Towards more sustainable approaches for protecting surfaces against wear

Kaveh Torkashvand
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Kaveh Torkashvand
Dedicated to my mother, the strongest and kindest person in my life…
Acknowledgements

I would like to thank the people who made this four-year journey fruitful and enjoyable for me. First and foremost, I would like to sincerely express my gratitude to my supervisors, Associate Prof. Mohit Gupta and Prof. Shrikant Joshi, for their consistent guidance and infinite patience throughout these years. I have learned valuable lessons from both of you on conducting higher-quality research, and I intend to carry those learning with me and apply them in my future professional endeavours. Mohit, thank you for prioritizing my PhD on numerous occasions and making yourself available even during your vacations. Many times, I perceived your heartfelt support when facing challenges or difficult situations during this four-year journey. Shrikant, I have always admired your meticulous care and attention to my research work during my PhD. I have learned from you to be precise and accurate in my technical talk and writing, to be passionate and dedicated, to be self-critical and to always strive to raise the bar and to be a bit better. And finally, I deeply appreciate the support and kind understanding I received from both of you during challenges in my personal life throughout these years spent in Sweden, far from my family.

My special appreciation goes to Prof. Richard Chromic and his group, particularly Dr. Bruno Castilho and Ms. Alejandra Encalada for providing me with the great opportunity to visit and access their facilities at McGill university. It was one of my most fruitful and effective experiences, and I learned and enjoyed everyday conversations and discussions with you on various topics, particularly Tribology. I would like to sincerely thank Mr. Stefan Björklund for his invaluable assistance in spraying samples. I am grateful for his insightful discussions and generous sharing of his extensive knowledge and experience in thermal spraying. Additionally, I would like to thank Mr. Magnus Sandberg for his kind support in spraying and sample preparation and laboratory support.

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Populärvetenskaplig Sammanfattning

Title: Mot mer hållbara metoder för att skydda ytor mot slitage

Nyckelord: Slitage; HVAF; WC-baserade beläggningar; Hållbar produktion; Bindemedelsskemi

WC-Co-beläggningar, med och utan kromtillsatser, används i stor utsträckning inom industrin i slitagekrävande applikationer. Oron för koboltförsörjningen och kobolts miljö- och hälsoeffekter har dock fått industrin att leta efter mer hållbara alternativ. Högastighetsflamsprutning med luft (HVAF) är en lovande sputteknik för att producera täta WC-baserade beläggningar med minimal materialpåverkan. Den låga temperaturen och den höga kinetiska energin hos partiklarna i lågan som sprutas med HVAF, kan möjliggöra användning av finare pulver, vilket potentiellt kan resultera i tätare och tunnare beläggningar med förbättrade prestanda. HVAF tekniken skulle även kunna vara en potentiell teknik för att åstadkomma koboltfria beläggningar. Slitageegenskaperna hos WC beläggningar som är koboltfria och som sprutas med HVAF är dock okänd. HVAF teknikens potential för att kunna ersätta höghastighetsflamsprutning med syre (HVOF), som är den teknik som dominerar på marknaden idag vid sprutning av täta slitagebeständiga beläggningar är även okänd. HVAF är ett intressant alternativ till HVOF eftersom metoden kräver mindre energi jämfört med HVOF. Vid sprutning med HVAF kan partiklarnas temperatur och hastighet i lågan påverkas med hjälp av processvariabler, munstyckskonfiguration och genom att variera tillsatsmaterialets storleksfördelning. Partiklarnas hastighet och temperatur i lågan påverkar i sin tur den sprutade beläggningens mikrostruktur som i sin tur påverkar beläggningarnas egenskaper. Även den kemiska sammansättningen hos tillsatsmaterialet kan spela en stor roll för beläggningsegenskaperna.

I detta arbete utvärderas slitageegenskaper hos HVAF-sprutade WC-CoCr-beläggningar där tillsatsmaterialet har olika storleksfördelning och olika munstyckskonfigurationer. Slitageegenskaperna jämförs med beläggningar som sprutats med tillsatsmaterial som saknar kobolt (NiMoCrFeCo, FeNiCrMoCu och FeCrAl).

Resultaten visar att HVAF-tekniken fungerar mycket väl för sprutning av WC-baserade tillsatsmaterial med olika storleksfördelningar, vilket möjliggör produktion av tätare och tunnare beläggningar jämfört med de beläggningar som produceras industriellt idag. Resultaten visar även att koboltfria beläggningar som sprutats med HVAF ger jämförbara, och i vissa fall, överlägsna prestanda avseende slitagebeständighet. Både HVAF tekniken och utnyttjandet av
WC-Co coatings, with and without chromium additives, are widely used in the industry for severe tribological applications. However, concerns about cobalt supply and its environmental and health impacts have led industries to explore sustainable binder alternatives. As a deposition technique, high-velocity air-fuel (HVAF) spraying technology offers a promising solution by producing dense WC-based coatings with minimal material degradation during spraying. Moreover, the combination of high velocity and low flame temperature in HVAF enables the deposition of finer powders, which are more susceptible to thermal damage, with minimal decarburization. This results in denser coatings with improved properties compared to conventional spraying techniques. Therefore, this thesis aims to evaluate more sustainable approaches to depositing WC-based wear-resistant coatings involving (a) HVAF as a less energy-intensive technique compared to other methods like high velocity oxy-fuel (HVOF), (b) alternative Co-lean/free binders, and (c) fabrication of thin ('flash') coatings from finer feedstock powders.

In HVAF spraying, particles' in-flight temperature and velocity can be influenced by the process variables including nozzle configuration as well as feedstock particle size distribution. On the other hand, the chemistry of metallic binder can also play a key role in determining both properties and performance of these coatings. In this thesis, characteristics and tribological behaviour of HVAF-sprayed WC-CoCr coatings were investigated by spraying feedstock powders with varying particle sizes (ultra fine: 15/5, fine: 20/5, medium: 30/5 and coarse: 45/5 um) employing different nozzle configurations (various lengths and divergence-convergence configurations). Additionally, different WC-based feedstocks, comprising alternative binders to traditionally used CoCr (namely NiMoCrFeCo, FeNiCrMoCu and FeCrAl) were investigated. Results showed that the HVAF spraying excelled in processing WC-based powders with various size distributions, enabling the deposition of thinner coatings from fine powders ('flash' coatings) with similar properties/performance as thick coatings. This leads to reduced material usage while offering potential for considerable component life extension, both of which are important elements of sustainability. Additionally, it was concluded that the Co-lean/Co-free binders demonstrated comparable, and in
Abstract

**Title:** Towards more sustainable approaches for protecting surfaces against wear

**Keywords:** Wear; HVAF spraying; WC-Based Coatings; Sustainability; Binder Chemistry


WC-Co coatings, with and without chromium additives, are widely used in the industry for severe tribological applications. However, concerns about cobalt supply and its environmental and health impacts have led industries to explore sustainable binder alternatives. As a deposition technique, high velocity air-fuel (HVAF) spraying technology offers a promising solution by producing dense WC-based coatings with minimal material degradation during spraying. Moreover, the combination of high velocity and low flame temperature in HVAF enables the deposition of finer powders, which are more susceptible to thermal damage, with minimal decarburization. This results in denser coatings with improved properties compared to conventional spraying techniques. Therefore, this thesis aims to evaluate more sustainable approaches to depositing WC-based wear-resistant coatings involving (a) HVAF as a less energy-intensive technique compared to other methods like high velocity oxy-fuel (HVOF), (b) alternative Co-lean/free binders, and (c) fabrication of thin ('flash') coatings from finer feedstock powders.

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some cases superior performance than the reference Co-based binder under various wear conditions. All of these together can represent a significant step forward towards more sustainable approaches for protecting surfaces against wear.
Appended Publications

Kaveh Torkashvand, Shrikant Joshi, Mohit Gupta

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Paper F. "High-temperature sliding wear performance of HVAF WC-based coatings with alternative binders", (Submitted to Wear).
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Abbreviations

HVAF: High Velocity Air-Fuel
HVOF: High Velocity Oxy-Fuel
APS: Atmospheric Plasma Spray
VPS: Vacuum Plasma Spray
LPPS: Low-Pressure Plasma Spray
HPPS: High Power Plasma Spray
SPS: Suspension Plasma Spraying
TS: Thermal Spray
CS: Cold Spray
DG: Detonation Gun
BoD: Ball-on-disk
CoF: Coefficient of Friction
WLI: White Light Interferometry
SEM: Scanning Electron Microscopy
EDS: Energy Dispersive X-ray Spectrometry
XRD: X-ray Diffraction
CRM: Critical Raw Material
PVD: Physical Vapor Deposition
CVD: Chemical Vapor Deposition
GDP: Gross Domestic Product
PM: Powder Metallurgy
Ultra fine coatings: Coatings deposited using ultra fine powder (15/5 µm)
Fine coatings: Coatings deposited using fine powder (20/5 µm)
Medium coatings: Coatings deposited using medium powder (30/5 µm)

Coarse coatings: Coatings deposited using coarse powder (45/15 µm)

C30: 30 µm thick coatings deposited from ultra-fine powder (15/5 µm), also referred as 'flash' coating

C240: 240 µm thick coatings deposited from ultra-fine powder (15/5 µm)
1 Introduction

The application of thermal spray metal matrix composites consisting of tungsten carbide (WC) grains and a metallic binder, capable of performing under high-temperature conditions up to 550 °C, is a popular measure to protect surfaces against severe wear conditions [1]. Traditionally, cobalt has been extensively used as a tough binder material to provide structural support for WC grains, and coatings involving WC-Co compositions, sometimes with chromium addition, have gained widespread industrial acceptance. However, growing concerns about the risk of assured cobalt supply and its potential adverse effects on environment and health have prompted industries to explore alternative binder materials that are more sustainable [2,3]. As far as thermal spray deposition techniques are concerned, high velocity air-fuel (HVAF) technology has shown promise in producing highly compact WC-based coatings. This is achieved along with minimal loss of carbon content, thanks to the combination of high kinetic energy and low temperature (below 1500 °C) of particles during the spraying process [4]. This can enable processing of powders with finer particle sizes, resulting in deposition of denser coatings with refined microstructures and improved properties. In this thesis, the performance of alternative binders as more sustainable options will be evaluated. Additionally, from a processing perspective, the possibility of spraying thinner coatings with enhanced properties will be explored. Alternative binders are aimed at reducing reliance on Co while thinner coatings are motivated by material savings that can accrue on the whole for the sake of enhanced sustainability and costs.

In the following sections, motivation and objectives for moving towards more sustainable approaches, followed by the formulation of research questions for this study, will be discussed in more detail.

1.1 Research motivation and objectives

In a WC-based composite system, the metallic binder plays a crucial role as a "cementing" agent, providing structural support to the individual hard carbide particles. Cobalt has traditionally been extensively used as the binder material for several decades [5,6]. It, however, presents numerous concerns regarding adverse effect on environment and health, as well as reliably future supply. It is recognized as a health-hazardous element, and some studies suggest it may be carcinogenic [7–9]. Moreover, due to its limited and geographically concentrated reserves, there are significant worries regarding its availability and cost, to the extent that it has
been classified as a critical raw material (CRM) [2,10]. Therefore, the search for Co-lean or Co-free binders can be a step forward in finding more sustainable solutions. However, any proposed replacement must be thoroughly assessed in various aspects. Hence, the first objective of this study is to evaluate the characteristics and tribological performance of different WC-based coatings using more sustainable alternative binders. It should be mentioned that concerns about supply risk also apply to Tungsten. Although there have been efforts to find replacements for WC using other carbides, its unique properties are still required in many industrial applications. Therefore, this thesis specifically focuses on substituting Co in WC-based coatings as one of its objectives.

High velocity oxy-fuel (HVOF) processing technique is the current state-of-the-art method in the industry for depositing wear-resistant WC-based coatings. In this technique, a combination of pure oxygen and fuel in the form of gas or liquid is utilized to produce a high temperature combustion jet, reaching temperatures up to approximately 3000 °C [11]. It can produce relatively dense, homogeneous, highly coherent, and well-bonded coatings that exhibit exceptional performance in wear-prone environments. However, exposure of WC-based powder to elevated temperatures reached during HVOF spraying can result in the oxidation of binder as well as formation of brittle phases, such as W\textsubscript{2}C, due to decarburization. Decarburization, in case of WC-based coatings, can be defined as loss of carbon from WC grains due to overheating [11]. While the extent of decarburization observed in HVOF coatings is considerably lower compared to plasma spray coatings, it is still acknowledged as a shortcoming of this method [12,13].

