ASPECTS CONCERNING THE WEAR AND CORROSION BEHAVIOR OF WC-COCR COATINGS AND RESPECTIVELY DLC/WC-COCR SYSTEMS

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Abstract

Industrial branches are developing the best materials for their applications. An important part of surface engineering is represented by Physical Vapor Deposition (PVD) and Thermal Spraying techniques. The present work aims to investigate and compare the properties of multilayer coating systems obtained from PVD deposited Diamond-like Carbon (DLC) films on top of High Velocity Oxy-Fuel thermal sprayed WC-CoCr cermet interlayers to those of as-sprayed cermet coatings. In order to determine the coatings characteristics, the morphology, microstructure and chemical composition have been analyzed by means of Scanning Electron Microscopy combined with Energy-dispersive X-ray Spectroscopy (EDX). The EDX line-scan analysis confirms the existence of a gradient coating. The adhesion layer is a mixture of carbides, nitrides and carbonitrides. The presence of the cermet interlayer has several advantages like promoting adhesion to the metallic substrate and exhibiting a gradual distribution of the metal into ceramic, offering a better opportunity for the phase distribution of the top layer. Therefore, a further used method for the characterization of the cermet coating was X-ray diffraction. Several transformations in the phase content were observed and a decomposition of the ceramic phase was detected. The coefficient of friction, measured with a Pin-on-Disc Tribometer, stabilized quickly and remained constant for the WC-CoCr coating, whereas in the case of DLC/WC-CoCr it showed a lower steady state value with light fluctuations. Polarization measurements revealed a considerable dissolution of the metallic binder in the case of WC-CoCr coatings. Meanwhile, the DLC/WC-CoCr multilayer system performed significantly better under the same electrochemical testing conditions.

Keywords: DLC, WC-CoCr, HVOF, sputtering, multilayer coatings

1. INTRODUCTION

The industry is constantly looking for new and improved ways and materials to increase quality of tools and to reduce equipment and components degradation and damaging caused by wear and corrosion. As engineering applications become ever more demanding, the requirements for composite coatings that both protect the substrate, to retain its mechanical strength, but also to enhance the resistance of the substrate to wear and corrosion are increasing. The development of wear- and corrosion-resistant high-performance coatings is important to improve mobile and stationary components used in the automotive industry, turbines, aerospace, and food processing industry, medical implants, hydraulic modules and many others [1]. New micro- and nanostructured coating materials and processes to obtain these coatings are developed in order to increase the performance of work pieces and components, to enhance durability, and to reduce maintenance and manufacturing costs. To increase the wear, erosion, and corrosion resistance of tribologically stressed functional surfaces, the use of hard, high performance coatings increases rapidly.

PVD Magnetron Sputtering and HVOF thermal spraying surface engineering techniques have been applied successfully to deposit composite coatings with high density, superior bond strength, without the degradation of the substrate [2]. This is possible due to the "low" temperatures induced during the deposition process. One of these processes is the High-Velocity Oxygen Fuel (HVOF) thermal spraying. Based on the high particle velocity a low porosity, high bond strength, and an increased hardness are the main advantages of the thermal spraying process.

During the last decades, using of diamond-like carbon films (DLC) poses great interest, due to their outstanding properties, such as high hardness, thermal conductivity and wear resistance, high transparency in IR range, chemical inertness and biocompatibility [3, 4]. This unique combination of physical, chemical and mechanical properties makes them suitable for use in a wide range of technological and industrial applications, such as microelectronic, optical, biomedical applications, wear-resistant and protective overcoats [5, 6, 7].

The present work concentrates on analyzing the wear and corrosion behavior of WC-CoCr coatings and the multilayer Diamond-like Carbon/WC-CoCr systems.

2. EXPERIMENTAL PROCEDURE

According to the test condition requirements different types of specimen geometries have been chosen for the coatings deposition. Furthermore, in the case of friction investigations (pin on disc test) standard Almen strips made from C67 steel were used. Additionally, disc-like specimens (Ø 14mm) were necessary in order to perform the corrosion tests.

2.1. Feedstock powder and methods for characterization

The SEM micrograph represented in the **Figure 1a** is demonstrating the shape and size of the WC-Co-Cr 86-10-4 powder. On the right side, in the **Figure 1b**, the X-ray diffraction analysis confirmed the predominance of a large percentage of ceramic phase, 62 wt.% of WC. Additionally, a substantial amount of cobalt and tungsten containing subcarbides as Co_2W_4C, was also recorded for all the investigated powders. Therefore, it can be observed that the quantity of metallic Co became lower (~ 4 wt.%).

