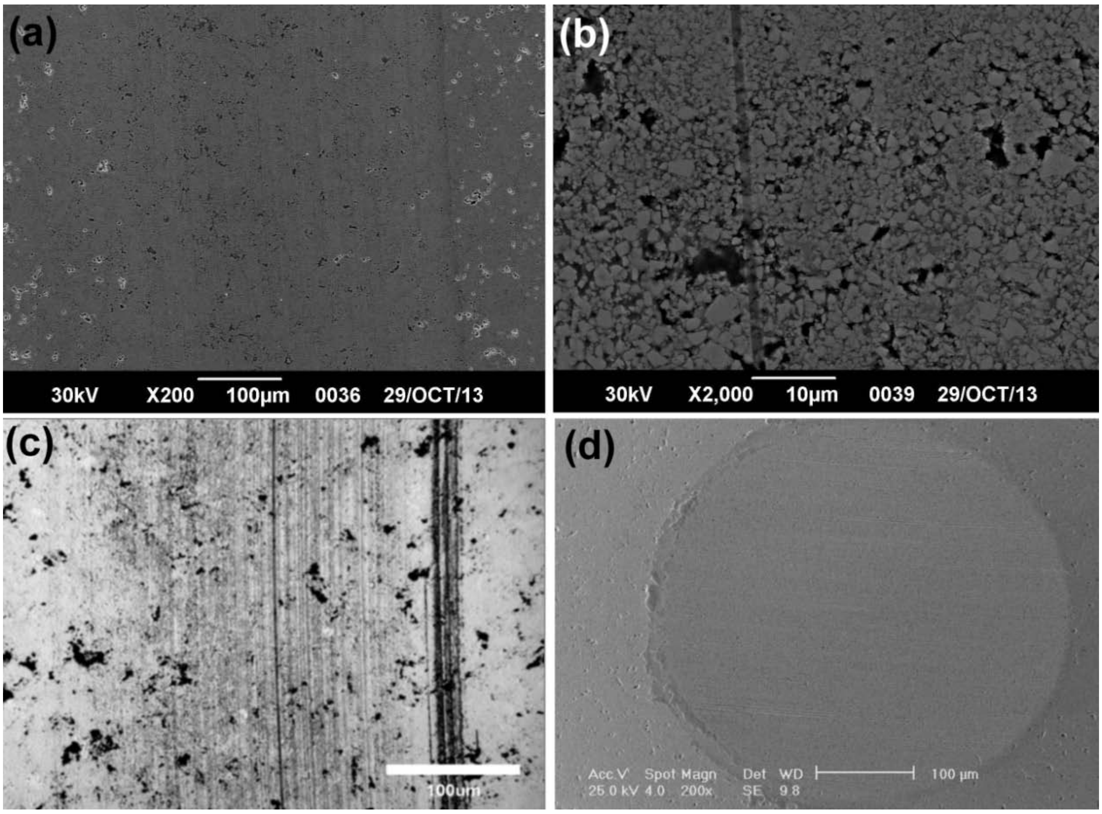
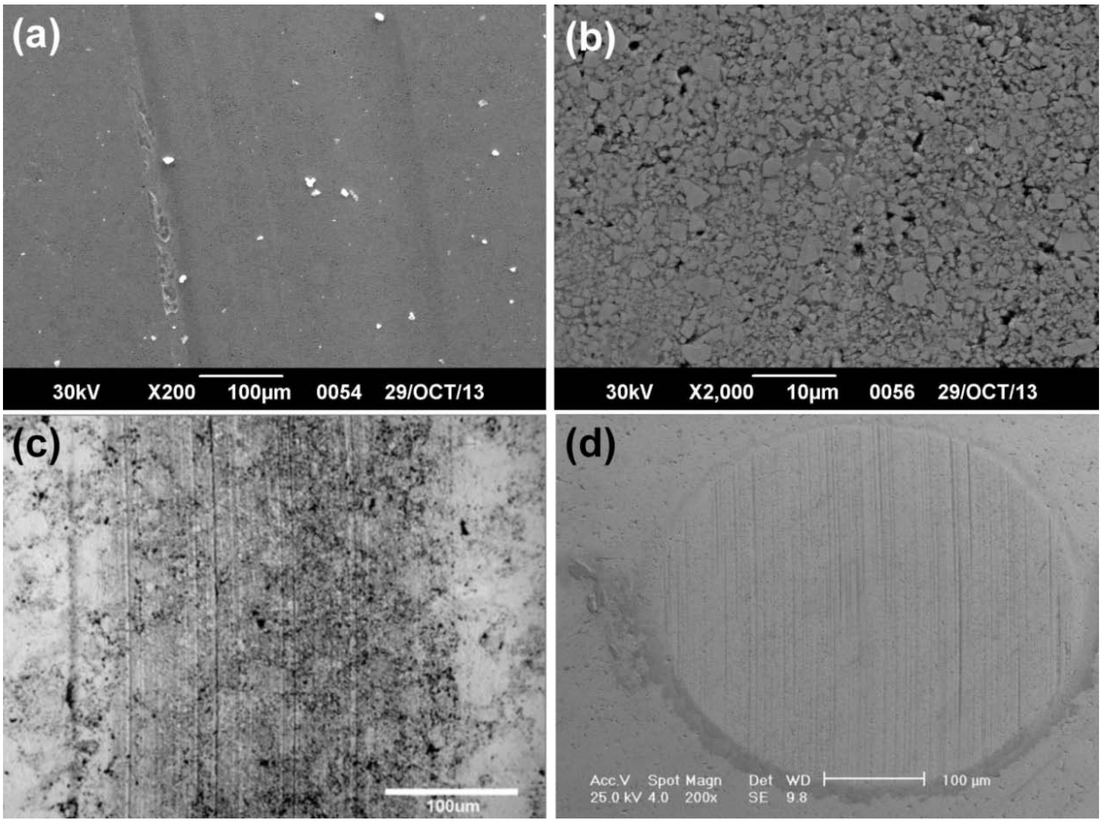