On the other hand, the HVAF technique has demonstrated significant potential in fabricating high-quality coatings with minimal material alteration, thereby leading to superior performance. When processing WC-based materials, one advantage of HVAF over HVOF is its lower flame temperature, which helps prevent changes in the phase constitution of the feedstock material due to decarburization and oxidation. Instead, higher kinetic energy, achieved by using high flow rates of compressed air necessary for combustion, compensates for the lower thermal energy resulting from reduced flame temperature and promotes the formation of dense and well-adherent coatings. Besides, the utilization of compressed air in HVAF, as opposed to pure oxygen in HVOF, makes it a less energy-intensive technique with a reduced carbon footprint, ultimately resulting in a more sustainable spraying route. Additionally, the lower flame temperature of HVAF paves the way for spraying feedstock materials with finer particles, in cases where the powder is more susceptible to decarburization [14–16]. This can be important since employing finer powders can result in even denser microstructure with improved characteristics and performance [17]. Through this
approach, it may be feasible to spray thinner coatings, leading to a substantial reduction in the overall material usage, including that of Co as a CRM element. However, optimizing the appropriate spraying parameters for different powders with varying chemistries or particle size ranges requires a fundamental understanding of how these factors impact the characteristics and performance of the resulting coating. Therefore, the second objective of this thesis is to conduct a comprehensive study with the aim of establishing a fundamental understanding of the influence of process variables, such as different particle sizes and various nozzle configurations, on coatings performance.

Based on the provided discussion, the two main objectives of this thesis are:

- To develop fundamental understanding of coating process parameters-microstructure-performance relationships in HVAF sprayed WC-based coatings by investigating the role of feedstock particle size and nozzle design.
- To evaluate characteristics and performance of more sustainable WC-based wear resistant coatings by exploring different binders as potential alternatives to Co.

1.2 Research questions

Based on the objectives of this study, the following research questions are framed to be addressed:

- RQ1: How do process variables influence characteristics of HVAF-sprayed WC-based coatings?
- RQ2: How do the proposed binder alternatives (to Co) perform in different wear environments?
- RQ3: How do process variables and alterations in binder chemistry influence wear mechanisms under different wear environments in HVAF-sprayed WC-based coatings?
2 Background

2.1 Wear and tribology

Various definitions of wear exist, typically following the form of this description by the Larousse Dictionary of Science and Technology [18]: "the process of losing material from two surfaces that have been rubbed against one another". In every instance of relative motion between two surfaces, a resisting tangential force, known as friction, inevitably emerges. The ratio of this tangential force to the normal force is referred to as coefficient of friction (CoF), usually denoted by $\mu$. On the other hand, tribology is defined as the science of two interfaces in contact with each other in relative motion. The science of tribology generally refers to friction, wear, and lubrication [19]. Various classifications for wear are suggested in the literature taking into account different perspectives such as the condition of the contact [20], material removal mechanisms [21,22], and tribological testing methods [19,23]. Variations in classifications and terminology may lead to minor differences in the way a tribosystem is described, but this does not alter the fundamental nature of wear as a phenomenon. In this context, it would be more convenient to categorize wear based on the nature of contact between two surfaces, resulting in three main modes: sliding (2- and 3-body), impact, and rolling wear. Each of these wear modes can be divided into various subcategories.

**Sliding wear**: progressive removal of material from a solid surface due to the forceful rubbing action of another solid surface. Sliding wear includes various wear modes, including abrasive, adhesive, fatigue, fretting, and polishing wear. Abrasive wear can be categorized into two-body and three-body abrasion [21]. Two-body abrasion occurs when rigid protuberances are firmly attached to the sliding surfaces. In contrast, three-body abrasion involves loose hard particles that have the freedom to roll/slide between two surfaces in relative motion. Adhesive wear occurs when material removal takes place due to localized bonding between solid surfaces in contact, rather than by intentionally introduced abrasive substances within the tribosystem. It is well-known that, in sliding tribosystems, wear debris is often generated as a result of repeated rubbing. When these wear debris particles come into contact with the rubbing surfaces, they can act as third-body abrasive media. Consequently, adhesive wear can transition into abrasive wear due to presence of wear products [19,21].

Using a mirror-polished surface tested against a shiny alumina ball, ball-on-disc (BoD) testing following standard ASTM G99) can simulate adhesive wear as the primary wear mode in the initial stages. However, as time progresses, the emergence of wear debris leads to a combination of both abrasive and adhesive

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Figure 1. Schematic illustrations and important testing parameters of a) BoD test based on ASTM G99, b) sand-rubber wheel test based on ASTM G65 and c) dry jet erosion test based on ASTM G76.
wear. On the other hand, standard ASTM G65 aims to simulate three-body abrasion by introducing abradant media between the specimen's surface and a rubber wheel (see Figure 1).

**Impact wear**: wear of a solid surface caused by repetitive dynamic contact from another body. Wear can occur through the repetitive impact of a single large body, as well as from the impact of numerous small particles (erosion), liquid droplets or gas bubbles (cavitation) on a surface.

ASTM G76 is the standard that examines the wear of a surface exposed to the repeated impact of numerous small solid particles, commonly known as erosion wear (see Figure 1).

**Rolling wear**: progressive loss of material from one or both solid surfaces, resulting from repeated compressive stresses applied on the contacting region by a rolling element.

Standard laboratory tests, including the tests shown in Figure 1, are designed to evaluate and rank material performance. Among these tests, the three standard wear tests; BoD, sand-rubber wheel and dry jet erosion, are of the most widely used experiments for evaluating the tribological performance of a surface. Results from these three tests can provide a fairly good indication and can be considered as benchmarks. However, it's essential to note that no single test can completely mimic all the wear conditions encountered in a real-life working conditions. This stems from the fact that wear isn't an inherent material property; instead, it's a response from the tribosystem [24]. It should also be noted that mechanisms of wear can differ depending on the particular application and operating conditions.
Consequently, it is often necessary to employ a combination of various tests to gain a comprehensive understanding of the wear behavior of a component [19,25].

### 2.2 Tribology and sustainability

There must be a fine balance between human/industry demand for energy and minimizing environmental impact it can cause. The idea is to mitigate environmental consequences by enhancing the efficiency of energy usage, or in other words, by minimizing energy loss through the exploration of more suitable methods. These environmental concerns include diverse aspects such as carbon footprint, greenhouse gas emissions, excessive utilization of CRMs, as well as the emission of pollutants (in form of liquid and dust) into soil and water [26,27]. Advancements in material science are expanding the possibilities for utilizing alternative substances in commercial applications. These substances have the potential to offer equivalent or improved benefits in terms of material loss (due to friction), performance and reliability. Consequently, this progress can lead to a reduction in environmental impact. By taking advantage of tribological principals, it is possible to move closer to achieving a balance between developing environmentally friendly solutions and minimizing systemic losses.

Preservation of surfaces in aggressive wear environments has been a long-standing concern in various industries and tribological applications. From everyday simple objects to advanced industrial machinery, wear can lead to significant economic losses and environmental impacts [28,29]. Finding precise data on energy consumption shares in the industry is challenging in the available literature. However, estimations suggest that approximately 20% of the world's total energy consumption is attributed to overcoming friction caused by wear [28,30]. The materials group of the US office of technology assessment (in 1976) estimated potential savings of approximately 0.86% of the gross domestic product (GDP) through improving wear resistance and optimized maintenance procedures. Also, on a global scale, the future potential for savings seems promising, as reduction of energy loss due to wear could result in annual savings of 8% to 8.6% of the GDP in developed countries [29,31]. Tribological advancements can contribute to similar trends in reducing material loss and particulate emissions. For instance, to minimize brake wear, PORSCHE introduced the porsche surface coated brake (PSCB) in 2017, which is a gray cast iron brake disc coated with a 100 µm thick WC-based coating. This innovative brake system generates approximately 90% less brake dust [32,33].

However, employing these wear protection measures can have their own environmental impacts, including the amount of energy used during processing,
the overuse of critical elements, and the use of elements that pose health risks to humans and animals. To avoid such impacts, traditional methods of surface protection should be replaced by advanced techniques. One way forward can be to explore more efficient techniques for surface protection, while also reducing reliance on critical elements in the protective materials. To achieve this, it is necessary to assess the feasibility of utilizing greener chemistries that involve less harmful elements or abundant resources. Also, the traditional spraying processes can be replaced by techniques that are less energy-intensive and provide equal or better quality surface protection [23]. Hence, it is crucial to explore more sustainable approaches that balance performance with environmental and economic concerns when it comes to protecting surfaces against wear.

2.3 Coatings for tribological applications

Coatings, employed as a surface engineering technique, can offer a promising solution for protecting surfaces that are prone to wear. Based on thickness, tribological coatings can be classified into two main groups: thin films and thick coatings [23].

2.3.1 Thin film coatings

Addition of a thin layer (typically ranging from a few nanometers to a few micrometers) of specific materials can greatly improve the surface properties. These coatings are applied using various techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Thin coatings such as TiN, CrN, WC/Co, AlTiN, NiSiC, etc., are mostly used to minimize wear in industrial components like cutting tools and machine elements [34]. There are several advantages to using thin coatings, such as their low material requirement, which leads to cost savings and resource conservation. Thin coatings also offer precise control over coating thickness, resulting in a smooth and uniform surface finish, which is important for applications requiring precise tolerances. Additionally, thin coatings have minimal impact on substrate dimensions, making them ideal for coating delicate or complex components while preserving their functionality and design [35,36]. However, the exceedingly low thickness of thin film layers can make them incapable of withstanding the contact stresses generated in certain conditions where high surface stresses are present. Thin hard coatings applied on soft substrates are particularly susceptible to coating fracture due to the stresses induced by substrate deformation [35]. Additionally, other disadvantages of thin films, such as sensitivity to surface preparation, cost and complexity of deposition techniques can make them less suitable for certain applications [23].
2.3.2 Thick Coatings

Thick coatings generally have a thickness ranging from tens to hundreds of micrometers. Thermal spraying, weld overlays, cladding, and electroplating are well-known deposition techniques used to apply thick coatings. Among these techniques, thermal spraying stands out as a highly versatile technology applicable in fabricating coatings for various applications, including wear, corrosion, high temperature environments as well as repair of components [37,38]. During recent years, various wear resistant materials and spraying processes have been developed to meet the specific service demands of different applications. The availability of numerous deposition routes, along with advancements in powder production technologies and feedstock chemistries, present new and promising opportunities for enhancing coating performance. However, the diversity of potentially promising candidate solutions as a result of the above has also made the selection of the right process and material combination more complex in order to achieve an optimal coating system [13]. Additionally, factors such as environmental concerns, the availability and price of both the feedstock materials as well as the processing techniques, add to the challenges involved in making the right selection. Materials for wear application that are possible to process using thermal spray can be divided into two main categories. This classification is based on the composition of the feedstock material, categorizing them as either purely metallic, intermetallic, or ceramic (single-phase), or as a combination of two or more of these materials (composite) [11].

Single-phase materials: This class of materials includes a wide variety of metals, alloys, intermetallics and ceramics. Superalloys, NiCr alloys, cobalt-based stellites, cobalt/nickel-based triballoys, NiCrBSi alloys, etc., are the most well-known metal alloys that can be applied by spraying techniques for wear applications. Also, a wide range of ceramics can be applied through thermal spraying for tribological applications. Metallic oxides including Al₂O₃, TiO₂, Cr₂O₃ and carbides like Cr₃C₂ and SiC are the most common ceramic wear resistant materials. Finally, intermetallics such as NiAl and MoSi₂ can provide thermal spray coatings with good wear-resistant properties[11].

Composite materials: To enhance performance, it is common to produce particulate-reinforced composites by combining suitable phases with different chemical and physical properties. Such combinations can offer mechanical properties that would not be achievable with individual phases alone. One widely recognized approach is the reinforcement of a metallic phase, which grants ductility and toughness, with a ceramic phase, which provide hardness and strength, leading to the formation of a material system known as cermet. Here, the term “ceramic phase” is defined as all type of hard and brittle materials [1].
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**BACKGROUND**

WC-Co/Ni, Cr₃C₂-NiCr, and TiC-NiCr are some of the most well-known cermet materials that can be applied using thermal spraying [1,11].

### 2.3.2.1 Thermally sprayed WC-based coatings

When dealing with severe wear conditions, where heavy loading is applied on the surface, the number of material candidates capable of tolerating excessive stresses is limited. Cermet materials excel as an outstanding choice for protecting surfaces in harsh tribological environments among the available alternatives. They can be tailored to meet the specific requirements of a wide variety of components that operate under various harsh wear conditions. Depending on the particular application, some of the key requirements include hardness, modulus of elasticity, toughness, fatigue strength, corrosion and oxidation resistance. These properties can be tailored through factors such as the chemistry and grain size of the carbides, the type and content of binder, and the deposition technique employed [1,39].

Among cermet chemistries, WC-Co coatings (deposited using thermal spraying) have demonstrated a unique combination of high hardness and fracture toughness, resulting in outstanding tribological performance in many industrial applications. Aerospace, oil and gas, automotive, medical, mining, wood and paper industries, among others, are some examples of industries that use WC-Co components [1,40].