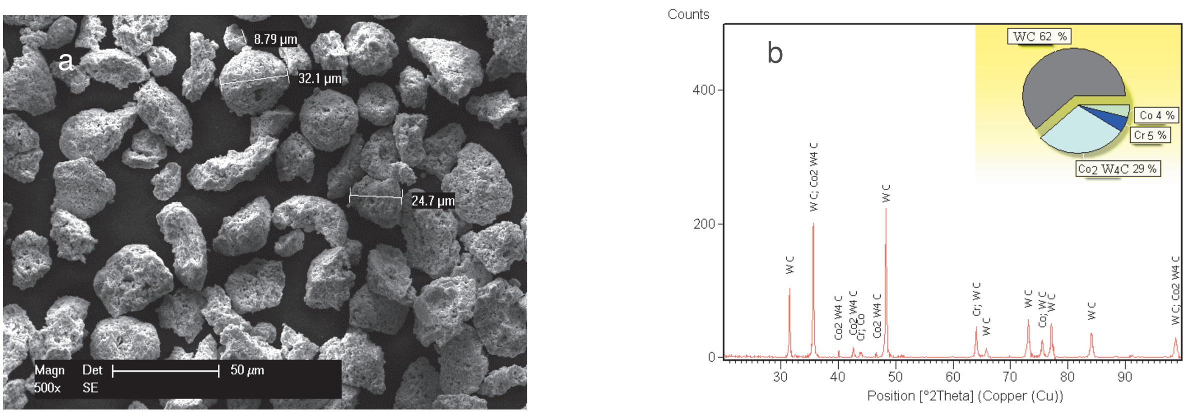

Figure 1 SE micrograph of the WC-CoCr powder (a) and its X-ray diffraction pattern (b)

This fact indicates that during the powder spheroidization a metallurgical reaction between Co and WC is created, diminishing thereby the content of the Co-phase and that of the WC phase as well. In terms of Cr content, the percentage detected by XRD corresponds with the theoretical one.

The characteristics of the obtained specimens were investigated by the means of Scanning Electron Microscopy (Philips XL 30 ESEM), using magnifications varying between 250x - 15000x, combined with Energy-dispersive X-ray spectroscopy (EDAX) and Light Microscopy (Leica DM-RME). The phase composition was determined by the means of X-ray diffraction measurements (Philips X'Pert).

2.2. Coating deposition processes

The commercially available agglomerated and sintered cermet powder from the industrial partner Thermico GmbH was used for the HVOF deposition. To obtain optimum adhesion between the sprayed layer and substrate, the substrate was degreased, grit-blasted and cleaned prior to the coating process obtaining roughness of approximately 3µm. Not to reduce the tensile adhesive strength due to oxidation or other environmental influences, the recently blasted component must be directly coated [8]. Feedstock powder from type WC-Co-Cr 86 10 4, with a granulometric fraction of -45 +20 µm was coated using a CJS gun. This powder is known to exhibit good wear resistance and high resistance against corrosion due to the ceramic phase [8].

The Unbalanced Magnetron Sputtered (UBMS) DLC films were deposited with the aid of a CemeCon CC800/9sinox ML PVD system on C45 steel discs. Field strength at the target surface is 0.065 T. Before the deposition target clearing by sputtering on the shutter was performed. The time, voltage and discharge current of UBM at clearing made 1 min, 470 V, 1.0 A, accordingly. As a working gas Ar was used at pressure in chamber of 0.1 Pa. Sputtering realized by UBM using as working gases Ar/CH_4 (99.98%) at common pressure in chamber 0.1- 0.2 Pa was performed in order to deposit the DLC coating.

2.3. Electrochemical and tribological tests

The electrochemical corrosion tests were carried out in 3.5% NaCl solution at room temperature with the aid of a potentionstat/galvanostat (VoltaLab PGP201). The applied potential was varied between -1000 and 1000 mV versus SCE (saturated calomel electrode) at a scan rate of 10 mV/min.

The friction tests were performed using a pin-on-disc arrangement (CSM Instruments TRIBOMETER). For all tests 6 mm WC-Co sintered ball was loaded against rotating C45 steel discs with a diameter of 40 mm and a thickness of 6 mm coated with the DLC/WC-CoCr multi-layer with a load of 10N. The sliding wear optimized parameters are presented in the **Table 1**.

