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MANUFACTURING NANOCOMPOSITE COATINGS AND WEAR EVALUATION IN CERMETS

Matheus A. DA CUNHA[1], Waleska C. GUAGLIANONI[1], Bruno F.A. BEZERRA[1], Felipe V. DE CAMARGO[1,2,*], Carlos P. BERGMANN[1]

[1]Federal University of Rio Grande do Sul, Porto Alegre, Brazil

[2]University of Bologna, Bologna, Italy

*Corresponding author: fevannucchi@gmail.com

Abstract: *This work investigates the wear rate of a cermet from a NiCr alloy that is added at 5 wt% to cobalt carbide. This carbide was milled for 3, 6 and 12 hours in a high energy mill to obtain different sizes of nanometer-scale crystallites, and high velocity oxygen fuel thermal spraying (HVOF) was used to deposit the coating onto a metal substrate. The feedstocks used to obtain the coating were characterized via morphology through scanning electron microscopy (SEM), crystallite size, and crystalline phases by X-ray diffraction (XRD) as well as particle size analysis. The coatings were evaluated for microstructure (optical microscope), Vickers hardness and thickness, and wear was performed by means of solid particle erosion and Ball-on-disc tests. The results showed that the crystallite size of WCCo significantly decreased in the first milling hours. The coatings milled for 3 hours and 12 hours showed a mass loss for the erosive test of approximately 50% less than the commercial coating at the 30° angle. For erosion, at 90° angle, the coating with lower mass loss was the compound milled for 3h. All cobalt carbide compositions displayed an improved behavior relative to that of samples made from the commercial feedstock.*

Keywords: *WCCo/NiCr coatings, Thermal spraying, Tribology, Wear, Erosion.*

1. INTRODUCTION

The preparation and modification of the surfaces of mechanical components that perform specific functions in an application, generally without significantly changing the dimensions of the components, are of great importance in the study of surface engineering. Surface engineering deals with the application of traditional or innovative technology to modify the properties of components and materials, creating a new composite material that combines the desirable characteristics of the surface and the base material in the same piece [1].

One way of modifying the properties of the surfaces is by depositing a coating using thermal spray techniques, which consists of a group of processes where metallic or non-metallic materials are sprayed in a molten or semi-molten condition on a prepared substrate forming a coating. The coating material may initially be in the form of powder, rod or wire and the formed coatings may be applied to provide wear resistance, electrical or thermal insulation or conductivity [2].

Several metallic and non-metallic alloys have been developed to be deposited through thermal sprinkling techniques. Cermet coatings consist of a mixture of a ductile metal

matrix that may be pure or in a blend composed of Ni, Cr or Co with WC or Cr_3C_2 particles dispersed within the metal matrix [3]. Nickel-based cermets are widely used industrially because of their superior mechanical strength as well as corrosion, erosion, and abrasion resistance. They are easy to manufacture, have lower production costs and the ability to coat substrates with any geometric design [4]. The wear resistance of the material is controlled by the proportion of carbide particles dispersed in the matrix, the carbide size and the hardness. These coatings require particles that can resist to wear. The best thermal deposition technique for coatings with these characteristics is HVOF spraying [5].

Most studies on WCCo coatings employ raw materials on traditional scales [6-8]. The literature does not present investigations on coatings that use nanostructured NiCr and WCCo together and in their composition. The performance of these coatings can be altered if one of these materials is used on the nanometer scale, in a way that the physical and mechanical properties of the materials become superior due to the high volumetric fraction of atoms present in the grain boundary due to the reduced size of the nanometer scale [9].

It is in this context that the present investigation is conducted, aiming to obtain raw materials based on WCCo/NiCr to constitute coatings through HVOF spraying and subsequent evaluation of the wear resistance in different techniques, thus pointing out optimal coating process parameters for the attainment of an enhanced performance of the composite against wear.

2. MATERIALS AND METHODS

The cermet consists of nickel-chromium (NiCr) and tungsten carbide-cobalt (WCCo) supplied by Sulzer Metco and sold commercially as Diamalloy 2001 and Woka 3652. Table 1 shows the chemical composition of these materials according to the manufacturer [10, 11].

