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Wear performance of graphene nano platelets incorporated WC-Co coatings deposited by hybrid high velocity oxy fuel thermal spray

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ABSTRACT

WC-Co coatings have been used as wear resistant coatings in aero engines for decades, and research is still ongoing to further improve the performance of these coatings through compositional modifications to reduce wear. The coatings are used for unlubricated sliding wear protection in aero compressor parts such as; compressor, disc mid-span stiffeners and compressor aerofoils. In this study, two different graphene nanoplatelets (GNPs) were introduced into the WC-Co (88–12 wt %) coating through a hybrid thermal spray technique. Under the correct injection conditions, hybrid HVOF thermal spray leads to in-situ powder mixing which eliminates the need for premixed powder. The addition of GNPs into the WC-Co coating led to an increase in the porosity of coatings. Both GNPs improved the wear performance of the system against alumina and reduced damage to the counter surface. Against the WC-Co counter body, although in a few cases the GNP incorporated coatings had a higher wear rate, lower deformation on counter bodies were obtained. When wear of counter surfaces and coatings were combined, GNPs improved the wear performance of the system as a whole.

1. Introduction

In engineering applications, the friction force between moving parts causes wear and subsequent material loss from the surfaces, which leads to degradation and loss of function. In many cases, it is neither possible nor economic to replace parts frequently and hence wear resistant coatings are used. Thermal sprayed WC-Co cermet coatings are widely used especially in the aerospace industry and land based turbine blades to protect the surfaces from wear without affecting the bulk mechanical properties of the materials [1]. WC-Co is well known for its hardness. strength, wear resistance [2,3], Plasma spray methods have been used until the 1980s for WC-Co cermet coating deposition. High processing temperatures during plasma spray led to decarburization and formation of the W₂C phase which has lower wear resistance properties than the WC phase. HVOF thermal spray methods have become more popular to deposit WC-Co cermet coatings nowadays, as they have lower processing temperatures compared to plasma spray and coatings have minimal W2C phase [1]. In addition to the type of thermal spray process, particle sizes carbide grain size, and binder to carbide ratio are the other important factors that affect the microstructure and hence the mechanical properties of the deposited coatings. Cobalt binder is a relatively soft phase compared to carbides. Therefore, increasing the cobalt content reduces the hardness and Young's modulus of the deposited WC-Co coating. On the other hand, fracture toughness and flexural strength increase slightly as cobalt is a ductile phase and has higher energy absorption capability. In addition to the effect on mechanical properties, increasing the cobalt content reduces the decarburization and formation of the W₂C phase. Cobalt has a higher specific heat value compared to WC, therefore in-flight particle temperatures are lower [4–7]. Feedstock powder size has an effect on velocity and temperature reached by the particles in flight during the deposition process. Studies performed showed that reducing the powder size, increases the temperatures of the particles and creates a more uniform heat distribution. This increases the deformation upon impact which leads to denser, less porous and harder coatings. However, as a result of higher temperatures oxidation, decomposition and decarburization happen at a higher rate which leads to the formation of undesirable phases that can affect the performance of the coatings [8–10]. Furthermore, carbide grain sizes also affect the mechanical properties and hence performance of the deposited coatings. WC-Co coatings with finer carbide grains perform better compared to medium or coarse carbide grains [10-12]. However, once the carbide grain sizes are at an extremely fine or nanostructured level, inconsistent results

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were reported on mechanical properties and performances of the coatings. Most studies reported a higher degree of decomposition as a result of a higher surface area to volume ratio in smaller grains. However, the morphology of the powder feedstocks can also influence the surface area to volume ratio and hence the heating of the particles. In some studies, fracture toughness and hardness are reported to be increased in nanostructured carbide grains as a result of increased density of grain boundaries, surface bonding with a binder material and reduced binder mean free path. However, some studies reported a reduction in hardness and fracture toughness as a result of higher decomposition rates. Higher decomposition rates of the WC phase leads to higher loss of C and dissolution of WC in the molten Co binder phase. In addition, it favours the W₂C phase which has lower fracture toughness (more brittle) than the WC phase. Furthermore, the wear performance of these coatings varies as the wear regime depends on the testing conditions and the type of wear mechanism taking place. Finer carbide grains can reduce the wear rate when the wear is dominated by WC grains pull out and third body abrasive behaviour of these grains. On the other hand, reduced hardness and fracture toughness increase the wear rate of these coatings as well under dry sliding and three body abrasive wear [10, 12-16]. Both mechanical properties and wear performance of WC-Co coatings on their own and combined with other metals have been studied extensively in the literature. However, these have not been studied using WC-Co together with the solid lubricant graphene. Graphene has promising results on friction and wear when it is used as a solid-state lubricant or reinforcement material for composite materials.

In 2004, Novoselov et al. managed to obtain a single layer of sp^2 hybridized carbon atoms inside a hexagonal lattice by mechanically exfoliating graphite [17] which was later on named as graphene. Graphene became an important and promising material since its discovery, as it is currently the strongest material known and has high Young's modulus and good thermal and electrical conductivity. In addition, graphene also has chemical inertness, enhanced surface properties and self-lubrication ability, which makes it a promising material to reduce friction hence improving wear resistance [18,19]. Graphene nanoplatelet (GNP) is a common name used to refer to a few layers of graphene (usually up to 20) [20]. Extensive studies were performed on GNPs and their incorporation into ceramic, polymer, metal and cermet matrix materials via various manufacturing methods. Mechanical properties of the materials and hence their performances are reported to increase as a result of GNP incorporation. However, these improvements are dependent on the GNP concentration, manufacturing techniques and main matrix materials [21-29]. The wear resistance of the GNP incorporated materials is also improved, as a result of improved mechanical properties such as hardness and fracture toughness which are important factors in wear processes. In addition, in some studies, a tribofilm formation was also observed as a result of GNP pull out [18,30-35]. In other studies, HVOF thermal spray methods were also used to produce pure GNP coatings, where massive reductions in coefficient of friction (down to around 0.1) and hence protection of the surfaces were observed [36-38].