Table 1 Pin-on-disc test parameters

Counterbody	normal load [N]	linear speed [cm/s]	rotational speed [rpm]	radius [mm]	stop condition [lap]	sliding distance [m]	test duration [s]
WC-Co ball	10	40	475	8	100 000	5040	12600

3. RESULTS AND DISCUSSIONS

As it is already known, the microstructure of an HVOF sprayed coating, represented in the **Figure 2**, is a complex mixture of lamellas formed from melted or semi-melted particles as well as from some irregularities. These types of coatings may typically contain oxides due to the oxidation of the particles in the hot flame and also some cracks due to the relaxation of residual stresses. It can be seen in the **Figure 2a** that the thickness of the coating is around 180 µm and in the **Figure 2b** that the size of the WC particles is between 450 nm and 1.2 µm respectively.

Three typical groups of porosity can be also in the **Figure 2** identified: interlamellar pores, interconnected pores and/or globular pores.

However, the XRD patterns, represented in the **Figure 3**, show a light transformation (~3%) of the WC-phase into the W_2C-phase, which normally by such coatings may occur more pronounced during the deposition process. A positive aspect, knowing that a high decomposition of WC leads to a fragile mixture of W_2C, WC and free carbon in the coating composition.

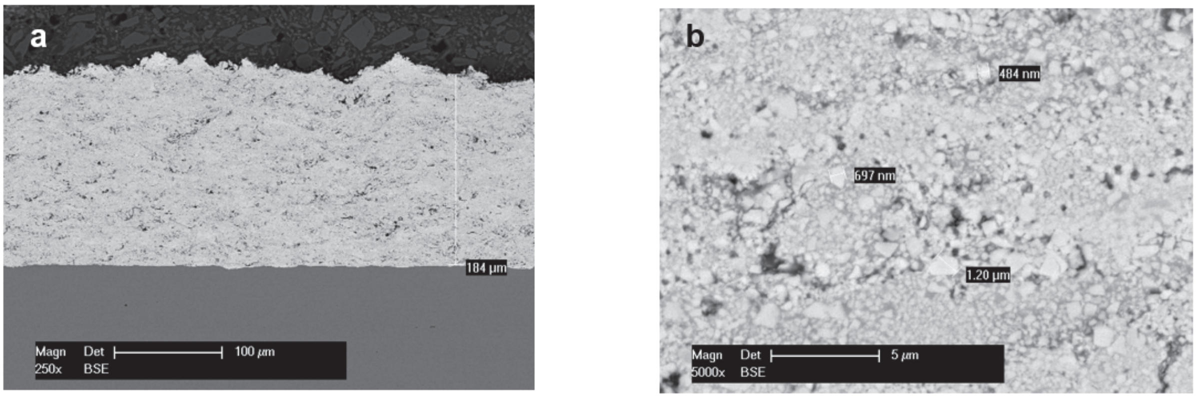

Figure 2 SEM micrographs of the as sprayed WC-CoCr coating as (a) overview and (b) size of the WC particles

The DLC/WC-CoCr multilayer coating systems were examined before the wear and corrosion tests by means of SEM and EDX analysis. The micrographs presented in the **Figure 4a** represent the fractured surface of the DLC/cermet layer system. The study of the DLC film at a higher magnification shows different grey levels, in that between the actual DLC layer and the cermet layer, there is a graded layer as the bonding layer.

