HVOF sprayed WC-CoCr coatings on aluminum: tensile and tribological properties

A Koutsomichalis¹, M Vardavoulias² and N Vaxevanidis³

¹ Hellenic Air-Force Academy, Department of Aeronautical Studies, Dekelia Air Force Base, TGA 1010, Attica, Greece
² Pyrogenesis S.A, Technological Park of Lavrio, GR 195 00, Lavrio, Greece
³ School of Pedagogical & Technological Education, Dept. of Mechanical Engineering Educators, GR 141 21 Heraklion, Athens, Greece

E-mail: vaxev@aspete.gr

Abstract. This paper provides a comprehensive assessment of the tensile and sliding wear behaviour of WC-10Co4Cr agglomerated and sintered powder deposited on aluminum by Hyper Velocity Oxy-Fuel (HVOF) process. Microstructural analysis (SEM) identified grains of tungsten carbide (WC) in the metal matrix of the cobalt-chromium (Co-Cr). A transformation of the WC in the $W_2C$ phase was observed and decomposition of WC in the metal matrix. The HVOF WC-Co-Cr coating was found to decrease tensile strength of the aluminum substrate. Transverse cracks were observed to initiate on the coating surface, increasing rapidly with the increase in tensile strain and stopped on the coating-substrate interface causing decohesion. Tribological properties were examined using the pin-on-disk method under various loads. The friction coefficient rose abruptly at the start-up phase and stabilized at almost the same sliding distance independently of the applied load. Both the friction coefficient and the wear volume were found to increase with increasing applied load. Study of the wear mechanisms revealed surface micro-cracking and fragmentation of flattened coating layers with subsequent gradual pull out of the carbide particles.

1. Introduction

Tungsten carbide coatings find a large variety of industrial applications for the protection of mechanical components against sliding and abrasive wear at various temperatures [1-3]. Tungsten carbide either in coated or sintered form is used for structural applications like cutting tools, plungers, bearings, gears, steam turbine, hydro turbines etc. [4]. The sprayed WC-Co coatings exhibit multi-phase microstructures, which are formed by the decomposition of WC-Co powders [5]. The degree of decomposition of WC-Co powders during spraying is related to carbide dissolution in the molten matrix with subsequent decarburization; it is also dependent on the temperature, the carbide grain size and the time (velocity) and is reported to influence wear characteristics [6]. The properties of WC-CoCr coatings depend on the powder size and volume fraction of WC powder feedstock and matrix composition [7]. The wear resistance properties of WC-Co-Cr coatings is dependent on the presence of hard, wear resistant WC grains in a CoCr based metallic binder phase, with the latter providing some toughness in the coating in comparison with pure ceramic coatings. Recent studies are focused on the tribological behaviour of composite cermet/metal coatings, in which the metallic phase...
participates not as binder metal, but as a distinct matrix of the product in percentages higher than 20% [8]. HVOF is widely used for the deposition of WC-based cermet coatings, since it retains a larger fraction of WC in the coating because of the short powder-flame interactions due to its hypersonic velocity that limits WC decomposition [9]. The WC decomposition to W$_2$C and metallic W is reported to decrease coating hardness and deteriorate wear resistance [10,11-16]. Recent studies are focused on the optimization of the deposition process parameters (e.g. spray distance, oxygen and flue flow rates) towards enhanced coating hardness [15,16].

The objective of this work was to investigate the friction and wear behaviour of HVOF WC-CoCr coating at different loads and identify the effect of load on the wear mechanism of the carbide coating. This paper also attempts to provide an in situ microscopic observation on the crack initiation, propagation and fracture behaviour of the coated system under uni-axial tensile loading.

2. Experimental researches

A commercially available WC-Co-Cr agglomerated and sintered powder (WOKA 3653) was deposited on the surface of Al-4%Cu alloy. The powder characteristics are given in table 1. SEM micrograph of agglomerated micro-structured WC-10Co-4Cr powder with EDX analysis is shown in figure 1.

| Table 1. Coating powder characteristics. |
|-------------------------------------------|
| **Composition** | WC: 86%, Co:10%, Cr: 4%, Fe<0.3% |
| **particle size** | -45+11 μm |
| **shape** | spherical |
| **density** | 14.7 g/cm$^3$ |

Two different types of specimens were prepared by the aluminum substrate: tensile specimens with dimensions 130x90x2.1 mm$^3$ and flat cylindrical test pieces for wear tests, 38.1 mm in diameter and 10mm thick. All specimens were grit blasted, prior to spraying, with aluminum oxide mesh 90.