Figure 3. (a) and (b) SEM photomicrographs illustrating the wear track morphology corresponding to the c-CNTs-36h coating. (c) Optical micrograph of the wear track (d) SEM morphology of the WC-6Co counterpart.



Figures 4 (a) and (b), SEM photomicrographs illustrating the wear track morphology corresponding to the c-36h coating. (c) Optical micrograph of the wear track. (d) SEM morphology of the WC-6Co counterpart.

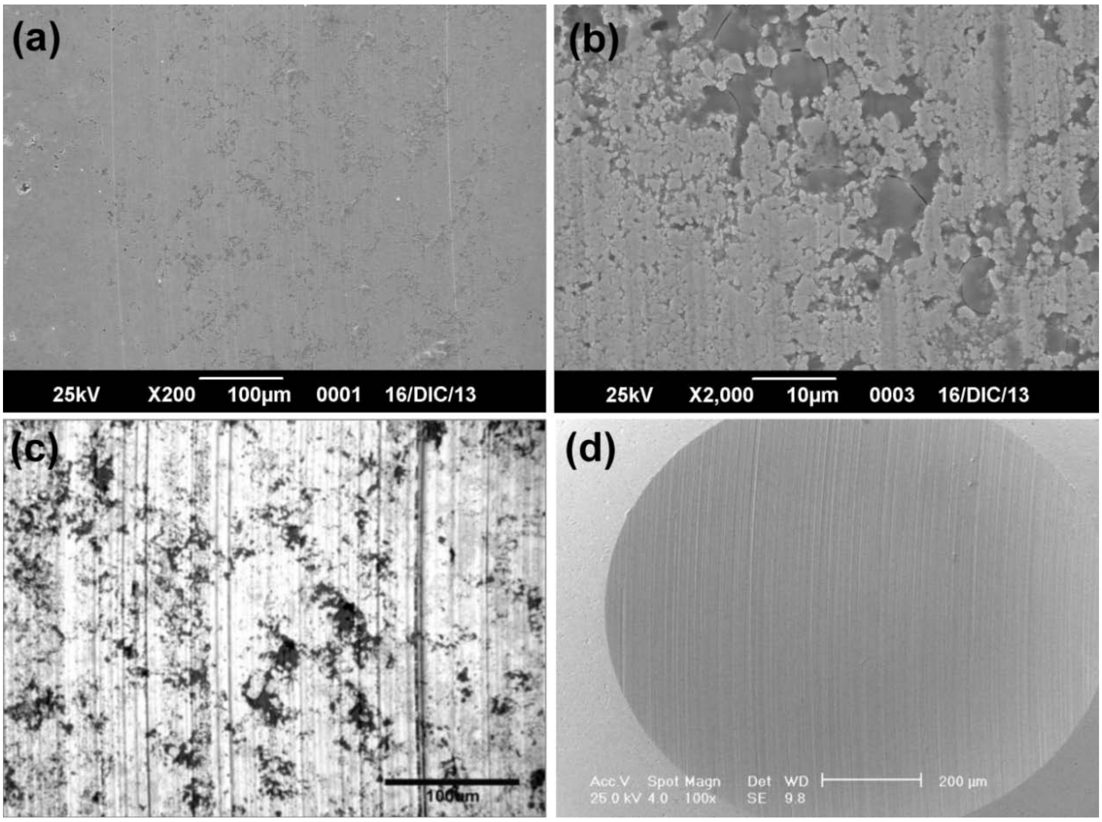


Figure 5 (a) and (b), SEM photomicrographs illustrating the wear track morphology corresponding to the WC-12Co coating. (c) Optical micrograph of the wear track. (d) SEM morphology of the WC-6Co counterpart.

Table 1 summarizes the results of the sliding wear tests, which include the worn volume (*V*) and wear constant "*k*" for each coating, as well as the maximum Hertzian contact pressure, Vickers hardness and elastic modulus. As can be observed, the wear volume and wear rate corresponding to c-CNTs-36h coating were approximately 32% and 87% less than those corresponding to the c-36h and WC- 12Co coatings, respectively. A wear rate of approximately 10^{-6} $mm^3/(Nm)$ was determined for the different coatings. According to Kato and Adhachi (2002) a wear volume of this magnitude indicates the predominance of a severe wear mode for these testing conditions.

In addition, Table 1 presents both the wear volumes and wear constants of the counterparts. Accordingly, the smallest wear occurred for the counterpart in contact with the c-CNTs-36h coating. These results indicate that both milling and the addition of CNTs have a positive effect on the wear resistance of the coated system. Another interesting feature of the investigated coatings is that both milling and the addition of CNTs give rise to an increase in P_{max} due to the increase in the coating elastic modulus. As can be seen from Table 1, the c-CNTs-36h coating exhibits the greatest P_{max} value, which indicates that the addition of CNTs to the WC-12Co powders could also give rise to an increase in contact severity as a consequence of the increase in the E value. However, as indicated by Zhang et al. (2004), the addition of CNTs could also give rise to an increase in the fracture toughness of the coating, which would counterbalance the increase in P_{max} and therefore, reduce the contact severity.