In this study, composite coatings of WC-Co and graphene nanoplatelets have been produced using a hybrid HVOF thermal spray. This technique allowed *in–situ* mixings of the submicron sized GNPs with the micro sized WC-Co inside the flame. Hardness and wear resistance of the WC-Co and self-lubrication ability of GNP with its ability to improve mechanical properties of composites have been combined in a single coating. The wear performance of coatings has been investigated by using the ball on disc wear test to analyse the effect of GNP incorporation, microstructure and mechanical properties of the coatings. The ball on disc wear test was chosen as it is a simple but elegant wear test technique in laboratory settings that provides reliable values of coefficient of friction (CoF) during the test. Here, the tracking of CoF is important for observing the formation of self-lubricating GNP tribofilms during the test.

2. Materials & methods

2.1. Feedstock materials

Three different feedstock materials, WC-Co (Amperit 518, H.C. Starck, Germany), graphene nanoplatelets (product no. AB 304022, ABCR Germany) and graphene nanoplatelets aggregates (product no. AB304025, ABCR, Germany), were used in this study. Amperit 518 was used in the powder form, while the other two were used to prepare suspensions.

Amperit 518 powder consists of agglomerated and sintered tungsten carbide (WC) particles with medium grain size (\sim 2.5 µm), in a cobalt (Co) binder. This composite powder was formed from 88 wt% tungsten carbide and 12 wt% cobalt, WC-12Co. Back scattered electron (BSE) micrographs of WC-12Co in both low (a) and high (b) magnification are shown in Fig. 1. From the low magnification BSE micrograph, spherical powder morphology and a homogenous distribution of powder particles can be seen. On the high magnification BSE micrograph, particles are seen as porous and tungsten carbide grains can be discerned from the cobalt matrix based on the contrast. Brighter areas, as marked with a blue arrow, represent WC grains, while dark grey areas, as marked with a red arrow, represent the cobalt binder matrix. WC-Co particles have a nominal size range of 15-45 µm with D90, D50 and D10 values of 48-58, 29-37 and 18-22 µm respectively, as stated by the manufacturer. The stated chemical composition of this tungsten-based powder is 11-13 wt % Cobalt, 5.2-5.6 wt % Carbon (C) and 0.2 wt % Iron (Fe). The powder was dried overnight inside a drying cabinet at ~100 °C before the thermal spray to eliminate the moisture and its effects on the flowability of the powder.

Deionised water-based suspensions of graphene nanoplatelets (labelled as GNP1 in this study) and graphene nanoplatelets aggregates (labelled as GNP2 in this study) were prepared using 0.3 wt % of each powder. GNP1 has 6–8 nm nominal thickness, 5 μ m average lateral size and a specific surface area of 118.8 m²/g. GNP2 consist of varied submicron sized particles with a specific surface area of 300 m²/g. Secondary electron (SE) micrographs of both GNP powders are shown in Fig. 2. Both GNP powders have angular flake shaped morphology. However, GNP2 powder is more agglomerated as a result of its high specific surface area, hence greater forces of attraction. Sodium dodecyl sulphate, SDS (product no. 71725, Sigma–Aldrich, United Kingdom) was added as a surfactant to promote dispersion of the GNPs. The amount of surfactant added was 1 wt % of the GNPs used. The suspensions were stirred using a FB-505 Ultrasonic Processor (Fischer Scientific, United Kingdom) which operates at 20 kHz with a 2 s pulse every 5 s for 1 h.

AISI 304 stainless steel substrates with dimensions of $60 \times 25 \times 2$ mm with nominal composition Fe-19.0Cr-9.3Ni-0.05C (all in wt. %) were used as substrates. Substrate surfaces were grit blasted with a blast cleaner from Guyson (Dudley, United Kingdom) at 3 bars with F100 brown aluminium oxide particles (0.125–0.149 mm). Prior to thermal spray, the substrate surfaces were cleaned with industrial methylated spirit (IMS) and compressed air.

2.2. Coating deposition

Coatings were deposited onto the grit blasted stainless steel substrates with a TopGun SS (GTV GmbH, Germany) HVOF thermal spray system. A custom attachment for the HVOF thermal spray gun shown in Fig. 3 was used for radial injection of the GNP1 and GNP2 suspensions. Amperit 518 powder was injected axially into the 22 mm long combustion chamber where the combustion between hydrogen and oxygen takes place, at a rate of 40 g/min. Hydrogen and oxygen flow rates were 660 l/min and 229 l/min respectively, which gives rise to a 75 kW and 70% stoichiometric flame. A hydrogen rich combustion was chosen to minimise the effect of WC decarburization during the thermal spray. Substrates were attached to a rotating carousel with a diameter of 260 mm and positioned at a 300 mm stand-off distance. The carousel rotates



Fig. 1. BSE micrographs of Amperit 518 (WC–12Co) agglomerated and sintered powders in low magnification (a) and high magnification (b). Brighter areas are WC grains (marked with blue arrow) while dark grey areas are the cobalt binder matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 2. SE micrographs of GNP1 (a) and GNP2 (b) powders. Both powders have angular flake shapes; however, GNP2 powder is more densely packed and agglomerated as a result of higher specific surface area.