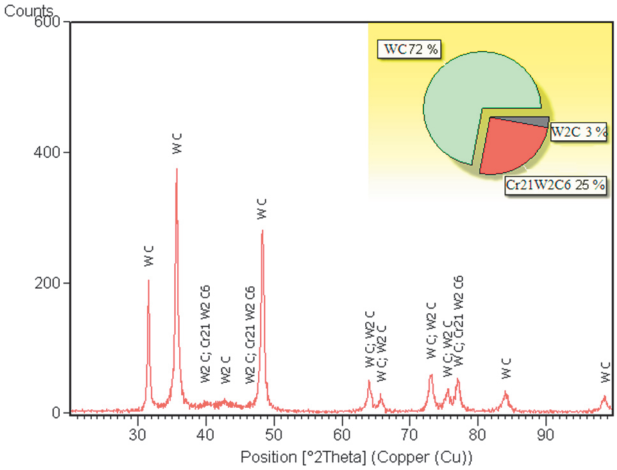

Figure 3 X-ray diffraction pattern of the WC-CoCr coating

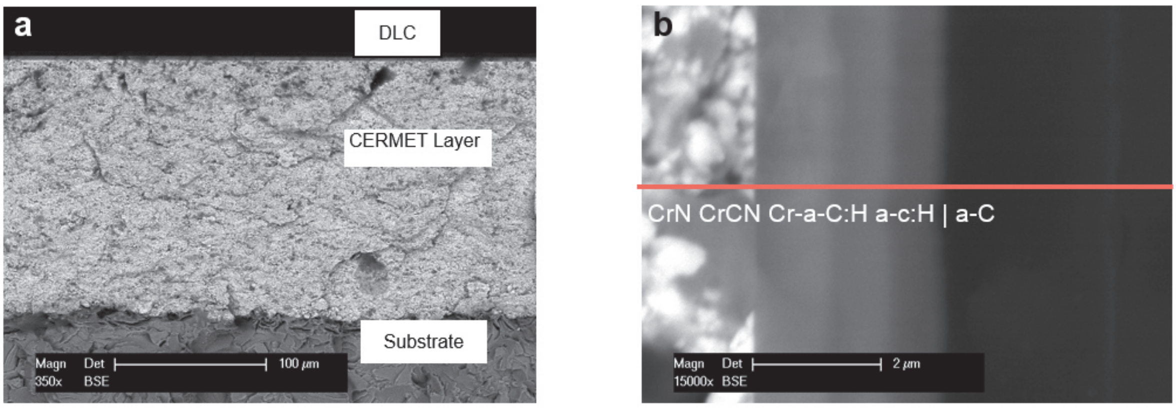

Figure 4 SEM micrographs of the cross-sectioned DLC/WC-CoCr coatings systems as (a) overview and of the (b) EDX line scan

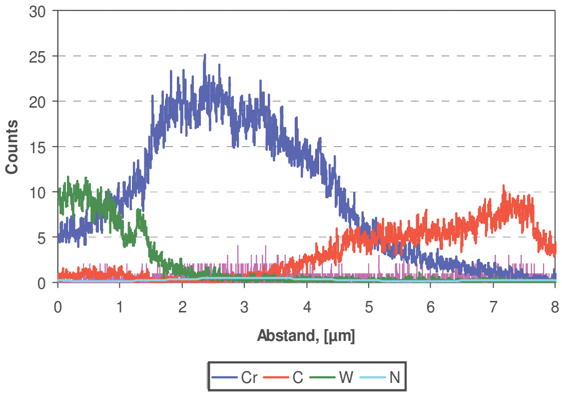

Figure 5 EDX line-scan of the DLC/WC-CoCr multi-layered coating

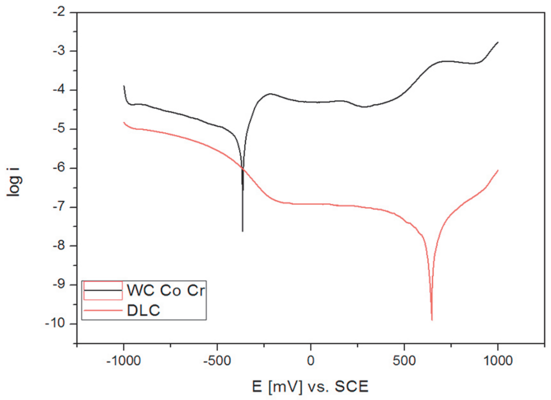

Figure 6 Tafel plots for WC-CoCr and DLC in 3.5% NaCl solution

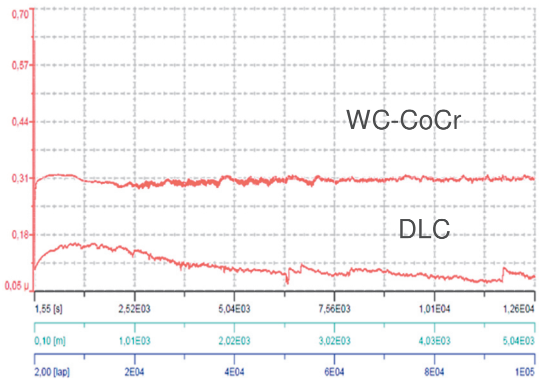

Figure 7 Friction coefficient of WC-CoCr and DLC coating

The EDX line-scan analysis, seen in the **Figure 5**, identified the presence of Cr, N and C in this area, a result which indicates a phase composition consisting of chromium carbides, chromium nitrides and chromium carbonitrides respectively. The line where the EDX scan was performed is represented in the **Figure 4b**. Regarding the corrosion, the **Figure 6** shows a comparison by overlaying the polarization curve of the WC-CoCr coating and the DLC/WC-CoCr coating respectively. As these investigated coatings have a complex composition, it can be mentioned that the possibility of micro-galvanic corrosion activity between the different microstructure and the composition is likely to undermine the surface integrity.