Figure 2 shows typical low- and high-magnification cross-sectional images of an HVAF-sprayed WC-based coating. In high-magnification image (Figure 2, right), the light grey particles represent WC, while the dark grey areas are identified as the metallic binder (CoCr), and the black spots correspond to pores.

![Figure 2. Cross-sectional SEM images of deposited WC-CoCr coating left) low magnification, right) high magnification image of coating.](image-url)
2.3.2.2 Binder selection for thermally sprayed WC-based coatings: moving towards more sustainable elements

WC-12Co and WC-10Co4Cr are two most popular compositions for thermal spray applications [41]. These HVOF-sprayed WC-based coatings with Co-based binders can yield an excellent coating with a Vickers hardness number ranging from 1100 HV to 1600 HV, along with a fracture toughness of 4-6 MPam$^{0.5}$ [42,43]. This combination of high hardness and high fracture toughness is highly desirable for tribological applications [44]. HVOF-sprayed WC-Co coatings exhibit an exceptionally low specific wear rate, typically around $10^{-6}$ (mm$^3$·N$^{-1}$·m$^{-1}$) [45], and in certain cases, even lower, ranging from $10^{-7}$ to $10^{-8}$ (mm$^3$·N$^{-1}$·m$^{-1}$) [46,47], when subjected to BoD wear testing.

However, as pointed out in previous sections, Co has raised environmental, supply, and economic concerns, leading to its classification as a 'critical raw material' or 'conflict element' by the European Commission (EC) and the Natural Environmental Research Council (NERC) [2,48]. Reports can be found in the literature that aim to identify Co-free binder compositions that exhibit mechanical properties and tribological performance comparable to Co [49]. However, a systematic assessment of coatings with alternative binders, deposited by state-of-the-art techniques under various wear environments, was identified as a research gap to be addressed in this thesis. There has also been a consistent progress in the evolution of processing techniques such as HVOF and HVAF for depositing this class of materials, with the aim of improving coating properties and reducing operational costs. A more detailed discussion on processing techniques is provided in section 2.4.

A potential binder candidate should not only meet environmental requirements, but also exhibit promising mechanical properties and tribological performance. During recent years, there have been several investigations involving Co-free binders which have shown comparable performance with Co. Ni as a stand-alone binder [50,51], with three main weight ratios of WC-10Ni, WC-12Ni and WC-17Ni [1], is commercially available as a binder in WC-based thermal spray powders. Using this element as a binder can result in a coating system with higher corrosion resistance compared to pure Co [52]. Although limited reports are available on wear performance of thermal sprayed WC with pure Ni as binder [1,51], there are several on Ni-based binders proposed as alternatives to Co. In thermal spray applications, nickel is often combined with additional elements, such as chromium or chromium carbides to enhance its oxidation and corrosion resistance, and address its lower wear performance when compared to WC-CoCr [50,53]. A list of varied WC-based feedstock compositions, investigated in powder metallurgy and thermal spray studies, and their specifications that can be found in the literature is provided in Table 1.
BACKGROUND

In case of HVOF spraying, some Ni-based and Fe-based binders have been reported to show promising characteristics and performance. For example, NiMoCrFeCo is one of the Ni-based binders that has shown comparable performance relative to WC-CoCr as reference [49,54]. Similarly, FeNiCrMoCu and FeCrAl are two Fe-based binders that have shown promise in various applications such as wood machining, metal cutting and mining [49,54,55]. However, a comprehensive study on mechanical properties and tribological performance of HVAF sprayed WC-based coatings with above proposed binders is lacking and has been identified as a research gap. Therefore, one of the main objectives of this thesis is to assess tribological behaviour of proposed Ni and Fe-based binders, specifically FeCrAl, FeNiCrMoCu and NiMoCrFeCo deposited using HVAF technique.

Table 1. Partial list of varied WC-based feedstock compositions investigated in powder metallurgy (PM) and thermal spray (TS) literature. Further details in Paper A.

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Composition (% Mass)</th>
<th>Particle Sizes (µm)</th>
<th>Service Temp.</th>
<th>Powder Type/Hardmetal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carbide size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80WC-10CoCr</td>
<td>Co: 10.5-13</td>
<td>Fe: Max. 0.2</td>
<td>30/5 - 90/45</td>
<td>Fine, Medium, Coarse,</td>
<td>Agglomerated and sintered/ Sintered and crushed, (TS)</td>
</tr>
<tr>
<td></td>
<td>C: 5.2-5.6</td>
<td>W: Bal.</td>
<td>Very coarse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60WC-10NiCr</td>
<td>Co: 8.5-11.5</td>
<td>C: 5.0-6.0</td>
<td>15/5 - 45/15</td>
<td>Nanometric, Sub-micron,</td>
<td>Agglomerated and sintered/ Sintered and crushed, (TS)</td>
</tr>
<tr>
<td></td>
<td>Cr: 3.0-5.0</td>
<td>O: Max. 0.2</td>
<td>Fine, Medium, Coarse</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe: Max. 0.6</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-12Ni</td>
<td>Ni: 11-13</td>
<td>WC: Bal.</td>
<td>45/15</td>
<td>Fine</td>
<td>Agglomerated and sintered, (TS)</td>
</tr>
<tr>
<td></td>
<td>Fe: 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-NiCr</td>
<td>Ni: 11.0</td>
<td>Fe: 1.0</td>
<td>45/15</td>
<td>Medium</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mo: 3.0</td>
<td>Co: Max. 0.8</td>
<td></td>
<td></td>
<td>Agglomerated and sintered, (TS)</td>
</tr>
<tr>
<td></td>
<td>Cr: 2.5</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73WC-20Cr-7Ni</td>
<td>Cr: 17-21</td>
<td>Ni: 6-5.8</td>
<td>30/5 – 53/20</td>
<td>Fine</td>
<td>Agglomerated and sintered, (TS)</td>
</tr>
<tr>
<td></td>
<td>C: 6.3-7.3</td>
<td>Fe: Max. 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O: Max. 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCrWMo</td>
<td>Cr: 20.5</td>
<td>Fe: &lt;1</td>
<td>53/11 and 53/20</td>
<td>Gas or water atomized, (TS)</td>
<td>&lt;875 °C</td>
</tr>
<tr>
<td></td>
<td>W: 10</td>
<td>C: 0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo: 9</td>
<td>B: 0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu: 4</td>
<td>Ni: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr3C2-37WC</td>
<td>C: 8.11</td>
<td>Fe: 0.23</td>
<td>30/10-45/15</td>
<td>Agglomerated and sintered, (TS)</td>
<td>&lt;700 °C</td>
</tr>
<tr>
<td>18Ni1CoCrFe</td>
<td>Ni: 11.63</td>
<td>Cr: 40.74</td>
<td>1.6/0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co: 3.63</td>
<td>WC: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85WC-15(FeCrAl)</td>
<td>Fe: 10.79</td>
<td>C: 5.58</td>
<td>45/15</td>
<td>Agglomerated and sintered, (TS)</td>
<td>[54,55,72]</td>
</tr>
<tr>
<td></td>
<td>Cr: 5.58</td>
<td>O: 0.16</td>
<td>Fine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al: 1.02</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-10,20FeNi</td>
<td>Fe: 9.18</td>
<td>Mo: 1.0</td>
<td>45/15</td>
<td>Agglomerated and sintered, (TS)</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>Ni: 1, 2</td>
<td>Cu: 0.2</td>
<td>Fine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WC: Bal.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-15FeCoNi</td>
<td>Fe: 9.75</td>
<td>Ni: 2.25</td>
<td>-</td>
<td>Hardmetal, (PM)</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Co: 3</td>
<td>WC: Bal.</td>
<td>0.21±0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-10FeMn</td>
<td>Fe: 9.84, 9.69, 9.38,</td>
<td>Mn: 0.16, 0.31, 0.62, 1.6</td>
<td>-</td>
<td>Hardmetal, (PM)</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>8.4</td>
<td>WC: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.4 Deposition processes

As mentioned in previous sections, cemented carbides have been widely deposited in the form of a coating by thermal spraying. In thermal spray techniques, using a spraying system, coating feedstock materials (in powder, wire, or suspension form) are heated and accelerated towards a prepared surface that is to be coated [11]. The thermal energy can be sourced from electricity (plasma and arc) or chemical combustion, and the kinetic energy is gained from the hot plasma/gas flow stream. The state of particles at the moment of impact with the surface depends on the specific spraying technique employed, ranging from fully melted to partially melted or softened. When the fully/partially melted or softened particles impact the substrate, they deform and create so-called “splats”. Subsequent splat deposition over one another at high impact velocities leads formation of coating [11,75]. The spray deposition process is schematically illustrated in Figure 3.

![Figure 3. Schematic illustration of coating deposition using thermal spraying method; adapted from [37].](image)

Thermal spray processes can be categorized into three distinct groups: one relies on combustion for heat generation, another utilizes electrical energy (plasma or arc), and the third is cold spray, a kinetic-energy-driven method [11]. Figure 4 presents categories of thermal spray techniques and their subsets.
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![Figure 4. various thermal spray techniques; adapted from [23].](image)

WC-based feedstocks can be sprayed using various techniques, including plasma spraying (APS, VPS, LPPS, HPPS and SPS) [76–78], cold spray (CS) [79] and high velocity spraying routes (HVOF, HVAF and DG) [80–82]. Over the past decades, APS technique has been commonly used for spraying WC-based feedstocks. However, it is now very well-known that APS sprayed WC-based coatings suffer from severe decarburization of carbide particles during spraying process [4,12]. Currently, HVOF spraying technique stands as the state-of-the-art method for depositing WC-based coatings and has gained extensive use in various industries. Nonetheless, in the pursuit of a more suitable method that minimizes decarburization and oxidation of WC-based coatings while also being less energy-intensive, HVAF has started to gain significant attention.

2.4.1 High velocity techniques for depositing WC-based coatings

High velocity routes, such as HVAF and HVOF in particular, are among the most attractive techniques for spraying WC-based materials due to their capability in preventing excessive overheating of the carbides during spraying. In high velocity techniques, the objective is to increase particle impact velocities and decrease flame temperature, leading to improved adhesion and mitigation thermal damage to feedstock. Unlike plasma arc processes, these techniques derive their energy source from combustion, resulting in inherently lower temperatures. Consequently, the flame conditions result in particles that are softened or partially molten, accelerating at high speeds towards the substrate. This process ultimately yields nearly fully dense coatings with improved mechanical and tribological characteristics [13,83].
As mentioned, a very dense, well-adherent WC-based coating can be achieved by HVOF and HVAF techniques, since they provide a suitable combination of high kinetic and adequate thermal energy [57,84]. The key difference between HVAF and HVOF spraying techniques is that HVAF primarily utilizes compressed air for combustion, while HVOF employs pure oxygen. As shown in Figure 5, the resulting flame issuing from HVOF nozzle can heat particles, ranging from 1500 °C up to 3000 °C, while simultaneously accelerating them to a velocity of up to 1000 m/s through the transferred kinetic energy [11,13]. The dissolution process of WC grains in the molten metallic binder and subsequent decarburization initiates at temperatures higher than the eutectic temperature, which is approximately 1350 °C for WC-CoCr [85,86]. Therefore, thermal energy in HVOF technique still remains sufficiently high to allow for decarburization.

Instead, employing compressed air in HVAF technique can keep particle temperature under 1500 °C while in-flight particles can reach a high speed of up to 1200 m/s (Figure 5) [87,88]. This provides a greater kinetic energy with lower particle temperature compared to HVOF technique, which helps in mitigating decarburization [15,16]. Hence, the combination of very high particle speed and relatively low flame temperature paves the way for deposition of exceptionally dense coatings, with significantly reduced feedstock material degradation due to thermal effects such as oxidation and/or decarburization [15,16,89]. Moreover, the desired combination of high kinetic and low thermal energy makes HVAF a suitable method for spraying feedstock powders with smaller particle/carbide sizes, which are more prone to decarburization at high temperatures due to their increased surface area-to-volume ratio. Utilization of powders with smaller particle/carbide sizes can significantly enhance the properties and performance of the deposited coating [57,90,91]. This is further discussed in section 2.4.1.2.

Figure 5. General range of particle velocity and temperature sprayed by HVOF and HVAF techniques [11,13,88].