Fig. 3. Image showing the GTV HVOF TopGun with the custom attachment for radial injection indicated with the arrow, where the injector was pointing 10 mm from the nozzle exit and 15° downstream.

with a speed of 73 rpm during the spray runs which gives rise to a 1 m/s linear velocity for the attached substrates. Simultaneously, the spray gun moves vertically with a traverse speed of 5 mm/s, which leads to a 4 mm overlap between tracks from subsequent passes [39]. GNP suspensions were injected at a rate of 170 ml/min radially through an injector with an internal duct diameter of 450 μ m pointing at 10 mm from the nozzle exit along the flame axis and 15° downstream to the flame direction, as

an optimised set of parameters from a previous project [37]. Three different runs were performed, the first one was just axially injecting Amperit 518 powder to obtain a WC-Co coating as a reference sample. Two more runs were performed by introducing the radial injection of GNP1 and GNP2 suspensions respectively to deposit composite coatings (WC-Co + GNP1 and WC-Co + GNP2).

2.3. Wear test

The top surface of the coatings was ground via a metal bonded diamond grinding disc of 20-µm particle size which corresponds to a grit size of ~P900. This process was followed by fine polishing in the order of Abracloth and Planocloth in the presence of 9- and 1-µm water-based diamond suspension, respectively. Final polished surfaces had surface roughness values (Ra) in the range of 0.02-0.05 µm. Unlubricated rotational sliding wear tests were performed using a rotary tribometer with a ball on disc arrangement (Ducom Instruments, The Netherlands). Tribological performance of polished coatings was investigated at a 60 N load against 6 mm alumina (99.9% aluminium oxide) and tungsten carbide (WC - 6 wt % Co) counter body (referred to as WC) balls (Dejay distributions, United Kingdom) which resulted in 10 mm diameter circular wear tracks. Both counter surfaces had a surface finish of 0.038 µm. Supplier provided hardness values were 91 in Rockwell A scale for tungsten carbide and 81 in Rockwell 45 N scale for alumina. Vickers hardness conversions for WC is ${\sim}1550$ HV and ${\sim}2000$ HV for alumina. Samples were rotated at 100, 200 and 300 rpm against the stationary balls which gives rise to 52, 105 and 157 mm/s linear speeds,

respectively. Tests were performed for a total sliding distance of 1 km. The loading condition, sliding speed and counter body materials were chosen to investigate an operating envelope where GNPs within the coating can lead to the formation of the tribofilm. Duplicate tests were conducted for all conditions. The coefficient of friction (CoF), which has an accuracy of 0.02 \pm 1%, was plotted against sliding distance.

2D transverse line profiles of each wear track were measured at four different points using Talysurf Form 50 contact profilometer (Taylor Hobson, United Kingdom) together with a diamond stylus with a tip radius of 2 μ m and lateral resolution of 0.5 μ m. Mountains map software was used to analyse these line profiles to calculate the cross-sectional area of the wear tracks, then these were converted into volume loss by multiplying with the circumference of the circular tracks which is the total length of the wear track [14,40]. In total eight different points were used to calculate the average and standard error of the mean for each sample. Material volume loss on the counter body was calculated (from two different measurements – one from each test) by following the assumption of a spherical cap of material removal method reported in the studies [5], and [6]. The specific wear rate of both the coatings and the counter bodies was calculated from the volume loss by dividing it by applied force and total sliding distance.

2.4. Material characterisation

Cross sectional analysis (microstructure, thickness and porosity) of the deposited coatings and observations of the morphology of the feedstocks and the worn surfaces were performed with a Quanta 600 scanning electron microscope, SEM (FEI, The Netherlands) in both SE and BSE modes with 20 kV accelerating voltage, a spot size of 5 and a working distance of 13 mm. Combined EDX software (Bruker, USA) was used for elemental composition analysis. Cross sectional samples of the coatings were prepared by cutting the samples with a diamond cutting disk, followed by sequential silicon carbide (SiC) grinding and diamond polishing with a final grit size of 1 µm. Porosity analysis of the coatings was performed on 5 different BSE micrographs for each coating obtained from the SEM at 2000X magnification from the centre of the coatings which gives rise to an area of 70 μm \times 60 $\mu m.$ Contrast threshold function on ImageJ software [41] was applied to the micrographs according to ASTM E2109 standard to estimate the percentage area fraction of the pores in each BSE micrograph. An average porosity along with the standard mean error was reported in all cases.

X-ray diffraction (XRD) was performed on coatings top surface and WC-12Co powder to analyse the phase changes upon the thermal spray. A Bruker D8 Advance diffractometer (Bruker, USA) with Cu K_{\alpha} radiation (1.5406 Å) in 0-20 Bragg-Brentano geometry was used with a step size of 0.02° and a time per step of 0.1 s in the $20^{\circ} \leq 20 \leq 100^{\circ}$ range. To quantify the decarburization, the carbide retention index was calculated for each coating and the values are presented in Table 1. Index of carbide retention was calculated using equation (1) and intensities of WC, W₂C and W peaks at 35.6°, 39°, 40.5° respectively [42].

$$\frac{Iwc}{Iwc + Iw2c + Iw}$$
(eq.1)

A LabRAM HR spectrometer (Horiba Jobin YVON, Japan), modified by the addition of an automated xyz stage (Märzhäuser, Germany) was used to perform Raman spectroscopy. Before the spectra collection, the instrument was calibrated using a standard Si (100) reference band at

Table 1 Summary of coatings properties including thickness, porosity and hardness.