The cermet powder was deposited by HVOF equipment. This step was accomplished by means of a Diamond Jet 2700 Sulzer Metco gun, employing a mixture of propane as fuel and oxygen. The spraying conditions are listed in table 2.

WC-CoCr coating was deposited on both sides of the tensile dog bone shaped specimens in equal thicknesses in order to enable balanced loading during tensile testing. Tensile testing was performed in accordance with ASTM E8 standard on an Instron 4482 apparatus using three specimens for each set.

Cylindrical wear test pieces were sprayed to an average coating thickness of 400 μm. The microstructure of the coated samples was observed under a metallographic microscope (Leica DMR) and SEM (Jeol); see figure 1 with image analysis software (Image Pro).

For the evaluation of friction and wear characteristics sliding friction tests were performed (according to ASTM G 99-05 standard) on a state-of-the-art pin-on-disc apparatus using, as counterbody, a cutting insert with a diamond-coated tip. Four normal loads were selected, namely 1N, 2N, 5N and 10N. All tests were conducted at 16 mm track radius and with constant linear speed of 0.6 m/s.

| Table 2. Spraying parameters. |
|-------------------------------|
| **Pressure** | Oxygen: 220 psi, Propane: 30 psi; Air 320 psi, Argon (carrier): 140 psi |
| **Flow rate** | Oxygen: 240 lt/min, Propane: 74 lt/min; Air: 800 lt/min, Argon (carrier): 30 lt/min; Coolant: 24 lt/min |
| **Powder feed** | 2.5 rpm |
| **Spraying distance** | 200 mm |
| **Revolutions** | 53 rpm |
| **Gun speed** | 0.044 m/s |
| **Flame temperature** | 2500 K |
3. Results and discussion

Figure 2 shows the cross section of the coating which is exhibiting dense structure, low porosity and is macro-crack free. Coating-substrate interface shows no gaps or cracks indicating good adhesion between the coatings and the substrate. The coating is built up by a deposit of lenticular splats, one over the other, in a uniform manner, throughout the coating. Pores appear black in the micrographs. The coating microstructure is observed to be composed of WC particles, which are uniformly distributed within the coating.

The coating microstructure typically consists of adjacent layers of dark and light areas (figure 3). The microstructure of the dark areas was revealed to be mostly Co particles with aggregate of WC, while the microstructure of the light areas was mostly consisted of sintered aggregate WC particles. Close examination of light areas of coatings showed very small WC particles forming larger particles. Tungsten carbide grains with sharp edges are attributed to their incomplete melting, while rounded carbide grains result from the dissolution of WC, due to local overheating, in the Co matrix.

It has been reported [17-21], that during spraying of WC-Co powder, particles are subjected to decarburization leading to a decrease of the total carbon content. The extent of the WC transformation has been associated with the starting powder type (size, morphology, and carbide size), the type of spray process, the amount of oxygen in the environment, and the spray parameters [22,23].
During decarburization tungsten carbide (WC) is transformed to tungsten semicarbide ($W_2C$) according to the following reactions [17]:

\[
2WC \rightarrow W_2C + C \\
W_2C \rightarrow 2W + C
\]

The XRD pattern of the coating, shown in figure 4, indicates the presence of both WC and the decarburized brittle $W_2C$ phase formed during deposition. These brittle phases have been correlated with reduced toughness and overall wear resistance [24] and are normally distributed in the peripheries of splats, leading to a weak interface between the splats [25]. The formation of hard crystalline phases and tough crystalline Co, without the consumption of a great deal of the WC phase, results in higher wear resistance coatings [26].