A comparison of decarburization ratios in case of the three spraying routes APS, HVOF and HVAF, reported in literature by various groups, is provided in Table 2.
Instead, employing compressed air in HVAF technique can keep particle temperature compared to HVOF technique, which helps in mitigating decarburization. Approximately 1350 ºC for WC-CoCr [85,86]. Therefore, thermal energy up to 1200 m/s (Figure 5) [87,88]. This provides a greater kinetic energy with lower initiation than the eutectic temperature, which is 1000 m/s through the transferred kinetic energy [11,13]. The dissolution process results flame issuing from HVOF nozzle can heat particles, ranging from 1500 ºC up to 3000 ºC, while simultaneously accelerating them to a velocity of up to 120 m/s as compared to a cylindrical nozzle with same length (named 4L0) [99]. The key difference between HVAF and HVOF techniques, since they provide a suitable combination of high kinetic and adequate thermal energy [57,84]. The key difference between HVAF and HVOF techniques is that HVAF primarily utilizes compressed air and HVOF employs pure oxygen. As shown in Figure 5, the temperatures and velocities of feedstock particles can be obtained [99]. For instance, equipping an HVAF gun with a convergent-divergent nozzle (for example 4L4) can increase average velocity of WC-CoCr feedstock particles by 120 m/s as compared to a cylindrical nozzle with same length (named 4L0) [99].

### 2.4.1.1 HVAF technique

Figure 6 shows schematic sketch of a typical HVAF gun. In this technique, compressed air and fuel are blended in a mixing chamber and directed into the combustion chamber through a ceramic insert. Feedstock powder is axially injected into the combustion chamber, heated up and accelerated through a flow stream in a De-Laval nozzle and subsequently deposited on a target surface. In HVAF, high kinetic energy causes the metallic binder in WC-based coatings to undergo plastic deformation upon impact with the substrate or underlying deposited layers. As can be seen in Figure 6, the air used for cooling the nozzle (Air 2) is combusted with the injected fuel (Fuel 2) through an afterburner system, thereby maintaining a high flame temperature for a longer period of time. In a HVAF gun, configuration design of combustion chamber and acceleration nozzle can be varied. Depending on volume of combustion chamber, length of employed nozzle as well as its convergent-divergent configuration, various in-flight temperatures and velocities of feedstock particles can be obtained [99]. Table 2. Decarburization ratio reported in case of APS, HVOF and HVAF spraying of WC.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Decarburization ratio (W_C/W_C)</th>
<th>Chemistry</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS</td>
<td>0.2</td>
<td>WC-17Co</td>
<td>[92]</td>
</tr>
<tr>
<td>APS</td>
<td>≈1</td>
<td>WC-17Co</td>
<td>[93]</td>
</tr>
<tr>
<td>APS</td>
<td>0.46</td>
<td>WC-Ni</td>
<td>[94]</td>
</tr>
<tr>
<td>HVOF (JK(1))</td>
<td>0.7</td>
<td>WC-10Co4Cr</td>
<td>[95]</td>
</tr>
<tr>
<td>HVOF (JP 8000)</td>
<td>0.12</td>
<td>WC-10Co4Cr</td>
<td>[95]</td>
</tr>
<tr>
<td>HVOF (JP 5000)</td>
<td>0.055</td>
<td>WC-10Co4Cr</td>
<td>[96]</td>
</tr>
<tr>
<td>HVOF (JP 5000)</td>
<td>0.14 – 0.16</td>
<td>WC-10Co4Cr</td>
<td>[97]</td>
</tr>
<tr>
<td>HVOF (DP(2))</td>
<td>0.114</td>
<td>WC-12Co</td>
<td>[96]</td>
</tr>
<tr>
<td>HVOF (DP 2700)</td>
<td>≈0.6</td>
<td>WC-12Co</td>
<td>[98]</td>
</tr>
<tr>
<td>HVOF (DP 2700)</td>
<td>0.13</td>
<td>WC-12Co</td>
<td>[89]</td>
</tr>
<tr>
<td>HVOF (HV-2000(3))</td>
<td>0.25</td>
<td>WC-12Co</td>
<td>[89]</td>
</tr>
<tr>
<td>HVOF (AK(4))</td>
<td>≈0</td>
<td>WC-10Co4Cr</td>
<td>[95]</td>
</tr>
<tr>
<td>HVOF (M2(5))</td>
<td>≈0</td>
<td>WC-10Co4Cr</td>
<td>[55]</td>
</tr>
<tr>
<td>HVOF (M3(6))</td>
<td>≈0</td>
<td>WC-12Co</td>
<td>[98]</td>
</tr>
<tr>
<td>HVOF (Aerospray(7))</td>
<td>0</td>
<td>WC-12Co</td>
<td>[89]</td>
</tr>
</tbody>
</table>

1JK (Jet Kote): Jet Kote™ III - NOVA-D & NOVA-FC
2JP 5000: Trademark of Praxair S.T. Technology, Inc.
3DJ (Diamond Jet): Trademark of Sulzer Metco Management AG
5AK: Trademark of Kermetico, Inc.
6M2 and M3: Trademarks of Uniquecoat Technologies, LLC
7Aerospray: Browning Thermal Systems Inc.
Also, in a study by Lyphout et al. [100], it was shown that employing nozzles with longer length can lead to improvement in performance of resultant WC-CoCr coating under abrasion test.

Figure 6. Schematic sketch of a HVAF gun (Uniquecoat Technologies LLC, Oilville, USA).

Spraying parameters such as air and fuel pressure, powder feeding rate etc. should be carefully adjusted depending on the employed gun configuration. Moreover, as discussed above, different gun configurations can result in varying in-flight particle velocities/temperatures and consequently affect characteristics of the sprayed coating. Hence, it is crucial to establish a fundamental understanding of how different gun configurations can potentially influence the characteristics and performance of the deposited coating.

2.4.1.2 Deposition of thin coatings by HVAF

Feedstock powders can differ in terms of morphology, carbide size, particle size distribution and apparent density [75,101]. As pointed out in previous sections, specific features of the HVAF technique make it viable for spraying powders with a finer particle size. In HVAF process, in-flight velocity and temperature of particles can be significantly influenced by their size [11,102]. In a study by Matikainen et al. [103], it was shown that decreasing WC-CoCr feedstock size range from 30/10 µm to 25/5 µm can result in an increase in the average velocity of particles by 30 m/s while their temperature was decreased by 50ºC, when spraying by HVAF technique. This can potentially affect the characteristics and consequently performance of the resultant coating. Bolelli et al. [17] conducted sliding and abrasive wear tests on HVAF-sprayed WC-CoCr coatings deposited from two different feedstock materials with particle size ranges of 30/5 µm and 45/15 µm, to study influence of particle size on tribological behaviour. In two wear conditions of sliding and abrasion, feedstock with finer particle size yielded superior wear performance. Thus, prior studies clearly suggest the importance of
particle size in governing the coating characteristics, and thereby their wear behaviour.

Possibility of fabricating coatings with refined microstructures, improved mechanical properties, and enhanced tribological performance may pave the way for reducing the required thickness of coatings in some industrial applications. When it comes to seeking more sustainable approaches for wear applications, reducing thickness of coatings becomes crucial from both energy and material utilization perspectives. Deposition of thinner coatings ('flash' coatings) also offers advantages in terms of processing time and cost-effectiveness. This becomes particularly significant when utilizing WC-CoCr as feedstock powder, considering the supply risk associated with W and Co elements, as well as the environmental concerns surrounding Co.
3 Experimental procedure

All the experimental steps ranging from spraying processes, microstructural characterization, mechanical and tribological testing as well as post-wear analysis are provided in this chapter. However, a more detailed explanation on each can be found in the appended papers: Paper B-F.

3.1 HVAF deposition of coatings

Table 3 shows all the feedstock powders sprayed in this study. WC-CoCr feedstock (as the reference) was used in four different particles size distributions. Also, there were three more powders with alternative binder chemistries. All the powders, acquired from Höganäs AB, were manufactured by agglomeration and sintering. Disk-shaped samples (diameter 25.4 mm and thickness 6 mm) and rectangular samples (50×25×6 mm) made from Domex 355 HSLA steel and Hastelloy X were used as substrates.

Table 3. Specifications of used feedstock powders (manufactured by Höganäs AB).

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Particle size (µm)</th>
<th>Particle size distribution (µm)</th>
<th>WC size</th>
<th>Trade name</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-CoCr 86-10-4</td>
<td>45/15 (Coarse)</td>
<td>D 10% 34  D 50% 62  D 90% 52</td>
<td>Fine</td>
<td>Amperit® 558.074</td>
</tr>
<tr>
<td></td>
<td>30/5 (Medium)</td>
<td>12 19 28</td>
<td></td>
<td>Amperit® 558.059</td>
</tr>
<tr>
<td></td>
<td>20/5 (Fine)</td>
<td>6 13 22</td>
<td></td>
<td>Amperit® 558.052</td>
</tr>
<tr>
<td></td>
<td>15/5 (Ultra fine)</td>
<td>- - -</td>
<td></td>
<td>Amperit® 558.090</td>
</tr>
<tr>
<td>WC-NiMoCrFeCo 82-18</td>
<td>45/15 (Coarse)</td>
<td>18-22 30-38 48-58</td>
<td>Medium</td>
<td>Amperit® 529.074</td>
</tr>
<tr>
<td>WC-FeNiCrMoCu 85-15</td>
<td>45/15 (Coarse)</td>
<td>17 28 45</td>
<td>Fine</td>
<td>Amperit® 531.074</td>
</tr>
<tr>
<td>WC-FeCrAl 85-15</td>
<td>17-21 29-37 49-57</td>
<td>Medium</td>
<td>Amperit® 618.074</td>
<td></td>
</tr>
</tbody>
</table>

All samples were sprayed by a M3 HVAF gun (Uniquecoat Technologies LLC, USA). As shown in Figure 7, five different nozzles with different configurations were employed for spraying the feedstock powders.
EXPERIMENTAL PROCEDURE

### 3.1 HVAF deposition of coatings

Table 3 shows all the feedstock powders sprayed in this study. WC-CoCr feedstock (as the reference) was used in four different particle size distributions. Also, there were three more powders with alternative binder chemistries. All the powders, acquired from Höganäs AB, were manufactured by agglomeration and sintering. Disk-shaped samples (diameter 25.4 mm and thickness 6 mm) and rectangular samples (50×25×6 mm) made from Domex 355 HSLA steel and Hastelloy X were used as substrates.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Particle size</th>
<th>Particle size distribution (µm)</th>
<th>D 10%</th>
<th>D 50%</th>
<th>D 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-CoCr</td>
<td></td>
<td></td>
<td>45/15</td>
<td>22</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiMoCrFeCo</td>
<td></td>
<td></td>
<td>82</td>
<td>18</td>
<td>45/15</td>
</tr>
<tr>
<td>NiMoCrFeCo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiMoCrFeCo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiMoCrFeCo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeNiCrMoCu</td>
<td></td>
<td></td>
<td>85</td>
<td>-</td>
<td>15/5</td>
</tr>
<tr>
<td>FeCrAl</td>
<td></td>
<td></td>
<td>85</td>
<td>-</td>
<td>15/5</td>
</tr>
<tr>
<td>FeCrAl</td>
<td></td>
<td></td>
<td>85</td>
<td>-</td>
<td>15/5</td>
</tr>
<tr>
<td>FeCrAl</td>
<td></td>
<td></td>
<td>85</td>
<td>-</td>
<td>15/5</td>
</tr>
<tr>
<td>FeCrAl</td>
<td></td>
<td></td>
<td>85</td>
<td>-</td>
<td>15/5</td>
</tr>
</tbody>
</table>

All substrates were cleaned and mounted on a rotating fixture for grit-blasting and coating. A target thickness of approximately 250 µm was set for all coatings deposited by the 4L2, 4L4, 5L2, and 5L4 nozzles, while coatings of various thicknesses ranging from 30 to 250 µm were sprayed using the 3L3 nozzle. Spraying angle was 90° in all cases. Spraying parameters corresponding to each powder and nozzle are presented in Papers B-F.

### 3.2 Material characterization and indentation testing

Various experiment procedures are briefly presented in this section and in section 3.3, with more detailed information provided in the annexed papers B-F.

**Material characterization:** Where deemed necessary, polished coatings, powders, and wear-tested samples were analyzed using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, and X-ray diffraction (XRD) to examine their microstructure, phase constitution, chemical analysis, and post-wear behavior.
Micro and nanoindentation: Vickers hardness of the coatings was measured by microindentation tests. Tests were done under a load of 300 gf and with a dwell time of 10 s in accordance with the ASTM E384 standard [104] at 300 ± 15 °C and room temperature (25 °C). Also, hardness and Young’s modulus of carbide grains and binders were measured employing nanoindentation testing at room temperature. The hardness was determined from the load-displacement data obtained through nanoindentation, while the elastic or Young's modulus was calculated using the method proposed by Oliver and Pharr [105].

3.3 Tribological tests and post-wear analysis

Tribological tests were conducted on the coatings under various wear conditions, including sliding wear, abrasion and erosion. These tests were performed using methods such as BoD, dry jet erosion, and sand-rubber wheel testing. After each test, post-wear analysis was performed on worn areas of the coatings’ surface. A brief information of the conducted tests is presented here and detailed information about each test and parameters is provided in the respecting appended papers.