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520.7 cm^{-1} and the Rayleigh line at 0 cm^{-1} . Spectra were obtained by using a red laser with the wavelength of 660 nm (for cross section) and a green laser which has a wavelength of 532 nm (for worn surfaces) together with a 300 µm pinhole and a 100x objective. Two different wavelengths were used to avoid the fluorescence effect. Green laser usage on cross sections disturbs the 2D band, which is important for proving the presence of GNPs. On the other hand, red laser usage on the worn surface disturbs the whole spectrum range. A 25% laser filter was applied to attenuate the intensity at the sample. A 300 lines/mm rotatable diffraction grating was employed for scanning a range of Raman shifts during each acquisition. The detection of signals to create spectra was done with a Synapse detector (Horiba, Japan). Each individual spectrum was collected for 20 s and repeated 3 times to eliminate artefacts (cosmic spikes) generated by cosmic rays and to improve the signal to noise ratio. Spectra were corrected by applying linear baseline subtraction to eliminate any residual fluorescence by using Labspec 6 software (Horiba Jobin YVON, Japan) and normalised. Presented spectra for worn surfaces are an average of 5 different spectra from each of the coatings' corresponding wear track surfaces.

The coating microhardness was measured via a Vickers microhardness indenter (Buehler, USA) on polished cross sections. 500 gf with a dwell time of 10 s was applied to create 5 indents in the centre of the coatings, parallel to the substrate. An average hardness value with the standard mean error was reported in all cases.

3. Results

3.1. Coating characterisation

The XRD diffractogram in Fig. 4 shows Amperit 518 powder was composed of hexagonal WC (PDF 00-051-0939) and cubic cobalt (PDF 00-15-0806) phases. The WC phase is still the dominant phase after the thermal spray. However, W_2C (PDF 01-071-6322) and elemental W (PDF 00-004-0806) phases were formed during the thermal spray



Fig. 4. XRD diffractograms of the Amperit 518 (WC–12Co) powder feedstock, as-sprayed WC-Co coatings and both GNP1 and GNP2 incorporated composite coatings.

| Dating Properties | | | | | |
|-------------------|----------------|---------------|--------------------------|-------------------------|--|
| Samples | Thickness (µm) | Porosity (%) | Vickers Hardness (HV0.5) | Carbide Retention Index | |
| WC-Co | 110±2 | 0.6±0.1 | 1191±57 | 0.67 | |
| WC-Co+GNP1 | 106±9 | $3.8{\pm}0.6$ | 1193 ± 60 | 0.69 | |
| WC-Co+GNP2 | 106±7 | $2.2{\pm}0.4$ | 880±71 | 0.67 | |
| | | | | | |

process. In addition, a slightly broad diffuse peak between the $37^{\circ}-45^{\circ}$ 2 θ is also present in the coatings which is a sign of decarburization and amorphisation. In addition, the calculated carbide retention index value for all three coatings was 0.67.

All three coatings had achieved a good bonding with the substrates and their thicknesses were all in the same range (105–110 μ m) as it can be seen from the SE micrographs of the cross sections in Fig. 5. The thickness of each coating was measured from the cross-section micrographs at 5 different locations, and values are presented in Table 1. The incorporation of the GNPs led to a more porous coating in both cases. Dark areas and lines on the BSE micrographs of the cross sections shown in Fig. 5 represent pores and cracks. The existence of the pores was also confirmed by SE micrographs (not shown). Porosity in both composite coatings was measured by the method described in section 2.3 and the values are presented in Table 1. Brighter areas marked with red arrows

represent the binder rich W (splats of molten metal) due to the high atomic weight of tungsten. Angular shaped tungsten carbide grains are also visible in all cross sections. Both WC-Co and WC-Co + GNP1 coatings have the same Vickers hardness of ~1190HV, however, WC-Co + GNP2 coatings hardness reduced to ~880HV.

Raman spectra were collected from both GNP incorporated coating cross sections shown in Fig. 6. Both Raman spectra were dominated by 3 bands. Those bands are D, G and 2D bands present at ~1350, ~1600 and ~2650 cm⁻¹ Raman shifts, respectively. D band arises from stretching while G band arises from expansion/contraction of sp² hybridized carbon-carbon bonds in hexagonal rings or chains. They can be present in carbides as well however, the 2D band is a characteristic band of graphene and only present in graphene and graphite containing materials [43,44].



Fig. 5. At the top, SE micrographs of (a) WC-Co, (b) WC-Co + GNP1 and (c) WC-Co + GNP2 coating cross sections in low magnification. At the bottom, BSE micrographs of (d) WC-Co, (e) WC-Co + GNP1 and (f) WC-Co + GNP2 coating cross sections in high magnification. Darker areas represent pores and cracks while brighter areas are W heavy grain, marked with arrows on BSE micrographs.



Fig. 6. Optical microscope images of (a) WC-Co + GNP1 and (b) WC-Co + GNP2 coating cross sections are shown and marked areas represent the points where corresponding Raman spectra were obtained. Spectra have been baseline corrected for fluorescence, normalised to the intensity of the G band for ease of comparison and shifted along the y-axis for clarity.