![Figure 3. SEM/EDS analysis of HVOF coatings.](image)

**Figure 3.** SEM/EDS analysis of HVOF coatings.

**Figure 4.** XRD diffractogram of the WC-Co-Cr coating.

Figure 5 shows the engineering stress – strain curves for the WC-Co-Cr coated Al substrate with various coating thickness. The presence of the WC-Co-Cr coating results in a lower tensile strength of the coated aluminum in comparison with the tensile strength of the uncoated aluminum. The reduction of the tensile properties may be attributed to the brittle characteristics of the coating, while fracture analysis revealed that brittle cracks, formed in the coating, are the primary cause of the tensile failure of the coated specimens. Tensile tests were conducted for a number of different coating thicknesses. The coated steel substrate with equal WC-Co-Cr coating thickness on both sides can be treated as a laminated composite stressed parallel to the lamellas with the coating and the substrate being the constituents, which determine the elastic and elastic-plastic behaviour.
Since the applied strain in the loading direction is same for all the components of the specimen, an iso-strain condition in the substrate and coating layers is assumed. According to the mixture law for composite materials, following relationship can be given for the present coating system:

\[ E_{cs}(h_{Al} + h_{WC}) = E_{WC}h_{WC} + E_{Al}h_{Al} \]  

(1)

where \( E_{cs} \), \( E_{Al} \) and \( E_{WC} \) are the Young’s modulus of the coated system, the substrate (Al) and coating layer (WC-Co-Cr), respectively, and \( h_{Al} \), \( h_{WC} \) are the thicknesses of the substrate and the coating layers. From the measured uniaxial stress–strain curves, the average Young’s modulus of three coated specimens, \( E_{cs} \), is 372 GPa. The Young modulus of the substrate is 70 GPa, as measured, and the reported Young modulus of the coating [27] is 310 GPa, the estimated Young’s modulus of the coated system, according to equation (1), is 400 GPa, which is in good approximation with the experimental values.

![Figure 5. Tensile stress–strain curves of HVOF WC-Co-Cr coated Al substrate with various coating thicknesses.](image)

During tensile testing the coating exhibited cracking in the transverse direction of the tensile load. After the saturation of the multiple cracks, the cracks stopped on the interface between the top coat and substrate. Cracks in the coating surface were observed prior to the transition in the plastic region and are attributed to its brittle nature. While tensile testing was deployed, cracks multiplied (figure 6a). Multiplication of transverse cracks in the coating proceeds until the applied strain reaches \(~1.6\%\) and then the crack-to-crack spacing rapidly decreases. As tensile strain increased, the initiated cracks propagate transversely towards the coating-substrate in tree like manner. When the initially nucleated cracks approach the interface, they stop and then new cracks form and propagate (figure 6b). The cracks upon reaching the interface deflect into parallel microcracks and propagate causing delamination of the coating especially if the coating thickness is increased. After the cracks propagate and pass through the coating-substrate interface, decohesion occurs just after the transverse crack tips arrive at this interface (figure 6c). The interfacial delamination cracks have been studied in coated
systems and are attributed to the linkage of previously formed cracks, are relative to the residual stresses and are associated with the fracture toughness of the coating [28,29]. The coating-substrate adhesion influences the tensile performance of the HVOF WC-Co-Cr coatings and is related to the substrate surface roughness (accomplished by grit blasting) which enables mechanical interlocking of the WC-Co-Cr splats with the substrate surface. Embedment of grit into the substrate or the presence of grit remnants may act as stress raisers and influence interfacial crack propagation and delamination of the coating upon stress induction.

![Figure 6](image)

**Figure 6.** (a) Plan view of the fractured coated system (b) transverse cracks in the cermet coating passing through the interface (c) enlargement of crack tip region in (b).

Figure 7 shows the friction coefficient of WC-Co-Cr coating for the four different loads 1 N, 2 N, 5 N and 10 N as a function of the sliding distance (or equivalently, time). Initially and for the first 250 m approximately the friction coefficient rapidly increases. After this initial running-in period [30], the friction coefficient tends to a constant steady-state value, for all the four loads applied. This constant value was found to be increasing with increasing normal load. More precisely, the steady-state friction coefficient value increases from 0.36 to 0.44 and to 0.55, as the normal load increases from 2 to 5 and to 10 N, respectively. During the application of the 10N load an increase of temperature was observed affecting the ductility of the coating thus leading in higher friction coefficient since as it has been elsewhere reported [31] even a relatively modest temperature increment can have a large effect on the tribological properties. The friction coefficient is in the same range with most literature values [32-34].