The high energy milling of WCCo was performed with a planetary mill using tempered steel milling bowl and AISI 52100 steel spherical milling bodies that are 10 mm diameter. The milling speed was 450 rpm using ethyl alcohol to cover the system. The milling times ranged from 15 min to 12 hours. After this step, the sample was dried at 50°C [12].

Table 1. Chemical composition of NiCr (Diamalloy 2001 [10]) and WCCo (Woka 3652 [11])

Material	Composition (%)					
NiCr	**Ni**	**Cr**	**B**	**Si**	**C**	**Fe**
	Balance	17.0	3.5	4.0	1.0	4.0
WCCo	**W**	**Co**	**Cr**	**C**	**Fe**	**-**
	Balance	8.5-11.5	3.4-4.6	4.8-5.6	0.2	-

The morphological analysis of the powders was carried using a scanning electron microscope (SEM) with a tungsten filament, and the crystalline phases were characterized via X-Ray spectroscopy. The instrument was equipped with a graphite monochromator and Cu-Kα radiation (λ = 1.5406). Crystallite sizes of the tungsten carbide in commercial form and after milling were determined via XRD technique using the Scherrer equation (Eq. 1):

$$D = (k.\lambda)/\beta.\cos(\theta) \qquad (1)$$

where D is the average dimension of crystallites; K is the Scherrer constant (usually assumed to be 1); λ is the wavelength of the X-ray source; and β is the integral breadth of a reflection (in radians) located at 2θ.

The manufacture used 95 wt% NiCr with 5 wt% WCCo. The powders were in the commercial form, and the process used 3 milling times (3, 6, and 12 h). The samples were mixed and agglomerated with 10% polyvinyl acetate. The heat treatment occurred in a 600°C oven with an argon atmosphere for 3 hours.

The coating deposited on on AISI 310 stainless steel was obtained via HVOF. The deposition parameters [13] are 0.385 L/min of kerosene flow, 58.2 and 0.3 mm^3/h of oxygen and feed flow, respectively, 300 mm of spraying distance and a 4 inches nozzle.

The coatings were evaluated for their microstructure and microhardness after thermal deposition. Samples were cut in a cross section after which they were sanded and polished. The microstructure was analyzed with a camera-embedded microscope. The Vickers microhardness tests employed a 3 N load for 10 seconds. Five indentations were made in the matrix region and another 5 were made in the carbide region.

The erosive wear tests were based on ASTM G76-13 [14]. The tests were performed at room temperature with 600 grams of erodent mass (electrofused alumina) and erodent impact velocity in the coating was approximately 30 m/s. The incidence angles between the surface of the coating and the erodent evaluated were 30° and 90°. Wear was determined by the difference between the final mass and the initial mass of the parts.

The tribological test was performed with a tribometer, providing both the wear rate of the coating and the coefficient of friction between the parts. The ball-on-disc test was performed according to ASTM G99 [15]. Three tests were performed for each group to evaluate wear rate. The test was conducted with alumina spheres after applying loads of 10 N, 15 N and 20 N with a linear velocity of 3.0 cm/s (without lubricant) and a distance of 33 m [16].

The wear rate was obtained based on the volume removed from the coating surface after tribological testing, dividing the worn volume (obtained with a contact profile model) by the product of the applied load and the distance.

3. RESULTS

The reduction of crystallite size as a function of milling time is shown in Figure 1, where samples submitted to milling for a few minutes did not present significant changes in their crystallite size, but the greatest variations were obtained with samples at 3 and 6 hours. Carbide milled for 12 hours has a crystallite size that is very close to sample milled for 6 hours. This small variation might occur because the material reaches the saturation point of deformation of the crystalline lattice at the atomic level and because of the increase in the density of defects in the crystalline lattice – a characteristic feature of the high energy milling process [17]. A recovery phenomenon can also occur during long milling times, where the density of defects in the crystalline lattice is reduced [18].