BoD test: Unidirectional and reciprocating BoD tests were conducted using a tribometer rig (Tribometer TRB3, Anton-Paar, Switzerland) on mirror polished surfaces of the coatings. Unidirectional tests were performed at room temperature and reciprocating tests were performed at both room and elevated temperatures (300±15 °C). Various loads ranging from 5-40 N were applied on the coatings for a sliding distance of 5000 m in case of unidirectional BoD. In case of reciprocating BoD, a normal load of 20 N was applied for a total sliding distance of 1500 m with stroke length of 10 mm. Alumina balls with a diameter of 6 mm were used as the counter body in both cases. Friction coefficient evolution during the tests was monitored using an in-situ sensor.

It's worth pointing out that WC-based coatings possess intrinsic properties such as high hardness and exceptional resistance against wear, resulting in minimal material removal during sliding wear tests [89,106]. This leads to the formation of very shallow wear scars, with depths ranging from hundreds of nanometers up to a few micrometers, and consequently low volume loss and specific wear rate. However, these factors can introduce sensitivities in both the selection of test conditions and the employed measurement procedure. Therefore, it is crucial to have a comprehensive understanding of the factors influencing the BoD test results and also their impact on the sliding wear behavior of WC-based coatings. In this context, various BoD tests were performed to evaluate the effects of different test variables, including angular velocity, load, and sliding distance, on the wear behavior of WC-based coatings fabricated from WC-CoCr feedstock.
The aim of the above exercise was to establish a reliable BoD testing routine (refer to Paper B).

**Erosion test:** Dry jet erosion tests were conducted using an air jet erosion rig (TR-470 test rig, DUCOM) on mirror-polished samples. Alumina powder with median size of 50 µm was used as erodent media. The tests were run for 2 minutes with a sand feed rate of 2 g/min, at two different velocities of 30 and 70 m/s. Erosion rate of the coatings was reported based on mass loss as well as volume loss.

**Sand-rubber wheel test:** Dry sand-rubber wheel tests were conducted on the rectangular samples. The samples were exposed to three body abrasion testing in their as-deposited state. Silica Quartz sand with particle size range of 100 µm – 700 µm was employed as third body abradant. The overall test duration was 30 min for each sample. The samples were weighed at 10 min intervals and the wear rate was reported based on mass loss.

**Post-wear analysis:** White light interferometry (WLI) technique was employed to measure volume loss and determine specific wear rate of the coatings in cases of BoD and erosion tests. Procedure of volume loss measurement and specific wear rate calculation can be found in Papers C, D and F. Also, surfaces and cross sections of wear scars from all wear tests were analyzed by SEM-EDS to investigate wear mechanisms.
Summary of results

In this chapter, an attempt is to briefly summarize the main results of the study so as to answer the key research questions identified. A more detailed information of the results is provided in the appended papers.

4.1 Coating characterization

Uniform and dense coatings were achieved by HVAF spraying in all the cases. As shown in Figure 8, the homogeneity and density of the coatings did not experience any considerable changes when using various nozzles (Paper C) or when spraying WC-based powders with alternative binders employing the same nozzle (Paper D). However, as depicted in Figure 9, a decrease in feedstock particle size led to a substantial improvement in density of the deposited coatings (refer to Paper C and E). Since the overall porosity content in HVOF- and HVAF-spray WC-based coatings is reported to be less than 1 per cent [107,108], a quantitative porosity measurement of these coatings is challenging. Hence, the aforementioned conclusions are drawn based on qualitative SEM analysis.

Figure 8. Cross-sectional SE-SEM images of four coatings with different binder chemistries. Clusters of binder material were detected in all coatings in the form of binder accumulation.
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![Figure 8. Cross-sectional SE-SEM images of four coatings with different binder chemistries. Clusters of binder material were detected in all coatings in the form of binder accumulation.](image)

![Figure 9. Cross-sectional BSE-SEM images of WC-CoCr coatings deposited using three different particle sizes: coarse (left), medium (middle) and fine (right). Pores are shown by arrows.](image)

Employing various nozzles did not significantly influence the hardness of coatings deposited using a given feedstock. However, the hardness experienced a considerable increase of approximately 400 HV$_{0.3}$ when the powder particle size was reduced (refer to Paper C). Additionally, the Vickers hardness of all four coatings with alternative binders was found to be within the range of 1100 HV$_{0.3}$ and 1300 HV$_{0.3}$, with WC-CoCr exhibiting the highest hardness and WC-FeCrAl demonstrating the lowest hardness (refer to Paper D).

Referring to the XRD analysis performed (Paper C and D), no significant phase changes were found to occur in any of the coatings sprayed using the HVAF technique, regardless of the feedstock particle size or the nozzle configuration used for spraying.

4.2 Test parameters for unidirectional BoD test

As explained in Paper B, a comprehensive investigation was conducted to establish a practical testing procedure which inspires confidence in the test conditions utilized to rank different WC-based coatings. By running fifteen tests on three samples at various wear track radii between 5 – 9 mm, it was shown that no significant difference is noted in the determined specific wear rate with change in radius from 5 mm up to 9 mm (changing angular velocity). The noted difference was smaller than the precision of measurement method itself. Also, increasing the normal load up to 40 N showed no major change in specific wear rate. Moreover, increase in sliding distance up to 10 km while the applied load is fixed at 20 N also did not show any significant change in specific wear rate when compared to other test conditions employed (Paper B). All these observations were rooted in the fact that there appeared to be no major change in dominant wear mechanisms or wear regime of sprayed WC-CoCr coatings under this window of test conditions.
4.3 Influence of HVAF process variables

4.3.1 Wear performance

4.3.1.1 Unidirectional BoD, influence of nozzle configuration and particle size

Influence of spraying parameters (by using four different nozzles) along with effect of particle size (by employing three different size ranges of WC-CoCr powder) on unidirectional BoD performance of deposited coatings were evaluated.

While no clear trend was identified for the coating obtained from coarse powder (45/15 µm), coatings from fine powder (20/5 µm) performed better when spraying with longer nozzle and also when using nozzle with bigger exit diameter (N2 or N4 instead of N1). On the other hand, the wear performance of the coatings fabricated from powder with intermediate particle size (30/5 µm) showed negligible sensitivity to the selection of nozzle configuration (Figure 10), with all four coatings showing relatively similar performance.

Moving to a finer powder size range (from coarse to medium), the average value of the specific wear rate of the coatings decreased regardless of the nozzle type. Further decreasing particle size (from medium to fine) led to a further decrease in the specific wear rate of the coatings sprayed using nozzles N2 and N4. The fine powder sprayed using nozzle N4 showed the highest resistance against wear.

![Figure 10. Specific wear rates of coatings deposited using three different particle size ranges and sprayed with four different nozzles (Paper C). N1: L=250 mm, D=18.9 mm; N2: L=250 mm, D=22.75 mm; N3: L=300 mm, D=22.4 mm; N4: L=300 mm, D=25.75 mm, where L and D represent nozzle length and diameter, respectively.](image-url)
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<table>
<thead>
<tr>
<th>Nozzle</th>
<th>L (mm)</th>
<th>D (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>250</td>
<td>18.9</td>
</tr>
<tr>
<td>N2</td>
<td>250</td>
<td>22.75</td>
</tr>
<tr>
<td>N3</td>
<td>300</td>
<td>22.4</td>
</tr>
<tr>
<td>N4</td>
<td>300</td>
<td>25.75</td>
</tr>
</tbody>
</table>

Figure 10. Specific wear rate of coatings deposited using three different particle size ranges and sprayed with four different nozzles (Paper C). N1: L=250 mm, D=18.9 mm; N2: L=250 mm, D=22.75 mm; N3: L=300 mm, D=22.4 mm; N4: L=300 mm, D=25.75 mm, where L and D represent nozzle length and diameter, respectively.

4.3.1.2 Unidirectional BoD, influence of coating thickness

For the case of ultra fine powder (15/5 µm) sprayed by the shortest nozzle (3L3), coatings were deposited with various thicknesses. Under 20 N normal load, a decrease in coating thickness from approximately 240 µm (C240) to 30 µm (C30) resulted in a slight increasing trend in the specific wear rate, which increased from $1.5 \times 10^{-8}$ (mm$^3$·N$^{-1}$·m$^{-1}$) to $4 \times 10^{-8}$ (mm$^3$·N$^{-1}$·m$^{-1}$). However, as shown in Figure 11, at normal loads of 5 N and 10 N (corresponding to an average Hertzian stress of approximately 1.18 GPa), the wear performance of both the thick and thin ('flash') coatings was comparable. It should be mentioned that the 'flash' coating with a thickness of 30 µm (C30) was initially sprayed with a target thickness of 50 µm, and 20 µm was removed during grinding and polishing.

Figure 11. Specific wear rates for C240 (240 µm thickness) and C30 (30 µm thickness) coatings tested under 20 N, 10 N and 5 N normal load.

4.3.1.3 Abrasion, influence of coating thickness

Figure 12 displays the mass loss of C240 and C30 coatings deposited from ultra-fine powder (15/5 µm). It also includes results from another 240 µm thick WC-CoCr coating (Thick-coarse) deposited from coarse powder (45/15 µm), under sand-rubber wheel testing for three time intervals of 10 minutes. Reasonably constant slopes of the mass loss vs. time plots for both the tests indicate that the tests nearly reached a steady-state situation after the first 10 minutes, and also reflect the repeatability of the tests. In the case of thick coating deposited from coarse powder, Thick-Coarse, it can be seen that, unlike C30 and C240,
steady-state situation was not achieved and mass loss shows a decreasing trend, with the mass loss during the first 10 min being the highest. The reason could be the rougher as-coated surface in the case of coatings deposited from the coarse powder and the consequent preferential removal of the significant surface asperities during the early stages of testing. However, a similar slope and, as a result, an almost identical total mass loss as C240 and C30 at the end of the tests suggested comparable abrasion wear performance of the thick and thin coatings.

Figure 12. Abrasion wear performance of the thick (C240) and thin (C30) coatings along with the thick coating deposited from coarse powder (Thick-Coarse) (refer to Paper E).

4.3.2 Wear mechanisms, unidirectional BoD

The influence of process variables, including nozzle configuration and particle size, on the wear behavior of deposited WC-CoCr coatings is discussed in this section.

As described in Paper C, when different nozzles were used to spray the same powder, no significant difference was observed in the sliding wear behavior and associated material removal mechanisms. However, wear mechanism of the WC-CoCr coatings varied depending on powder particle sizes, including coarse (45/15 µm), medium (30/5 µm), and fine (20/5 µm). Decreasing the particle size from coarse to medium resulted in a significant change in the wear behavior of the corresponding coating. As shown in Figure 13, wear mechanism for coarse coatings begins with crack propagation around defects within the coatings, leading to the breakage of coating material and then becoming entrenched in the adjacent pits. Subsequent sliding of the ball potentially causes first fragmentation and removal of these particles, which can then act as third-body particles and result in the formation of relatively deep grooves on the surface. As shown in Figure 14 (a) and (b), in medium and fine coatings, no pits were observed. In these
two coatings, the wear process seemed to initiate with removal of binder, with subsequent fragmentation of unsupported carbides and as a result removal of crushed carbide grains.

This difference in removal mechanisms in the fine, medium and coarse coatings can be rooted from the higher number of defects in form of pores and binder accumulations in the coarse coatings, as was described in section 4.1. SEM analysis on debris particles (Paper C) confirmed this difference, as debris in the case of coarse coatings was much coarser as compared to that observed in medium and fine coatings. It should be mentioned that coatings deposited from ultra fine powder (15/5 µm) showed similar wear mechanism behaviour as the medium and fine cases.

![Figure 13. Damage mechanism in coarse coatings: breakage of coating material and transferring into the adjacent pit (Paper C).](image)

![Figure 14. Removal mechanisms in coatings deposited using medium and fine powders: a) medium, b) fine, (Paper C).](image)
4.4 Influence of binder chemistry

Wear performance of HVAF-sprayed WC-based coatings with four different binder chemistries (see Table 3) was evaluated by exposing them to various wear environments including sliding, erosion and abrasion.

4.4.1 BoD sliding wear performance

4.4.1.1 Unidirectional BoD, room temperature

Figure 15 shows average specific wear rates along with the standard deviation (obtained from three repetitions in each case) for the four coatings (WC-CoCr, WC-NiMoCrFeCo, WC-FeNiCrMoCu and WC-FeCrAl) under unidirectional BoD test performed at room temperature. The specific wear rate for all the four coatings was in the order of $10^{-7} - 10^{-8}$ (mm$^3$·N$^{-1}$·m$^{-1}$), which is considered as extremely low. The coating WC-NiMoCrFeCo clearly showed the best performance, while the coating WC-FeCrAl showed the least resistance against wear under unidirectional BoD sliding wear conditions.