3.2. CoF and specific wear rates

The coefficient of friction behaviour of all three coatings against the WC and alumina counter body is given in Fig. 7 and Fig. 8, respectively. There is not an obvious trend in the coefficient of friction graphs as a result of GNP incorporation to the WC-Co matrix. For instance, against the WC counter body at 100 rpm Fig. 7(a) WC-Co + GNP2 coating has higher steady state CoF (\sim 0.6) while WC-Co + GNP1 coating has similar CoF as reference WC-Co coating (\sim 0.4). On the other hand, steady state CoF for WC-Co + GNP1 coating is the highest (\sim 0.6) while WC-Co + GNP2 coating has similar to reference (\sim 0.4) during the repetition tests at the same condition in Fig. 7(d). Furthermore, against the alumina counter body, CoF for GNP incorporated coatings are similar to the reference coating. The only exception to that is the repetition tests performed at 100 rpm in Fig. 8(d) where both GNP incorporated coatings achieve nearly 0.2 lower CoF compared to the reference WC-Co coating after a significant running in period for the WC-Co + GNP1 coating. The only noticeable effect of sliding speed on the CoF behaviour is the slight increase in CoF values of all three coatings at 200 rpm against both counter bodies. Measured CoF values against the alumina counter body of all three coatings are slightly higher than their counterparts against the WC counter body. This difference is expected as each counter body has different hardness and composition, which can lead to different wear mechanisms and surface deformation, hence roughness. Running in periods are also present in CoF graphs of all coatings in all cases. Running in periods for coatings against alumina counter body is shorter in distance compared to their counterparts obtained against WC counter body. Against alumina counter body running in periods are always shorter than 100 m and mostly limited to the first few meters of the wear test. On the other hand, most of the running in periods are 250 m against the WC counter body. Another difference in the running in periods is the shape of the CoF curve. CoF values during the running in periods against the alumina counter body have a sharp increase to the highest values in the first few meters then gradually decreases and stabilises. However, this is not the only trend existing in CoF graphs obtained against the WC counter body. In many cases, CoF values increase gradually then stabilises around the peak value for the rest of the tests. The reason for different types of running in periods is associated with a number of changes in the tribosystem such as surface roughness, surface work hardening, oxide film formations and subsurface defect structure. CoF graphs starting with a low CoF value and gradually increasing toward a stable CoF (such as WC-Co + GNP1 against WC counter body at 100 rpm in test 1) suggests smoother contact surfaces. On the other hand, graphs starting with a higher CoF value and gradually decreasing towards a stable CoF or reaching a peak then decreasing to a stable value (such as WC-Co against WC counter body at 100 rpm in test 1) suggest rougher contact surfaces [45]. Overall, neither GNP1 nor GNP2 incorporation improves the CoF performance of the coatings. In addition, there is no sign of lubrication due to GNP exposure, hence only the WC-Co reference coatings worn surface characterisations was performed via SEM micrographs to analyse the wear mechanisms and effect of both speed and counter surface on the wear mechanism.

Averaged specific wear rates of all three coatings in all cases, corresponding counter bodies and also combined wear rates are given with



Fig. 7. Coefficient of friction graphs for all three coatings against WC counter body from both test 1 and test 2. On the left graphs obtained during test 1 at 100 (a), 200 (b), and 300 (c) rpm. On the right, graphs obtained during test 2 at 100 (d), 200 (e), and 300 (f) rpm.

the standard error of the mean in Fig. 9. Against the WC counter surface, WC-Co + GNP1 coating has a lower average specific wear rate compared to the reference WC-Co coating at all speeds Fig. 9(a). However, the difference in average wear rates is all in the range of standard error of the mean except at 100 rpm. The WC-Co + GNP2 coating has a lower average wear rate than the reference coating at 200 rpm only, which, is also the lowest wear rate achieved by a significant margin for this set of tests. On the other hand, average specific wear rates of the WC counter bodies Fig. 9(b) are reduced in both WC-Co + GNP1 and WC-Co + GNP2 coatings in all speeds. However, the range of error bars was increased significantly when the rotational speed increased to 200 and 300 rpm, as the wear becomes more aggressive. In addition, an effect of sliding speed on average wear rate is not observed. Against the alumina counter surface Fig. 9(d), both GNP containing coatings have lower average specific wear rates than the reference coating at all speeds. The difference in average wear rates is all in the range of standard error of the mean except for WC-Co + GNP2 coating at both 200 and 300 rpm. Alumina counter surface average specific wear rates Fig. 9(e) also follow

the same trend as coating specific wear rates. The effect of sliding speed is more obvious when the alumina counter body was used, as increasing the sliding speed leads to higher average specific wear rates, this increase is only marginal between 100 and 200 rpm. However, at 300 rpm, the reference WC-Co coating and the WC-Co + GNP1 coatings exhibit a significant increase in average specific wear rates, which is not observed for the WC-Co + GNP2 coating. When the combined average specific wear rates Fig. 9(c) and (f) are taken into account both GNP1 and GNP2 incorporation improved the wear performance in all three sliding speeds and against both WC and alumina counter surfaces. In summary, against WC counter bodies GNP1 incorporation improved the wear resistance of both the coating and the counter surface, while GNP2 incorporation mostly improved the wear resistance of the counter surface. Against alumina counter bodies both GNP1 and GNP2 incorporation improved the wear resistance of both the coatings and the counter surfaces with WC-Co + GNP2 at 300 rpm showing the biggest improvement over the baseline. However, the main improvements were obtained at 100 rpm against the WC counter body by both GNP1 and GNP2 incorporation and



Fig. 8. Coefficient of friction graphs for all three coatings against Alumina counter body from both test 1 and test 2. On the left graphs obtained during test 1 at 100 (a), 200 (b), and 300 (c) rpm. On the right, graphs obtained during test 2 at 100 (d), 200 (e), and 300 (f) rpm.

by GNP2 at both 200 and 300 rpm against the alumina counter body. Although there was a wide range of error for the wear rates, these obtained a lower wear rate outside the range of errors.