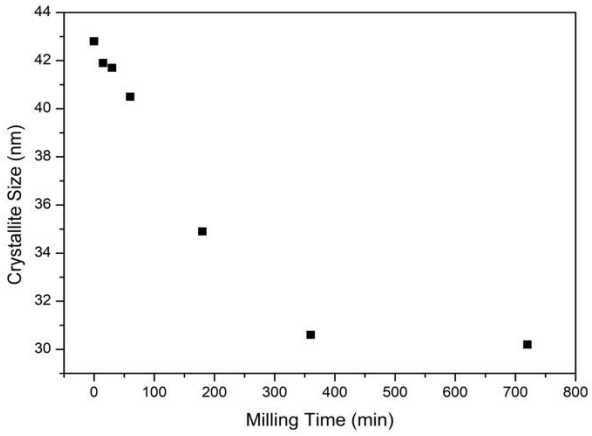


Figure 1. Crystallite size of WCCo as a function of milling time

Different crystallite size values can be found in similar studies when using distinct weight ratio of milling bodies to powder [17], or due to different milling rotation speeds [19].

XRD analysis did not show new phases even after milling. However, it is possible to see in Figure 2 that grinding broadened the diffraction peaks of the carbides. The crystallite size is refined and the internal strain has increased as a result of this enlargement.

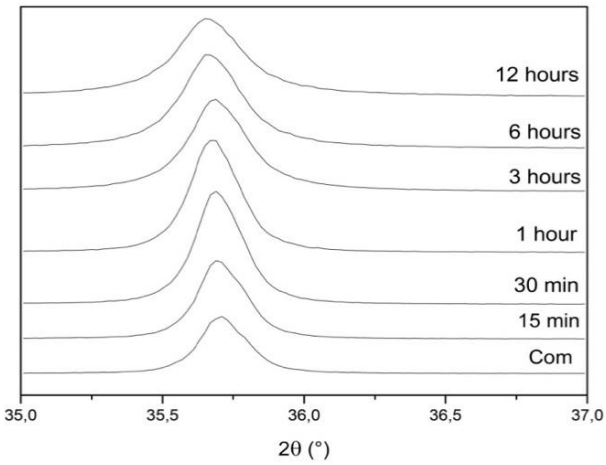
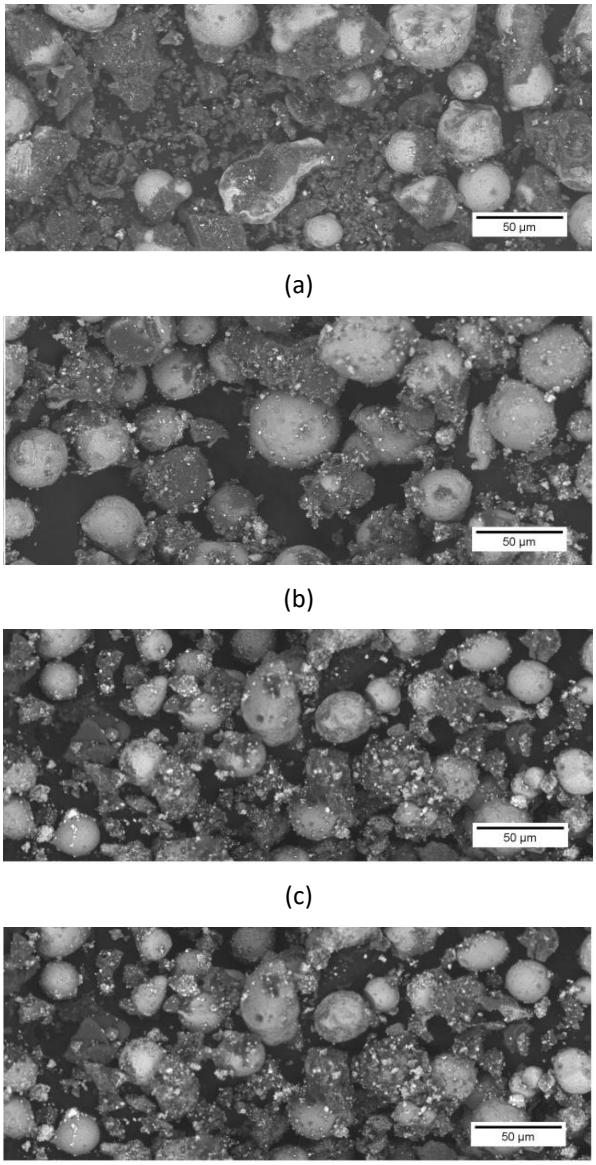


Figure 2. X-ray diffraction patterns of the first peaks of the commercial WCCo samples after different grinding times

The amplification of the diffraction peaks of carbide with increasing grinding time indicates a reduction of the crystallite size [20]. The peak shifted to the left suggesting insertion of tensile stress in the crystalline structure [21]. This behavior has been seen by other researchers using low [22] and long grinding times [17].