The wear volume loss after 10000 m sliding versus the applied load is shown in figure 8. It is evident that wear volume (equivalently wear mass losses) increases with increasing applied normal load following the Lancaster model [35]:

\[ V = k \cdot s \cdot N \]  

(2)

where \( V \) is the volume wear, \( s \) is the total sliding distance, \( N \) is the normal load and \( k \) is the wear coefficient or specific wear rate.

For relatively low normal load applied (2 N), the pressure at the contact area does not exceed the fracture stress of the ceramic coating; during sliding, friction obeys to the classical mechanical mechanisms leading to higher friction coefficient values due to the high roughness of these coatings. At the level of the contact area, sliding follows the topography of the coating’s protrusions and wear takes place through micro-cutting. For high normal load applied (10 N), the pressure at the contact area exceeds the fracture stress of the ceramic leading to lower friction coefficient values, since extensive micro-fragmentation at the level of the coating’s protrusions results in an intermediate layer of debris that facilitates sliding. For intermediate normal load applied (5 N), the pressure at the contact area exceeds only locally the fracture stress of the ceramic, e.g. at the level the higher protrusions leading to a mixed friction wear mechanism.
Stereoscopic analysis showed that the wear tracks become wider with increasing normal load and during sliding material is removed and deposited on the groove edges (figure 9). These are indicative of typical abrasion wear, encountered when a ceramic counterbody (diamond tip) is sliding against an elastoplastic metallic surface (WC-Co-Cr coating) [36].

The WC-Co-Cr coating consists of hard particles into a tough matrix and consequently the wear behaviour is related to the initial removal of the binder phase and the subsequent uprooting and exclusion of the hard WC particles and thus the wear loss can be explained by the delamination from the interface [37]. As a consequence of that the wear debris are trapped between the coating surface and the counterbody. While the wear debris is small, damage along the wear groove is low. Polishing lines along the sliding direction, together with micro-ploughing traces are clearly seen in figure 10a.
Figure 9. Plan view of the wear tracks (a) 1 N, (b) 2 N, (c) 5 N, (d) 10 N. The decohesion of the metallic matrix led to pull-out of the tungsten carbides, as also observed previously [6], that remained on the worn surface during testing (figure 10b). Further observation of the wear tracks revealed that the coating was worn out through the normally expected material removal via debris creation.

Figure 10. SEM top-view micrographs of worn surfaces.

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SEM observations on composite coatings cross sections revealed subsurface coating damage as well. Cracks were developed at the wear track boundaries on the contact surface and propagated parallel to the coating surface (figure 11a and b), practically splitting them and resulting in partial decohesion. Such cracks have been reported elsewhere [34, 38] but are found to propagate perpendicular leading to eventual splat exfoliation and consequently to relatively increased wear rates. In this case cracks are localized to surface and were not found to reach the coating-substrate interface. EDX microanalysis showed that the debris layer consists of a mixture of metallic and carbide components occurring from the simultaneous wear of both (figure 11c, d). The carbides particles in the debris act as a third abrasive body, destroying locally the tribo-layer that acts as an in-situ lubricant.
4. Conclusions

1. The tensile strength of the WC-Co-Cr coated aluminum was lower than that of the uncoated one indicating that the presence of the WC-Co-Cr coating reduces the tensile strength. During tensile loading, cracks first initiated in the outer layer of the coating and transversely propagated towards the substrate, and then cracks multiplied and saturated in the coating; finally interfacial decohesion occurred at the coating - substrate interface.

2. The variation of the friction coefficient with the sliding distance followed similar patterns for four loads applied (1, 2, 5, 10N). After an initial running-in period, the friction coefficient tends to a constant steady-state value, for all the cases examined. This steady-state value was found to be increasing with the applied normal load.