3.3. Worn surface characterisation

Wear tracks that were created by the WC counter surface at 100, 200 and 300 rpm in both SE and BSE micrographs are shown in Fig. 10. At 100 rpm in the SE micrograph, some parts of the coatings top surface still have smooth regions (marked with blue arrow). While, some areas were deformed by removal of flake shaped particles, where delamination regions (marked with red arrow) were formed. In the BSE micrographs, these delamination regions correspond to a darker grey contrast. EDX analysis shown in Table 2 on the area marked with a red dot shows oxygen and tungsten are the main elements present with small amounts of cobalt. This suggests tungsten (III) oxide, WO₃ formation and cracks can be seen around those oxides. Smooth regions cannot be seen on the surface at 200 rpm where nearly all parts of the wear track deformed. Once the rotational speed was increased to 300 rpm, the surface was aggressively damaged as can be seen from the pullouts, cracks and fractures forming on the surface. Wear tracks that were created by the alumina counter surface at 100, 200 and 300 rpm in both SE and BSE micrographs are present in Fig. 11. A similar trend was observed here as well. Increasing rotational speed from 100 rpm to 200 rpm has slightly increased the damage on the surface, while at 300 rpm the surface was again aggressively damaged. EDX analysis performed on the area marked with a red dot shows a higher concentration of oxygen and also the presence of aluminium. EDX confirmed the material transfer from the counter body to the worn surface of the coatings and the amount was increased with the rotational speed. Cracks were not observed around



Fig. 9. The specific wear rate values with standard error of the mean for all coatings obtained from averaging results of test 1 and test 2. On the left specific wear rates of the coatings against WC counter surface (a), specific wear rates of the WC counter body (b) and combined specific wear rates (c). On the right specific wear rates of the alumina (e) and combined specific wear rates (f).

and within the oxides in BSE micrographs this time. In both cases, delamination regions and the formed pits are seen on the wear track surfaces. In the case of the WC counter surface, formed pits were filled with oxides of tungsten as a result of triboxidation. On the other hand, against alumina counter surface pits were filled with transferred alumina particles. Both GNP containing coatings have wear track surfaces similar to the presented micrographs in this study and the presence of GNPs has not been observed on the wear track surfaces. Therefore, those micrographs were not reported in this study.

Raman spectra obtained from all three coating wear tracks formed with the WC counter body at three different speeds are shown in Fig. 12. Spectra were dominated by seven bands. Two of those bands are D and G bands from carbides present at 1350 cm⁻¹ and 1600 cm⁻¹ respectively. The rest of the bands present are oxide bands arising from tungsten (III) oxide WO₃ (800 cm⁻¹) and cobalt tungstate, CoWO₄ (700 cm⁻¹,875

cm⁻¹ and 975 cm⁻¹). In addition, the band observed at the lowest Raman shift (250 cm⁻¹) is also arising from oxides and according to the literature it can be from either WO₃ or CoWO₄. Furthermore, no noticeable trend was present in Raman spectra as the ratio between the carbide and oxide bands fluctuate at different speeds and in different coatings, same as the average specific wear rate data. Raman spectra obtained from all three coating wear tracks formed with the alumina counter body at three different speeds are present in Fig. 13. These spectra were noisier than the previous ones. As there is a material transfer and also a grooving wear mechanism taking place, wear surfaces were rougher which affects the signals to noise ratios. Spectra were dominated by four bands this time. D and G bands for the carbides are still present at the same Raman shifts. The remaining two other bands are the oxides present on the wear track surface. WO₃ band at 800 cm⁻¹ is still present in this case; however, it integrates into a bigger oxide

Fig. 10. On the left, SE micrographs of WC-Co wear tracks against WC counter surface at 100 rpm (a), 200 rpm (b), and 300 rpm (c). On the right, BSE micrographs of the same areas at 100 rpm (d), 200 rpm (e), and 300 rpm (f). Dark grey areas on BSE micrographs marked with red arrows represent WO3 phases. Cracking around those phases can also be seen in BSE micrographs. Blue arrow on image (a) represents smooth region while red arrow represents delamination region. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Table 2

Elemental composition obtained by EDX from marked areas inside the wear tracks shown by red dots in Figs. 10 and 11.

| Elements | Elemental composition (wt. %) | |
|----------|-------------------------------|----------------------|
| | WC Counter Body | Alumina Counter Body |
| W | 74.1 | 41.5 |
| Co | 4.9 | 7.9 |
| 0 | 21.0 | 37.4 |
| Al | Na. | 13.2 |

band at 900 cm⁻¹ Raman shifts. This band is tentatively assigned as a complex oxide which probably includes aluminium and cobalt oxides and a different oxide of tungsten. The band around 950 cm⁻¹ corresponds to a double bond between tungsten and oxygen [46]. This also

suggests a change in the structure of tungsten oxides found against the WC counter body compared to the ones formed against the alumina counter body. There is a trend present in these Raman spectra which is compatible with the trend for the average specific wear rates. Increasing the rotational speed from 100 to 200 rpm does not have a significant effect; however, at 300 rpm, the ratio of the carbide bands to oxide bands decreases significantly which suggests surfaces were deformed more aggressively and covered with more oxides instead of carbides. Another noticeable trend is in all cases WC-Co + GNP2 coating has the highest carbide to oxide ratios and also it is the coating that worn less in all cases. This again confirms the theory of wear track surfaces being predominantly carbides instead of oxides. The 2D band at ~2650 cm⁻¹ Raman shift could not be plotted to comment about the presence of GNPs on the wear tracks, because of the fluorescence effect.