![Figure 15. Specific wear rates of four WC-based coatings with different binders under unidirectional BoD tests performed at room temperature, (Paper D).](image)

4.4.1.2 Reciprocating BoD, room and high temperature

Figure 16 displays the specific wear rates (with their corresponding standard deviations) for the four coatings obtained from the reciprocating BoD tests conducted at both room and elevated temperature. The reciprocating specific wear rate for the four coatings at room temperature was of the order of $10^{-8}$ (mm$^3$·N$^{-1}$·m$^{-1}$) and comparable in magnitude to the wear rate of the reference HVAF WC-CoCr coating obtained from unidirectional BoD. However, the wear rate for the HVAF-sprayed WC-FeCrAl coating at room temperature was reduced...
from $1.8 \times 10^{-7} \text{ (mm}^3\text{N}^{-1}\text{m}^{-1})$ during unidirectional testing to $5 \times 10^{-8} \text{ (mm}^3\text{N}^{-1}\text{m}^{-1})$ during reciprocating BoD testing (compare Figure 15 and Figure 16).

Specific wear rates of tests conducted at elevated temperature were significantly higher than those at room temperatures. The coatings WC-CoCr, WC-NiMoCrFeCo, and WC-FeCrAl exhibited wear rates that were one order of magnitude higher than those observed during the room temperature tests. High temperature wear performance of all three coatings was comparable and in the range of around $2.5 \times 10^{-7} - 3.5 \times 10^{-7} \text{ (mm}^3\text{N}^{-1}\text{m}^{-1})$. In the case of WC-FeNiCrMoCu, the wear rate was about two orders of magnitude higher than that of the reference WC-CoCr, with the high temperature specific wear rate for the coating reaching around $1.1 \times 10^{-6} \text{ (mm}^3\text{N}^{-1}\text{m}^{-1})$.

4.4.2 BoD sliding wear mechanisms

4.4.2.1 Unidirectional BoD, room temperature

Figure 17 displays SEM micrographs of wear tracks from room temperature unidirectional BoD tests captured at three different magnifications. The presence of pits on the top surface of the WC-CoCr and WC-FeNiCrMoCu samples indicated local delamination of the coating material. From the SEM images, it was evident that the occurrence of these pits was notably higher in the WC-CoCr sample compared to the WC-FeNiCrMoCu coating. No detectable signs of pitting were observed in the WC-NiMoCrFeCo coating, and there were only a negligible number of pits in the WC-FeCrAl coatings, which were significantly smaller in size compared to those on the WC-CoCr and WC-FeNiCrMoCu samples.
Notably, pitting of these two coatings has been reported in other studies [49,109] too when they were sprayed using HVOF.

Figure 17. SEM micrographs of worn surfaces of four coatings WC-CoCr, WC-NiMoCrFeCo, WC-FeNiCrMoCu and WC-FeCrAl with three different magnifications, (Paper D).

4.4.2.2 Reciprocating BoD, room temperature

A different trend was observed in terms of wear mechanisms of the four coatings when tested under room and high temperature reciprocating BoD. Figure 18 shows SEM micrographs of wear tracks from room temperature tests captured at two different magnifications. Ripple patterns were found on the worn surface of all the coatings except WC-FeCrAl. Looking at the higher magnification SEM images (column b), the ripple patterns seemed to be formed as a result of the interaction between wear products and the coating surface. Besides the formation of ripple patterns, frequent carbide pull-outs can be detected on the worn surface which is a common material removal mechanism in this type of coating [3,110]. Removal of the carbide grains can pave the way for the formation of pits and as
a result material removal on a larger scale (see high magnification SEM micrographs of WC-FeNiCrMoCu and WC-FeCrAl) in Figure 18.

Comparing Figure 17 and Figure 18, formation of pits was less frequent and smaller in size in the reciprocating sliding wear tests as compared to the unidirectional sliding wear test performed on the same coatings deposited using the same technique.
4.4.2.3 Reciprocating BoD, high temperature

SEM micrographs in Figure 19 depict wear tracks from elevated temperature tests at two different magnifications. The WC-CoCr coating exhibited severe networks of cracks, while the WC-FeNiCrMoCu coating displayed less severe cracking but with a similar pattern. The WC-NiMoCrFeCo coating had parallel semi-circular fatigue cracks within the track, and the WC-FeCrAl coating showed rare cracks and frequent carbide pull-out. Cracks in the WC-CoCr coating originated from defects and stress-concentrated areas, spreading throughout the coating. The WC-FeNiCrMoCu coating exhibited cracking on a smaller scale than the WC-CoCr coating. In the case of WC-NiMoCrFeCo, the notably different cracking behavior compared to other coatings was attributed to the limited pit formation during wear. Therefore, semi-circular cracks formed in regions of high tensile stress behind the moving contact point, likely due to shear stresses. The WC-FeCrAl coating displayed intergranular and transgranular cracks. However, large pits observed in the WC-CoCr coating were absent in the WC-FeCrAl coating.
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4.4.3 Erosion wear performance

Jet erosion tests were conducted under three test conditions: A (particle velocity: 30 m/s, time: 10 min, impact angle: 90°), B (particle velocity: 30 m/s, time: 10 min, impact angle: 45°), and C (particle velocity: 70 m/s, time: 4 min, impact angle: 90°). Figure 20 illustrates the mass loss and erosion rate for the four coatings under the three jet erosion test conditions A, B, and C. For test conditions A and B, WC-CoCr exhibited the least amount of average mass loss, while WC-NiMoCrFeCo showed the highest. However, the overlap in error bars (representing standard deviation) hinders a clear ranking based on the results from these two test conditions. Regarding the erosion rate for the four coatings, WC-CoCr demonstrated the most superior performance against erosive wear, whereas WC-NiMoCrFeCo exhibited the lowest resistance to dry jet erosion. WC-FeNiCrMoCu and WC-FeCrAl coatings, on the other hand, displayed similar behavior under the erosive wear environment.
4.4.4 Erosion wear mechanisms

Post-wear analysis of erosion pits revealed that binder chemistry can have a slight influence on the material removal mechanism of coatings when tested under erosion wear conditions. Figure 21 presents SEM images of the surface morphology of erosion pits at three different magnifications for the four coatings with different binder chemistries under test condition A. At low magnification, the coating WC-NiMoCrFeCo displayed a smooth surface with a lower number of pits and bulges. The protuberances in the other three coatings appeared relatively similar. Looking at the medium magnification images, the removal mechanisms of the coatings exposed to erosion wear conditions can be identified. Four main removal mechanisms, namely pitting (I), ploughing (II), shoveling (III), and chipping (IV), were observed on all surfaces [21]. The coatings WC-CoCr, WC-FeNiCrMoCu, and WC-FeCrAl exhibited mostly similar behavior.

Figure 21. Morphology of the erosion pits for four coatings tested under test conditions A, (Paper D).
4.4.5 Abrasive wear performance

Figure 22 displays the mass loss for the four WC-Co-based HVAF coatings with different binder chemistries when subjected to dry sand-rubber wheel abrasion wear testing. WC-CoCr coating demonstrated the best performance among all the coatings, followed by WC-NiMoCrFeCo, WC-FeNiCrMoCu, and finally WC-FeCrAl. It is notable that, for all the coatings, the mass loss vs. time plot exhibited a steeper slope during the first 10 minutes of the test. This can be attributed to the presence of surface asperities in the as-sprayed samples, resulting in a higher rate of material loss during the initial stages of the test. As the test progresses into two subsequent 10-minute intervals, the slope of the mass loss significantly decreased and remained relatively constant, suggesting the attainment of a steady-state condition. The nearly identical slopes observed for all coatings between 10-30 minutes indicate that the steady-state wear rate was approximately the same for all four coatings.

![Figure 22. Abrasive performance of four coatings, (Paper D).](image)
5 Conclusions and future works

5.1 Summary and conclusions

This study was conducted with the aim of investigating the influence of process variables on the characteristics and behavior of HVAF-sprayed WC-based coatings. Additionally, it aimed to evaluate the performance of more sustainable binder chemistries as a replacement for Co, as well as the performance of coatings with reduced thickness achieved by depositing fine particle powders using the HVAF method. The findings indicated that the HVAF technique excelled in processing WC-based powders of different size distributions, allowing for the production of thinner coatings ('flash' coatings) using fine powders. Moreover, it was determined that the Co-lean/Co-free binders exhibited similar or better performance under different wear scenarios. These results represent an advancement towards sustainable methods of surface protection, as they reduce dependence on critical materials.

The main findings of this study are summarized in the following three categories, which provide answers to the research questions RQ1, RQ2, and RQ3.

RQ1: How do process variables influence characteristics of HVAF-sprayed WC-based coatings? (Paper A, C and E):

- Reduction in particle size led to an increase in coating density, homogeneity, and subsequently, the hardness value of the coating. No significant difference was observed among the coatings deposited in this study using various nozzles, which confirms the reliability and robustness of the HVAF technique.
- Superior wear performance of the coatings was observed by decreasing the feedstock particle size.
- Coatings with reduced thickness (~30 µm instead of the typical 200 µm) exhibited similar performance when the Hertzian stress was less than 1 GPa under BoD test. Furthermore, thin coatings showed similar performance under sand-rubber wheel abrasion testing.

RQ2: How do the proposed binder alternatives (to Co) perform in different wear environments? (Paper D and F):

- Comparable hardness values were obtained for all the alternative binders compared to the reference Co binder.
- Superior or comparable performance was achieved for the FeNiCrMoCu and NiMoCrFeCo binders compared to the reference Co-based binder.
under room temperature unidirectional BoD conditions. When comparing the reference Co-based binder with other alternatives, the FeCrAl binder showed comparable erosion and abrasion performance.

- Under high temperature (300 ± 15 °C) reciprocating BoD test, the NiMoCrFeCo and FeCrAl binders exhibited comparable performance to the reference CoCr binder, with specific wear values ranging from approximately $2.5 \times 10^{-7} – 3.5 \times 10^{-7}$ (mm³·N⁻¹·m⁻¹).

RQ3: How do process variables and binder chemistry influence wear mechanisms under different wear environments in HVAF-sprayed WC-based coatings? (Paper B-F):

- Ploughing, grooving, and pitting were the main removal mechanisms observed in coarse feedstock coatings, while ploughing was the dominant wear mechanism in medium and fine feedstock coatings during sliding wear conditions.

- The dominant wear mechanisms observed for the reference WC-CoCr coating during sliding wear testing were deep grooving, excessive cracking, and subsequent pitting. In contrast, the WC-NiMoCrFeCo and WC-FeCrAl coatings did not exhibit material removal in the form of pitting under sliding wear conditions. Instead, material ploughing was the dominant wear mechanism for these coatings. WC-NiMoCrFeCo exhibited slightly different behavior in terms of erosion mechanism.

- The dominant phenomenon observed during room temperature reciprocating BoD tests was the presence of ripple-like patterns on the surface. However, during elevated temperature reciprocating BoD tests, a wider range of wear mechanisms was observed. These included macro excessive cracking of the coating material, the formation of micro fatigue cracks, as well as pitting and the development of severe oxide formation on the surface.

- During high-temperature reciprocating BoD testing, the main wear mechanisms observed for both the WC-CoCr and WC-FeNiCrMoCu coatings were the formation of macro-scale networks of cracks, which originated from pits, micro fatigue cracks, and carbide pull-outs. In WC-NiMoCrFeCo, distinct crack formation arose from limited pit formation during wear, resulting in semi-circular cracks in regions with high shear stresses. Notably, the WC-FeCrAl coating exhibited a considerably higher frequency of excessive tribolayer formation compared to the other coatings.
5.2 Future works

Based on the groundwork laid during the present study, the following areas seem to be of interest for future studies:

- Given the high potential of the HVAF technique in preserving the original composition of the feedstock intact, exploring the spraying of WC-based powders with smaller carbide grains could be interesting. Evaluating the characteristics and performance of such coatings could clarify previous doubts regarding the influence of carbide grain size. Most studies in this area have been conducted with HVOF, where decarburization of smaller carbides poses a significant challenge.
- It is suggested to conduct a systematic parametric study on HVAF spraying parameters, including spray distance, air and fuel pressure, combustion chamber and nozzle configuration, particle size, etc. Design of experiment techniques can be employed to facilitate this study.
- Performing regular BoD and three-body abrasion tribological tests under more severe loading conditions on WC-based coatings with alternative binders could provide more insights into their performance. Additionally, supplementary tribological tests such as slurry erosion, slurry abrasion, etc., may also be of interest.
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Appended Publications
Advances in thermally sprayed WC-based wear resistant coatings: Co-free binders, processing routes and tribological behaviour

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Paper A

Advances in thermally sprayed WC-based wear resistant coatings: Co-free binders, processing routes and tribological behaviour

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Advances in Thermally Sprayed WC-Based Wear-Resistant Coatings: Co-free Binders, Processing Routes and Tribological Behavior

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Abstract A growing understanding of wear behavior of various thermally sprayed ceramic–metallic matrix coatings has occurred over recent years. This has resulted from the continuous evolution in spraying methods as well as material feedstock, and the corresponding new aspects of the field that have been thoroughly explored. This paper aims to review recent developments in thermally sprayed tungsten carbide-based coatings, with specific emphasis on evaluating alternative binders, processing routes and tribological behavior of the coatings. A comprehensive evaluation of various compositions as binders for WC-based coatings, considering environmental concerns and market requirements has been carried out. The properties and performance of various potential alternatives for cobalt as a conventional binder for these coatings have been assessed. Moreover, different thermal spray methods have been reviewed, particularly highlighting the role of processing parameters, phase change and feedstock characteristics in the high-velocity oxy-fuel (HVOF) and high-velocity air fuel (HVAF) techniques. A comparison is made between HVAF and HVOF coatings in terms of their performance under different wear environments. Finally, various scenarios of material removal in HVAF and HVOF coatings, under various wear conditions, have also been reviewed.