3. Wear volume increases with increasing applied normal load. The wear mechanism was micro-cracking of the metal binder leading to tungsten carbide particles pull-out. Cracks were developed at the wear track boundaries on the contact surface and propagated parallel to the coating surface causing partial decohesion.

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References

[1] Davis J R 2004 Handbook of Thermal Spray Technology (Ohio: ASM International)
[2] Legg K, Graham M, Chang P, Rastagar F, Gonzales A and Sartwell B 1996 Surf. Coat. Technol. 81 99-105
[3] Bolelli G et al 2015 Surf. Coat. Technol. 265 125-144
[4] Stewart D, Shipway P and McCartney D 2000 Acta Mater. 48 1596-04
[5] Qiao Y, Liu Y and Fischer T 2001 J. Therm. Spray Technol. 10 118-125
[6] Kumari K, Anad K, Bellacci M and Giannozzi M 2010 Wear 268 1309-19
[7] Strachowiak B and Stachowiak W 2010 Int. J. Refract. Met. Hard Mater. 28 95-105
[8] Kekes D, Psyllaki P, Vardavoulia M and Vekinis G 2014 Tribology in Industry 36 375-383
[9] Verdon C, Karimi A and Martin J 1998 Mater. Sci. Eng., A 246 11-24
[10] Morks M, Gao Y, Fahim N, Yingqing F and Shoeib M 2005 Surf. Coat. Technol. 199 66-71
[11] Xie M, Zhang S and Li M 2003 Appl. Surf. Sci. 273 799-805
[12] Hong S, Wu Y, Wang B, Zheng Y, Gao W and Li G 2014 Mater. Des. 55 286-291
[13] Li H, Khor K, Yu L and Cheang P 2005 Surf. Coat. Technol. 194 96-102
[14] Bolelli G, Cannill V, Lusvarghi L, Rosa R, Valarezo A, Choi W, Dey R, Weyant C and Sampath S 2012 Surf. Coat. Technol. 206 2585-01
[15] Al-Mutairi S, Hashmi M, Yilbas B and Stokes J 2015 Surf. Coat. Technol. 264 175-186
[16] Venter A, Oladijo O, Luzin V, Cornish L and Sacks N 2013 WC-Co Thin Solid Films 549 330-339
[17] Xie M, Zhang S and Li M 2013 Appl. Surf. Sci. 273 799-805
[18] Guilemany J, Dosta S and Miguel J 2006 Surf. Coat. Technol. 201 1180-96
[19] Adamson A W 1982 Physical Chemistry of Surfaces (New York: John Wiley) p 404
[20] Wang H, Song X, Liu X, Wei C, Gao Y and Fu J 2012 Surf. Coat. Technol. 207 117-122
[21] Wang Q, Li L, Yang G, Zhao X and Ding Z 2012 Surf. Coat. Technol. 206 4000-10
[22] Watanabe M, Owada A, Kuroda S and Gotoh Y 2006 Surf. Coat. Technol. 201 619-627
[23] Rabiei A and Evans A 2003 Acta Mater. 48 3963-76
[24] Qian L, Zhu S, Kagawa Y and Kubo T 2003 Surf. Coat. Technol. 173 178-184
[25] Zhu S, Guan X, Shibata K and Iwasaki K 2002 Metall. Mater. Trans. A 33 1292-95
[26] Veverkova J and Hainsworth S 2008 Wear 264 518-525
[27] Zhao D, Lekatou A and Vardavoulia M 2009 Surf. Coat. Technol. 204 15-27
[28] Cho J, Kim T, Jung Y and Lee K 2009 J. Ceram. Proc. Res. 10 344-350
[29] Keke D, Psyllaki P and Vardavoulia M 2014 Tribology in Industry 36 361-374
[30] Lancaster J 1967 Wear 10 103-107
[31] Mourlas A, Psyllaki P and Vardavoulia M 2014 Proc. 8th Intern. Conf. on Tribology, Sinaia pp 506-512
[32] Lee C, Han J, Yoon J, Shin M and Kwun S 2010 Surf. Coat. Technol. 204 2223-29
[33] Sharma P and Majumdar J 2013 Metall. Mater. Trans. A 44 372-380