4. Discussion

4.1. Coating microstructure

Microstructural evolution of the WC-Co coatings deposited by the HVOF thermal spray process has been studied extensively in another study [15]. Decarburization of WC-Co and formation of unwanted W₂C and W phases formed as a result of high temperature and the oxygen rich nature of the thermal spray system. WC-Co particles heat up, although they spend very little time inside the hot gas jet and cobalt melts. WC phases dissolve in molten Co and C also escapes from the system as a result of oxidation into CO. Fast cooling rates of splats formed on the substrates causes the formation of amorphous and/or nanocrystalline binder phase which leads to the formation of the broad diffuse peak between the 37°-45° 20 angles in the coatings. Furthermore, precipitation of W₂C and W phases also takes place as a result of carbon loss during the spray [11,14,15,47]. The calculated carbide retention index value (0.67) and the presence of W phases inside the coatings prove a higher level of decarburization during the thermal spray process. The presence of GNPs did not noticeably affect the carbon retention index. Liquid fuelled HVOF thermal sprayed WC-Co coatings are supposed to have less decarburization and undesirable phase changes [48] because in liquid fuelled HVOF thermal spray systems powder is injected after the combustion chamber. In this study, hydrogen gas is used as a fuel and gas fuelled HVOF thermal spray systems axially inject the powder into the combustion chamber which subjects the powder to high temperatures during the process. The presence of GNPs was confirmed by Raman, which means GNPs survived the thermal spray process. As a result of the radial injection, GNPs spent a reduced amount of time in the hotter, central part of the flame, which also reduces the chances of oxidation. In addition, in other studies where GNPs were axially injected into the combustion chamber, these GNPs still managed to survive in that condition without changing their unique structure [30,37,38,49].

GNP incorporation slightly reduced the thickness of the deposited

seen on SE micrographs marked with red arrows. Dark grey areas on BSE micrographs represents alumina and other complex oxides formed during the wear tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 12. Raman spectra obtained from wear tracks created by the WC counter body at 100 (a), 200 (b) and 300 (c) rpm.

coatings and increased the surface roughness which led to a slightly larger scatter around the mean value of the thickness than the WC-Co reference coating. In addition, GNPs prevents the bonding between successive splats which led to the formation of pores and cracks inside the coatings cross section. WC-12Co powder was in a molten or semimolten phase during the thermal spray, while GNPs conserved their shape and form. GNP particles positioned themselves between successive splats which prevented the interlocking mechanism between them, and pores were created around GNPs. Raman spectra shown in Fig. 6



Fig. 13. Raman spectra obtained from wear tracks created by the alumina counter body at 100 (a), 200 (b) and 300 (c) rpm.

confirm this theory as the characteristic 2D band of GNPs at 2650 cm⁻¹ is present inside the pores of both composite coatings' cross sections. The WC-Co + GNP1 coating has the highest porosity, but it still has the same hardness as the reference coating. On the other hand, a nearly 25% reduction in hardness of WC-Co + GNP2 coating was observed. Hardness measurements were performed by using a 500 gf (5 N) load. This load was chosen as it creates indents with measurable diagonals without cracking in the middle of the coating cross section. However, it is relatively high to form the indent within a single splat [11]. Therefore,

porosity and the bonding strength between the successive splats can affect the hardness value of the coatings. Although both coatings are porous only GNP2 incorporation reduces the hardness suggesting that the GNP particle sizes and surface areas are the main contributor to the hardness and hence on bonding between the splats. GNP2 has a higher specific surface area leading to more forces of attraction so bigger aggregates of GNP particles. This can create bigger/wider pores which can explain the reduced hardness and bonding strength between splats.

4.2. Wear performance

4.2.1. Effect of sliding speed

The coefficient of friction values for all coatings, against both counter bodies, generally increased as the rotational speed increased from 100 rpm to 200 rpm, and then decreased at 300 rpm. There are a few exceptions such as WC-Co coating against WC during the first test, as a result of high sensitivities to small changes such as humidity, temperature and coating inhomogeneities. Increasing rotational speed from 100 to 200 rpm causes more damage, deformation and asperity formations on the surface leading to a slightly rougher surface, and as a result, CoF increases. However, at 300 rpm the surface undergoes severe deformation and becomes significantly rougher as CoF decreases compared to 200 rpm (Figs. 7 and 8). The speed influences the interface temperature during a wear test and at higher speeds, a limited amount of heat can be conducted away from the interface. Higher interface temperature leads to the rapid growth of oxides as a result of chemical reactivity and also reduces the mechanical strength of asperities and near surface materials, which reduces the effect of increased surface roughness on the CoF behaviour [50]. Increasing the rotational speed did not have a noticeable impact on the wear rates when a WC counter body was used; however, a trend related to the speed was observed against the alumina counter body, there is a directly proportional relationship between the rotational speed and specific wear rate. There was a sharp increase in wear rate at 300 rpm, which was a result of the brittle nature of the alumina. At 300 rpm, the alumina counter body deforms catastrophically, which leads to a massive increase in the contact area and more alumina transfer from the counter body to the coating. An increase in contact area made the wear tracks wider, while more alumina transfer created more ploughing grooves on the surface and made the wear tracks deeper. As the wear tracks are getting deeper and wider at the same this leads to a more than five times increase in specific wear rate. The WC-Co + GNP2 coating was the only exception to that, which will be explained in section 4.2.3.