Table 1. Sliding wear results

CONDITION	***V (mm³)***	***k* mm³/(N.m)**	**P_{max} (MPa)**	***Hv* (GPa)**	***E* (GPa)**	**Porosity (%)**	***μ***
c-CNTs-36h	$1.21x10^{-6} \pm 3.49x10^{-7}$	$0.24x10^{-10} \pm 6.98x10^{-12}$	2564	15 ± 0.8	485	0.54 ± 0.18	0.25 ± 0.01
c-36h	$1.77x10^{-6} \pm 1.27x10^{-7}$	$0.36x10^{-10} \pm 2.55x10^{-12}$	2270	14 ± 0.6	354	0.92 ± 0.15	0.31 ± 0.01
WC-12%Co coating	$8.97x10^{-6} \pm 1.98x10^{-6}$	$1.79x10^{-10} \pm 3.96x10^{-11}$	1949	12 ± 0.5	392	1.11 ± 0.15	0.60 ± 0.04
WC Ball/c-CNTs-36h	$5,34x10^{-4} \pm 2,13x10^{-5}$	$1,07x10^{-8} \pm 4,26x10^{-10}$					
WC Ball/c-36h	$5,48x10^{-4} \pm 7,60x10^{-5}$	$1,10x10^{-8} \pm 1,52x10^{-9}$					
WC Ball/WC-12Co	$1,84x10^{-2} \pm 1,01x10^{-3}$	$3,69x10^{-7} \pm 2,02x10^{-8}$					

4. Conclusions

Sliding wear tests conducted at room temperature against WC-6Co counterparts allowed the determination of a wear rate of the order of 10^{-6} mm^3 / (Nm) and a friction coefficient of ~ 0.25 for a WC-12Co coating reinforced by CNTs. The value of the wear rate was found to be 87% less than that of the WC-12Co conventional coating and 32% less than that of the WC-12Co coating obtained from milled powders. The predominant wear mechanism observed in all coated samples against the static WC-6Co counterparts was mainly of the abrasive type. The static counterparts used in the different tests presented values of a higher wear constant that are in the range of 10^{-8} to 10^{-7} $mm^3/(Nm)$. The improvement in the wear behavior of the coatings reinforced by CNTs could be attributed to their intrinsic characteristics such as relatively lower porosity, higher hardness and possibly higher fracture toughness, in comparison with the conventional coating.

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