Keywords Co-free binders · HVAF · HVOF · tribology · WC-based coatings · wear mechanisms

Introduction

Tungsten carbide (WC)-based metal matrix composite coatings are the most popular materials used as a thermally sprayed wear-resistant layer (Ref 1, 2), thanks to their excellent performance in severe wear environments (Ref 1, 3, 4). These coatings consist of two main phases: first, WC grains as a hard phase to resist against wear and, second, a metal matrix that acts as a ductile binder phase to hold the carbide grains together and provide them physical support (Ref 5). Embedded WC grains in a tough binder offer a hard composite system that has a high overall toughness (Ref 3). Cobalt is the most commonly used binder in the cemented carbide coatings (Ref 6, 7). However, apart from supply risk and economic reasons, this element is also not desired as it is known to be a carcinogenic material (Ref 8, 9). Consequently, during recent years, there has been extensive research to find a suitable substitute for Co as a binder in WC-based wear-resistant coatings. A comprehensive review is performed on hardmetal compositions for thermal spray coatings in (Ref 7) discussing various binder chemistries used in their systems. In another review by Wood et al. (Ref 10), mechanical properties (i.e., hardness and fracture toughness) of Co and Ni as binder with various fraction ratios are compared. Mechanical properties of WC-based hardmetals with iron-based alloys as binder were reviewed by Ojo-Kupoluyi et al. (Ref 11). However, an update on existing potential candidates considering the processing route, mechanical properties and how they perform when comparing to the reference Co binder seems essential.

Thermal spray technique is the most frequently used processing route to deposit a WC-based coating on a substrate. Thermal spray techniques can be categorized based on the amount of thermal and kinetic energy transferred...
from the high-temperature, high-velocity gas stream to the feedstock particles. These transport processes control the particle temperature and velocity, having a huge effect on the resulting coating microstructure and its performance. In a thermal spray system, once the feedstock material (in its powder form) is injected into the plasma flame (in case of plasma spraying) or the combustion flame (in case of high-velocity techniques), heat transfer takes place from the gas stream to the surface of the feedstock particles through convection and the inside of the particles heats up through conduction. The final temperature of the particle at impact depends on the temperature and heat transfer coefficient of the flame, feedstock chemistry and morphology (which determines particle’s thermal conductivity), and size distribution of the used feedstock particles. On the other hand, depending on the flame stream velocity, the amount of kinetic energy transferred to the particles can be different, which can determine the impact velocity of the particle. For a given feedstock composition, this velocity also depends on the size distribution of feedstock particles which governs mass of the particles. Atmospheric plasma spray (APS), high-velocity oxy-fuel (HVOF) and high-velocity air fuel (HVAF) are some of the most commonly used process routes for applying WC-based coatings. According to several reports, it is very well known that APS-sprayed WC-based coatings suffer from severe degradation (i.e., oxidation, decarburization, etc.) of the feedstock material during the spraying process (Ref 12-14). Among all thermal spray methods, high-velocity routes (i.e., HVAF and HVOF) provide a suitable combination of very high kinetic energy and adequate thermal energy to deposit dense, well-adherent coatings ideal for wear and corrosion applications. Due to velocity being high, the resulting coating is highly dense, and the porosity is minimized (Ref 15, 16). However, utilizing these techniques to build up a composite coating system demands a thorough understanding of the influence of process parameters on microstructure characteristics and, as a result, wear performance of the resultant coating. A typical microstructure image of HVOF- and APS-sprayed WC-Co coating is shown in Fig. 1(a) and (b), respectively. The mean carbide grain size of the feedstock powder used in APS coating was $17.5 \pm 7 \mu m$, and carbide grains of fine size ($\sim 2 \mu m$) were used in the HVOF coating. It can be seen that, in the HVOF coatings, even the small carbide grains were retained while in plasma spray coatings they were not, because of the considerably higher temperature encountered. Also, there are a large number of visible pores in the plasma spray coating, whereas the coating deposited by HVOF method exhibits a denser microstructure. Review studies can be found in literature discussing how the selected spraying route can influence in-flight state of feedstock powders and consequently microstructure characteristics as well as degradation in phase composition of WC-based coatings (Ref 1, 14, 17, 18), by mainly focusing on HVOF and APS as processing technique. Given the high potential of HVAF technique in retaining phase constitution of feedstock powders, due to its practical lower flame temperature, it seems vital to perform a review on its capability, challenges and competitiveness in processing this class of materials. Moreover, a detailed review is crucial to evaluate effective factors during spraying process by focusing on limitations and possibilities of HVOF and HVAF as the two processing routes for spraying WC-based materials.

WC-based coatings are usually exposed to a variety of wear environments, including two- and three-body abrasion, sliding, erosion and impact conditions. Sliding and abrasion are the most frequently encountered wear modes, with abrasion being reported to be the most common wear mode accounting for more than 50% of wear problems in the industry (Ref 21). Erosion and impact also can be problematic wear phenomena for a variety of applications such as turbine blades, pipelines, propulsors, etc. (Ref 22, 23). Generally, in a wear process, more than one wear mode prevails, amplifying the complication of the phenomenon. Besides, having WC-based composite coatings comprising hard carbide grains with irregular shapes dispersed randomly throughout the coating as a wear counterpart makes the wear process even more complicated (as...
comparative to homogeneous material). There have been several investigations conducted to evaluate tribological behavior of WC-based coatings under various wear conditions. Ahmed et al. (Ref 6) reviewed sliding wear performance of thermal spray WC-12Co coatings with the focus on coating microstructure, carbide and binder characteristics, post-treatment and test environment. Also, reviews have been performed to evaluate effect of feedstock characteristics (Ref 24, 25) on wear behavior of WC-Co coatings as well as tribocorrosion performance of thermal spray WC-based coatings (Ref 10). However, a comprehensive assessment of wear performance of WC-based coatings, taking processing route and wear conditions into account, seems essential. Besides, a fundamental understanding of different mechanisms of material removal in each of the three wear conditions seems crucial to design and develop an improved coating microstructure suitable for the desired application.

The emerging market pull for an alternative that meets environmental concerns and supply challenges has also contributed to the growing challenges to be addressed. In response to the above, a large variety of different feedstock materials have been introduced as a “green” binder for WC coatings. However, the wear performance of the proposed alternatives in comparison to the benchmark Co is not fully reviewed yet. Also, there have been successive efforts in progress of deposition techniques, reviewing the success of the recent processing routes such as HVOF and HVAF, which are increasingly acknowledged as being most promising for depositing cermet coatings, seems meaningful at the moment. Moreover, considering several contradicting reports regarding the comparability of the performance of HVOF and HVAF methods, conducting a review on the latest comparative investigations seems vital. Finally, conducting a review on wear mechanisms of thermally sprayed WC-based coatings can provide a comprehensive understanding of the material removal of WC-based coatings under different wear environments. As discussed, it is acknowledged that there have been several reviews performed (Ref 1, 6, 7, 10, 11, 14, 17, 18, 24, 25) on the subject. However, no comprehensive review exists to provide an overview of these different factors (binder chemistry, spray process and tribological behavior) in a single article. Considering these different aspects together is often necessary to select and achieve an optimal coating. In this paper, a comprehensive review is done to identify the most recent investigations in the field and to highlight the necessity of further attention to the ground. In the next section, a review is provided on binder selection and concerns in this regard. In “Processing Routes” section, the deposition techniques and parameters are provided with an emphasis on HVOF and HVAF methods. In “Tribological Behavior” section, a comparison on the performance of HVOF versus HVAF coatings is provided. Additionally, a discussion on different wear mechanisms under sliding, abrasive and erosive wear environments is reviewed, followed by “Summary and Conclusions” section.

Binder Selection

Binder, in WC-based composite coatings, acts as “cement” by firmly holding the hard carbide grains together. The desired cemented carbide composite coatings should have a combination of properties such as high strength, toughness and hardness which are crucial for wear applications. These performance parameters are necessary conditions but not sufficient. There are other determining factors such as supply risk, price and most important among them is environmental considerations (Ref 9). So, the selection of binder can critically influence the performance, sustainability and environmental aspects of the WC-based coating. In this section, different compositions as candidate binders will be presented and discussed.

Cobalt as a Conventional Binder

Co is the most common element used as a binder in cemented carbide coatings, deposited by different thermal spray methods such as plasma spray and high-velocity techniques, over the past decades (Ref 14, 26, 27). It shows excellent wetting during the sintering process, and good adhesion properties, leading to a strong carbide–binder bonding in both hardmetals as well as coatings (Ref 28, 29). Its ability to impart excellent wear performance when blended together with WC and outstanding mechanical properties such as ductility, malleability and strength makes Co the desirable choice as a matrix material to derive the best performance from cemented carbide coatings (Ref 30, 31). WC-Co feedstock deposited using HVOF technique can result in a hard coating with Vickers hardness number in the range of 1100 HV to 1600 HV and fracture toughness of 4 MPam^{0.5} to 6 MPam^{0.5} which is a desired combination for tribological applications (Ref 32, 33). HVOF-sprayed WC-Co coatings exhibit a very low specific wear rate, typically in the order of 10^{-6} \text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1} (Ref 34, 35) and in some cases even lower in the range of 10^{-7} to 10^{-8} \text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1} (Ref 36, 37), when exposed to sliding wear testing. The sliding wear tests were conducted at room temperature using ball-on-disk rigs with alumina and tungsten-based balls as counter bodies, under various loads ranging from 10 to 100 N, and for sliding distances up to 5000 m. Also, it has been reported to show promising performance under abrasion and erosion wear (Ref 38, 39). Performance of WC-Co will be discussed in
more detail in the following sections, and it is selected as the reference coating for deliberations on alternate binder chemistries in this paper.

Cr is typically added to Co in the binder when high requirements for corrosion and oxidation resistance are present, because of the relatively poor corrosion resistance of the latter (Ref 6, 40). The two compositions of WC-10Co4Cr and WC-6Co8Cr are commercially available for thermal spray (Ref 41, 42). WC-10Co4Cr, in particular, is nowadays extensively used in thermal spray coatings for combined wear and corrosion resistance purposes (Ref 7, 43). However, there have been some environmental, supply and economic concerns around Co for it to be frequently labeled as a “critical raw material” or “conflict element” by the European Commission (EC) and National Environmental Research Council (NERC) (Ref 9, 44).

Environmental risk: Cobalt is classified as carcinogenic and genotoxic by the International Agency for Research on Cancer (IARC) (Ref 45) and by the Department of Health and Human Services (Ref 46). It can lead to higher toxicity when combined with WC (Ref 46, 47). It can also promote some immune reactions such as inflammation in exposed tissues (Ref 48). There is a particularly higher risk with Co used in wear applications, because it potentially produces particles in the nanosize dimension in the form of wear debris, which can be disseminated systematically through the lymph and vascular system (Ref 48-50).

Supply risk: Co is generally mined as a by-product of other elements (Ref 9, 51). Most of the Co reserves are in the seafloor, and not economically efficient to mine (Ref 52). According to Fig. 2, around 70% of Co produced worldwide in 2018 was from Congo. Moreover, this country accounts for more than 50% of the Co reserves (Ref 53). This makes the role of other countries limited in terms of planning against supply risk of this element.

Price: Although efficient recycling of the metal by industries as well as using Co-free alternatives are two strategies to reduce raw Co dependency and to keep Co price relatively stable in the long run, there has been a dramatic recent increase in its price. For example, the price has risen by 36 and 54% during 2017 and 2018, respectively (Ref 54).

It should be mentioned that the latter two considerations, i.e., supply risk and price, are true for Tungsten too. This motivates the assessment of other carbides as a suitable alternative (Ref 52, 53), although this particular review only focuses on substituting Co in WC-based coatings.