4.2.2. Effect of counter bodies

Now looking into the effect of Counter bodies, CoF values obtained against the alumina counter body are slightly higher than the ones obtained against the WC counter body. This is an expected result as both materials lead to different wear mechanisms and similar results reported in another study [51]. Using different counter bodies changes the type of wear mechanisms taking place. Against WC counter body in all coatings and at all speeds, the WO3 phase was obtained on the wear track surfaces. As a result of contact stresses, coatings were pulled out at the contact area around the weakly bonded splats and decarburised areas, leaving behind pits. Pulled out coating fragments, as well as debris from the counter body, oxidise into WO₃, as a result of friction and heat generation between the coating and the counter body. This oxidised wear debris fills the pits formed on the surface [52,53]. However, against the alumina counter body, the top surface of the coatings is mostly covered with aluminium oxide particles suggesting a material transfer taking place between the bodies in contact. Alumina grains pulled out during the wear test as a result of intergranular and/or transgranular crack propagation depending on the grain sizes when the critical contact pressure was reached [54]. During the wear tests against the alumina counter body, weakly bonded splats and decarburised areas were pulled out [55,56]. This leaves behind small pits which were filled

with the alumina debris in this study. However, there is no paste or tribofilm formation observed such as the one mentioned in Ref. [56].

4.2.3. Effect of GNPs

Broad error ranges obtained for wear rates affected by the inhomogeneity of the coatings as a result of GNP addition. Plastic deformation and hence wear rate is dependent on localised properties such as subsurface defects at the contact point, porosity, the formation of cracks, grain pull outs and surface roughness. The presence of the randomly distributed pores and crack around the contact area as a result of GNP addition can lead to higher wear rates, however, the presence of GNPs around the contact area can also lead to exposure of GNPs and the formation of GNP tribofilm or a solid-state lubricant which can reduce the wear rates. The fluorescence effect in Raman masks the 2D band if there is any, which could be used to confirm the presence of GNPs inside the wear tracks. This limitation prevents conclusive comments to be made on the presence of GNPs inside the wear tracks and the formation of a lubricative tribofilm. However, CoF graphs do not show a reasonable reduction which suggests there was no lubrication as a result of GNPs, or the amount of GNPs exposed during the tests were so small that it is not enough to create a tribofilm and protect the surfaces in contact. In addition, the wear tracks formed during the test were not deeper than 10 µm which reduces the chances of GNP exposure from the underlying layers of the deposited coatings. Although tribofilm formation or the lubricative ability of GNPs are not observed, the significant improvement obtained in WC-Co + GNP2 coating at 300 rpm against alumina counter body is a result of GNP addition. The incorporation of GNPs introduces porosity and reduces the hardness of WC-Co + GNP2 coatings which makes it 25% softer than the other two coatings. As this coating is softer than the others, less deformation is happening on the alumina counter body. Therefore, the contact area between the surfaces remains smaller and less material transfer between the surfaces prevents the damage of the coatings.

5. Conclusion

In this study, composite coatings of WC-Co with graphene nanoplatelets were produced by using two different feedstocks simultaneously via hybrid injection HVOF thermal spray. Using two different feedstocks eliminates the powder mixing and/or suspension preparation stages before the thermal spray. This also allows spraying submicron sized particles in a suspension together with micron sized powders. There was a significant amount of decarburization and dissolution of WC-Co during the process. Both composite coatings have a porous microstructure and Vickers microhardness of WC-Co + GNP2 was reduced by 25%. However, the wear performance of both coatings is promising. Both composite coatings showed improved wear performance against alumina counter surface at all speeds and also counter surfaces were less damaged as well. Against WC counter body, just WC-Co + GNP1 coating wore less than the reference WC-Co coating in all three cases. However, when combined wear rates are considered, both coatings outperformed the reference one in all cases again against WC as well. Wear rates obtained against WC in all three speeds and against alumina in both 100 rpm and 200 rpm are relatively in the same range. However, against alumina at 300 rpm, there was a significant increase in wear rates. Different wear mechanisms hence different oxide formations took place as a result of different counter bodies. Furthermore, rotational speed did not have a significant effect on the wear rate unless it reaches a critical level which causes catastrophic deformation of ceramic alumina counter surface. Neither lubricative ability of GNPs nor tribofilm formation were observed, which suggested that the wear performance improved due to alteration of mechanical properties as a result of GNP addition. This study suggests GNP incorporation into WC-Co coatings has promising results for improving the wear performance of the popular WC-Co cermet coatings used in many industries. Further work on optimising the amount of GNPs present inside coatings are

required to analyse if an increased number of GNPs inside the coatings can contribute the GNP pull out and tribofilm formation to contribute further to wear resistance properties.

CRediT authorship contribution statement

K. Derelizade: Formal analysis, Writing – original draft. **F. Venturi:** Writing – original draft. **R.G. Wellman:** Supervision, Writing – review & editing, Funding acquisition. **A. Kholobysov:** Supervision, Writing – review & editing. **T. Hussain:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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K. Derelizade et al.

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