Considerable micro-galvanic corrosion occurred between the hard WC particles and the metallic binder, and uniform corrosion occurred in the binder materials. After the potentiodynamic polarization testing it was determined that the DLC/WC-CoCr exhibited lower values for the corrosion current density which means a better corrosion resistance.

The field of protecting components against corrosion remains a challenge for the HVOF process due to the risk of interconnected pores, which lead to a very difficult corrosion rate estimation. Therefore, the corrosion effect on coated components working in aggressive environments will be hard to anticipate. These coatings can be recommended to be used against corrosion only for components that do not affect other parts in case of coating spallation and can be easily overhauled by respraying.

The coefficient of friction, shown in the **Figure 7**, was continuously monitored during the POD tests. The WC-CoCr coatings exhibited a stable frictional behaviour, with no evidence of a significant increase of friction coefficient after 100.000 laps. Throughout the first 2500 laps the friction coefficient raises to a maximum of approximately 0.32 and afterwards it decreases and remains stable. The DLC coating increases in the first 2500 laps to a maximum of 0.17 and then it starts to get stable at 5 000 laps. The average value of the stabilized coefficient of friction is around 0.07. According to Hainsworth et al, DLC films from highly discharged plasmas can have very low friction coefficients, under 0.03 [9]. The low coefficient of friction can be attributed to the absence of strong covalent bond interaction between the sliding surfaces. The wear tracks, showed in the **Figure 8**, measured for the WC-CoCr coating was at around 330 µm whereas the DLC one exhibited a value around 230 µm. The better wear track performance of the DLC coating can be attributed to the characteristics of the formed tribofilm during the pin-on-disc test, lowering the friction and the wear consequentely.

a) b)

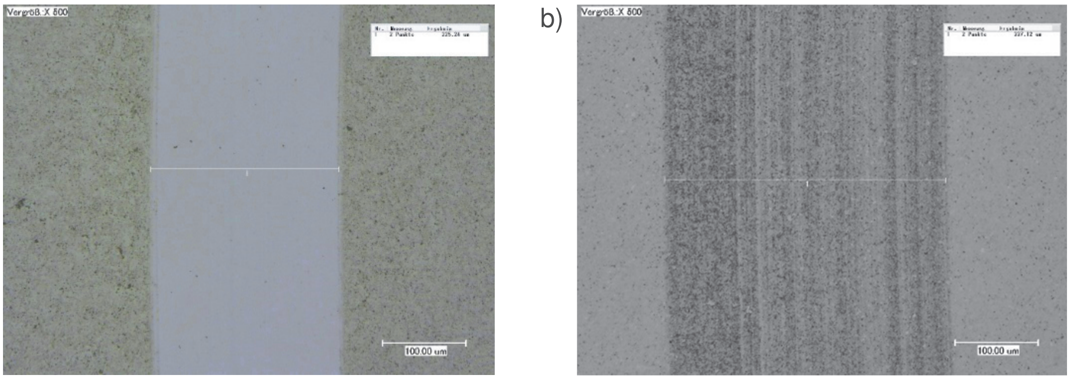

Figure 8 Wear track of the (a) WC-CoCr and the (b) DLC coating respectively

CONCLUSION

The conclusions are based on analyzing the morphology, corrosion and wear behavior of the WC-CoCr and DLC coatings. The EDX line scan identified the presence of Cr, N and C a result which indicated a phase composition consisting of chromium carbides, chromium nitrides and chromium carbonitrides respectively. A better corrosion behavior was determined at the DLC/WC-CoCr coating through the analysis of the corrosion current density. The width of the wear track of the DLC/WC-CoCr coating was 30% smaller than the as sprayed WC-CoCr one. The DLC/WC-CoCr systems exhibited considerably lower values for friction coefficient in comparison with that of the cermet coating. However, the latter one reached earlier the steady state. Although the DLC/WC-CoCr system demonstrated a better corrosion and wear resistance it can be seen that cermet layers can be considered for similar applications. The geometry of the component to be coated is not always convenient for DLC coatings that is why HVOF technology is still used and it can present certain advantages.

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