Figure 3a to 3d show scanning electron microscope (SEM) images upon addition of 5% WCCo to the NiCr alloy, illustrating that most of the ground fraction adhered to the surface of the NiCr alloy.



(a)

(b)

(c)

(d)

Figure 3. WCCo-NiCr with 5% WCCo (500x): commercial (a); with WCCo grinding for 3 hours (b); 6 hours (c); and 12 hours (d)

Figure 4a to 4d show the microstructure of coatings obtained by thermal spraying for all 5 % WCCo/NiCr samples. The coating layer is formed with NiCr (light part of the images) and carbides (dark regions). The coatings made with WCCo milled for 6 and 12 hours showed relatively greater thickness than the other samples. The coatings formed via carbide grinding for 3 hours or for 12 hours showed more dispersed carbides in the metal matrix.

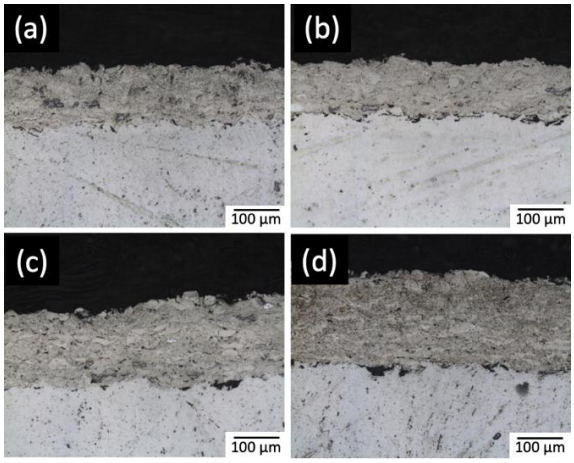


Figure 4. Microstructure of the cross section of the WCCo-NiCr alloy coating with 5% WCCo (200x): commercial (a); with WCCo processed for 3 hours (b); for 6 hours (c); and for 12 hours (d)

The average thicknesses for coatings obtained by HVOF with 5% WCCo added to the NiCr were measured 5 times along two pieces of each coating. The commercial coating and the ones with WCCo milled for 3, 6 and 12 hours had, respectively, 130 ± 12, 134 ± 8, 206 ± 7 and 194 ± 9 mm.

The microhardness measurements were performed in the matrix and the carbides regions. The average values for commercial coating and the ones with WCCo milled for 3, 6 and 12 hours had, respectively, are 423 ± 7, 403 ± 8, 406 ± 7 and 409 ± 4 HV for the matrix, and 876 ± 22, 637 ± 11, 823 ± 14 and 598 ± 12 HV for the carbide.

Figure 5a shows that the presence of small grains and the well-defined shape of the four indentation edges are observed in the indentation region in the point with the highest microhardness value (823 HV) for the coating. On the other hand, Figure 5b shows the indentation performed in the region of the matrix of the coating formed with WCCo for 3 hours. The microhardness value (403 HV) indicates that this region of the coating is

more ductile. The indentation has elongated diagonals, which validates the lower hardness value of the coating. Similar hardness results were attained by other researchers [23].

Table 2 shows the mass loss for the erosion test of coatings obtained with 5% WCCo and the results of the wear rate obtained with the ball-on-disc test with normal loads of 10 N, 15 N and 20 N.

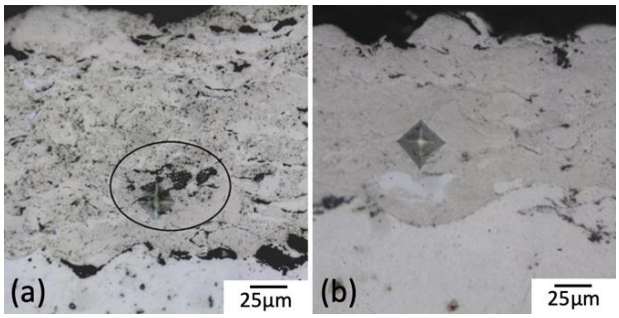


Figure 5. (a) Indentation in the carbide region for the WCCo-NiCr alloy with 5% WCCo grinding for 6 hours (500x); and (b) on the matrix for coating WCCo-NiCr with 5% WCCo grinding for 3 hours (500x)

Table 2. Erosive wear (at 30 ° and 90 °) and tribological tests for normal loads of 10 N, 15 N and 20 N in coatings with 5 wt% WCCo in different sizes of crystallites

Wear		5% WCCo comm.	5% WCCo (3 h)	5% WCCo (6 h)	5% WCCo (12 h)
Erosion (g)	30°	0.102 ± 0.004	0.052 ± 0.002	0.086 ± 0.019	0.052 ± 0.002
	90°	0.068 ± 0.007	0.065 ± 0.011	0.079 ± 0.007	0.091 ± 0.002
Tribology (mm^3/Nm)	10 N	1.73 ± 0.44	1.09 ± 0.15	1.51 ± 0.16	1.10 ± 0.14
	15 N	1.32 ± 0.29	0.91 ± 0.29	1.18 ± 0.12	0.70 ± 0.17
	20 N	2.33 ± 0.19	1.73 ± 0.17	1.26 ± 0.21	0.95 ± 0.21

In tests conducted at an angle of 30°, the coatings obtained with grinded WCCo had less mass loss than the ones with commercial WCCo. The coatings composed of WCCo grinded for 3 and 12 hours showed similar performance and 50% lower mass loss than the commercial coating, because the second had a smaller crystallite size.

The coatings formed with commercial WCCo and milled 6 hours presented higher erosive wear at 30° than at 90°, showing ductile material behavior. On the other hand, the coatings with WCCo milled for 3 and 12 hours demonstrated greater mass loss at 90°, indicating a fragile behavior. Rateick et al. [24] studied the mechanism present in the erosive wear of a cermet WC-Co, observing that the fragile and ductile nature of WC-Co cermets (rigid carbides embedded in a soft matrix) make it difficult to predict the effect of erodent particles and the impact angle on the erosion rate and the erosion mechanism, once results showed both weak and fragile responses.

The smaller erosions at 30° after 3 and 12 hours of milling are attributed to the fact that the carbides are better dispersed in the NiCr matrix, which favors the endurance of the material under such impact angle.

It is possible to see that for all normal loads the commercial specimen presented the worst performance regarding resistance to wear due to the fact of presenting larger crystallite size. By analyzing only the results of the tests with a load of 20 N, it can be seen that the wear rate decreased as the size of the crystallite decreased and consequently the coating containing the carbide benefited for 12 hours obtained the lowest rate of wear.

For the tests carried out with a normal load of 15 N, the coating containing the smallest crystallite size (WCCo 12 hours) also presented the highest resistance to wear. It can be seen that the tested coatings with WCCo milled for 3 hours and 6 hours showed a reversal in their wear resistance behavior, which can be attributed to better dispersion of the carbide in the coating providing a lower wear rate.

For the tests carried out with a load of 10 N it was observed that the coatings composed of carbides benefited for 3 and 12 hours had practically the same rate of wear, that is, the coatings were the most resistant to wear. Due to the better distribution of the carbides along the coating, the WCCo sample at 3 hours showed a lower wear rate than the other samples.

4. CONCLUSIONS

Coatings obtained with 5% WCCo milled for 3 hours and 12 hours showed the most dispersed carbides in their matrix. On the other hand, in coatings with 5% WCCo milled for 6 hours and in the commercial form, the carbides were observed in concentrated areas.

Erosive wear for a 30° angle of attack was higher for 5% WCCo milled for 6 hours and in the commercial form. At the same erodent impact angle, the 5% WCCo 3-hour-milled coating presented in the erosion test a 50% lower mass loss than the commercial coating, demonstrating that in order to improve the wear resistance of this coating, unduly long millings are dispensable.

The higher erosive wear at 30° than at 90° of coatings formed with commercial WCCo and milled 6 hours, demonstrates the predominantly ductile behavior of the material. Instead, when milled for 3 and 12 hours, greater mass losses are identified at 90°, indicating a fragile behavior.

Tribology ball-on-disc tests showed that coatings from 5% WCCo commercial had the highest wear rates independently of the loads applied. On the other hand, coatings that had 5% WCCo grinded for 12 hours had the lowest wear rate for normal loads of 15N and 20N and the carbide coating grinded for 3 hours obtained the lowest wear rate with a normal load of 10 N.

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