Substitution of Cobalt

Several reports can be found in the literature trying to find a binder composition that is comparable to Co, in terms of mechanical properties and tribological performance. In this section, some of the recent investigations in this area are provided.

Alternatives Produced by Powder Metallurgy Techniques

Although the material compositions discussed in this section were prepared using conventional powder metallurgy methods, the results can provide useful insight into the performance of these compositions since they are all possible to be thermally sprayed. One short-term solution for moving toward Co-free binders is to reduce Co content in WC-Co cerments by partially replacing Co with other

![Fig. 2 Amount of Co production and estimated reserves in different countries around the world (based on data from (Ref 53))](image)
elements such as Ni. In WC-CoNi composite samples produced by powder metallurgy method, with various contents of Ni and Co, when Co content is between 0 and 10 wt.%, an increase in Ni content first leads to a decrease in wear resistance, but further increase up to 20 wt.% results in improvement in wear performance of the hardmetal (Fig. 3). When Ni is at 20 wt.% in the binder phase, the maximum wear resistance occurs at around 10 wt.% of Co. Then, from this point, a continuous decrease in Ni with simultaneous increase in Co results in better wear performance (Ref 55). Tarrago et al. (Ref 56) studied fatigue properties of WC-based hardmetal samples by using Ni binder as a substitution for Co. It was shown that fatigue sensitivity of WC-Ni was comparable to that of the Co binder.

A systematic study on a Fe-based binder alloyed with Ni, Mn and Co was performed by Schubert et al. (Ref 57) by using powder metallurgy production technique. Their results showed that the two compositions WC-8.5Fe1.5Ni, with carbide size of 0.5 μm, and WC-7Fe2Ni1Co, with the same carbide size, exhibited the best hardness–toughness combination. Figure 4 shows a combination of wear performance and Vickers hardness for samples with different binder compositions. Several binder alternatives were found to yield comparable wear performance as the reference WC-Co. It may further be noted from Fig. 4 that despite similar hardness values, wear performance can significantly vary and vice versa, i.e., several alternatives exhibited comparable wear rate in spite of different hardness values. There have also been attempts to “engineer” the composition of binder materials by changing the percentage of various elements of the same compositions.

Liu et al. (Ref 58) used the calculation of phase diagram (CALPHAD) method to investigate the best possible composition of Fe-Ni-Co to act as an alternative to Co. Four compositions including 72Fe28Ni, 50Fe25Co25Ni, 70Fe12Co18Ni and 82Fe18Ni were selected because of their increased hardness due to being close to the martensitic transformation line (from austenite) in ternary diagram. Also, 15Fe85Ni was chosen because of its large carbon window (possibility to change the carbon content over a wide range without precipitation of γ-phase or graphite). Since a combination of high hardness and fracture toughness is desired for wear applications (Ref 11), this was used as the criterion to rank different compositions. 82Fe18Ni binder showed the best combination of hardness and fracture toughness among all initially selected compositions (see Fig. 5). Ni content being high, leading to a softer binder, was found to be the explanation for worse hardness and fracture toughness combination of 15Fe85Ni. Based on results shown in Fig. 5, they suggested that, for samples with a lower hardness range, fracture toughness of the hardmetals strongly depends on binder composition, while for hardness values above 1400 HV0.3, the fracture toughness is similar regardless of binder composition (graphs b and c in Fig. 5). Other Fe-based (WC-40vol%(-FeAl-B) and Ni-based (WC-40vol%(Ni3Al-B)) binders, as potential substitution of Co, have also been reported to show promising results (Ref 59).

Ni-Based Alternatives Processed by Thermal Spray

Ni as a stand-alone binder, with three main weight ratios of WC-10Ni, WC-12Ni and WC-17Ni, is commercially available in thermal spray grade WC-based feedstock (Ref 7, 60-62). While this element as binder can result in coating systems with higher oxidation resistance compared to Co (Ref 63), employing it in pure form does not provide desired oxidation and corrosion resistance. Although limited reports are available on wear performance of thermal spray WC-based coatings with pure Ni as binder (Ref 7, 61), several studies can be found on Ni-based compositions with some additional elements. For thermal spray, because of poor oxidation resistance (Ref 64) and corrosion resistance of pure Ni as binder (Ref 60, 65) as well as its inferior wear performance compared to WC-CoCr (Ref 61, 66), it is used typically with addition of other elements such as chromium or chromium carbides (Ref 67, 68). The composition 73WC-20CrC7Ni is an example with high chromium content in a way that the high content of Cr can lead to the formation of (W, Cr)2C phases (Ref 7, 63). The feedstock powder with a composition of WC-(W, Cr)2C-Ni was one of the first to be thermally sprayed as a coating with the general composition of 70WC24Cr26Ni (Ref 7, 69). Although there could be slight variations in the content of different constituents, commercial feedstock powders of this composition are currently available with designations of WC-CrC Ni, WC-Cr2C Ni or simply WC-NiCr (Ref 70). Unlike WC-Co and WC-CoCr, high

![Fig. 3 Wear performance of WC with NiCo binder at different ratios (Ref 55)](image-url)
resistance against oxidation makes it possible to spray these feedstocks at relatively higher temperatures (Ref 71).

Addition of 4 wt.% of Cr to HVOF-sprayed WC-Ni can increase the Vickers hardness value by around 150 HV0.3 (Ref 61). Although Cr can provide some benefits to the coatings, i.e., improvement in corrosion performance (Ref 60) and enhancement mechanical properties such as hardness, there is no known meaningful correlation between addition of Cr and improvement in wear performance of the coatings. As exhibited in Fig. 6, the performance can be inferior or superior to that of WC-Ni and WC-Co (both produced by agglomeration and sintering technique), depending on the content of elements in the feedstock composition. In Fig. 6, Cr content decreases from 4% in “WC-NiCr-1” to 3.5% in “WC-NiCr-2” and its content is 1.5, 4 and 8% in “WC-CoCr-1”, “WC-CoCr-2” and “WC-CoCr-3”, respectively (Ref 61). While WC-NiCr-1 showed inferior wear performance, WC-NiCr-2 exhibited superior performance compared to both WC-Ni and WC-Co. Al-Hamed et al. (Ref 72) attempted to reduce the amount of...
Co in HVOF-sprayed WC-based coatings by adding varied proportions of Inconel 625 alloy. It was shown that a composition of 75% WC-12Co (with nanosize WC grains) and 25% Inconel 625 exhibited the best wear performance followed by a blend of 12.5% WC-12Co (with nanosize WC grains) and 12.5% WC-12Co (with micro-WC grains) together with 75% Inconel 625.

Despite the addition of Cr to WC-based coatings with Ni (or Co) as binder, corrosion performance is still not satisfactory (Ref 7). To reach good corrosion resistance, more complex binders such as NiMoCrFeCo and FeCrAl entered the market (Ref 73, 74). The latter is categorized as Fe-based binder and discussed in the next section. Hastelloy C-type Ni-based NiMoCrFeCo binder has been shown to exhibit promising performance compared to the reference WC-CoCr (Ref 75, 76). HVOF-sprayed WC-NiMoCrFeCo shows similar performance to WC-CoCr reference under sliding wear conditions and comparable performance under three-body abrasion wear environments with the reference. This alternative is shown to outperform WC-CoCr in 3.5% NaCl aqueous solution because of its better pseudo-passivation ability (Ref 75).

**Fe-Based Alternatives Processed by Thermal Spray**

Fe-based binders, involving Fe alloyed with Al, Mn, Mo, Ni, Cr, etc., such as FeCrAl and FeNiCrMoCu are the other alternatives showing promising tribological performance. Testa et al. (Ref 75) evaluated wear and corrosion performance of HVOF-sprayed WC-FeNiCrMoCu in comparison to WC-CoCr as the benchmark. Although it showed slightly inferior corrosion resistance compared to WC-CoCr in a 3.5% NaCl solution, it exhibited similar sliding wear performance and comparable performance under high-stress abrasion condition. Nahavi and Jafari (Ref 67) studied microstructural and mechanical properties of WC-based coatings with two alternative binders, Fe-based and Ni-based, applied by HVOF technique. They employed Fe-based FeCrAl and Ni-based NiMoCrFeCo as a binder and compared their performance with Co. They found that the WC-FeCrAl coating system accounts for the highest microhardness among all the three with values approaching 1500 HV0.3. However, both proposed alternatives yielded a substantially lower fracture toughness as compared to conventional WC-Co. Considering that the WC phase accounts for around 80-85 wt.% of WC-based coatings, it is crucial to discuss how mechanical properties such as microhardness and fracture toughness are influenced by properties of the binder. Besides, the employed processing routes and powder characteristics, like size range of carbide grains, can also influence properties of the coating (Ref 6) which is discussed in “Role of Feedstock Characteristics” section. So, in spite of promising mechanical properties of the alternatives, it is crucial to critically evaluate differences in performance attributable to use of alternative binders. Bolelli et al. (Ref 77), in their study investigated the mechanical and tribological behavior of WC-based coating with Fe-based matrix as an alternative to WC-CoCr by conducting sliding wear and cyclic impact tests. Also, different oxygen-fuel ratios were used to apply the coatings by HVOF spray technique. The most desirable combination of as-sprayed compressive residual stresses in the coating, its oxidation ratio and hardness–modulus ratio was set as the criteria to judge the best combination of oxygen and fuel. Sliding wear and impact resistance of the WC coating with FeCrAl binder were comparable to those with a CoCr binder, while abrasion resistance of the coatings with FeCrAl binder was inferior due to increased brittleness of the coating resulting from oxide inclusions. The hardness–modulus ratio of WC-FeCrAl was higher, as desired for wear applications, compared to WC-CoCr reference, although the coatings were more oxidized.

A partial list of varied WC-based hardmetals produced by powder metallurgy technique (PM) as well as WC-based coatings deposited employing thermal spray methods (TS) is provided in Table 1. As can be seen in the table, a fair variety of different compositions have been evaluated. However, a search for suitable alternatives to Co as a binder demands a comprehensive evaluation of mechanical and tribological properties. Mechanical and tribological properties of most of the existing potential chemistries are yet to be fully explored. Also, a vast majority of prior studies involve coatings deposited using HVOF method and hardmetals produced using powder metallurgy technique, and the employment of HVAF as an emergent method for applying these potential substitutions has not yet been fully evaluated.
### Table 1: Partial list of varied WC-based feedstock compositions investigated in powder metallurgy (PM) and thermal spray (TS) literature

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Composition, %Mass</th>
<th>Particle size, μm</th>
<th>Service temp., °C</th>
<th>Powder type/hardmetal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>WC grain size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fine, medium,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>coarse, very coarse</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>88WC-12Co</td>
<td>Co: 10.5–13</td>
<td>Fe: Max. 0.2</td>
<td>30/5–90/45</td>
<td>&lt; 500</td>
<td>Agglomerated and sintered/ sintered and crushed (TS)</td>
</tr>
<tr>
<td></td>
<td>C: 5.2–5.6</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Ref 16, 78-80)</td>
</tr>
<tr>
<td>86WC-10Co4Cr</td>
<td>Co: 8.5–11.5</td>
<td>C: 5.0–6.0</td>
<td>15/5–45/15</td>
<td>&lt; 500</td>
<td>Agglomerated and sintered/ sintered and crushed (TS)</td>
</tr>
<tr>
<td></td>
<td>Cr: 3.0–5.0</td>
<td>O: Max. 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe: Max. 0.6</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-12Ni</td>
<td>Ni: 11–13</td>
<td>WC: Bal.</td>
<td>45/15</td>
<td>&lt; 500</td>
<td>Agglomerated and sintered (TS)</td>
</tr>
<tr>
<td></td>
<td>Fe: 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-NiCr</td>
<td></td>
<td>38/53</td>
<td></td>
<td></td>
<td>Mechanically milled (TS)</td>
</tr>
<tr>
<td>WC-NiMoCrFeCo</td>
<td>Ni: 11.0</td>
<td>Fe: 1.0</td>
<td>45/15</td>
<td></td>
<td>Agglomerated and sintered (TS)</td>
</tr>
<tr>
<td></td>
<td>Mo: 3.0</td>
<td>Co: Max. 0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr: 2.5</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73WC-20CrC-7Ni</td>
<td>Cr: 17–21</td>
<td>Fe: Max. 0.3</td>
<td>30/5–53/20</td>
<td>&lt; 750</td>
<td>Agglomerated and sintered (TS)</td>
</tr>
<tr>
<td></td>
<td>Ni: 6.5–8</td>
<td>O: Max. 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C: 6.3–7.3</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCrWMo</td>
<td>Cr: 20.5</td>
<td>Fe: &lt;1</td>
<td>53/11 and 53/20</td>
<td>&lt; 875</td>
<td>Gas or water atomized (TS)</td>
</tr>
<tr>
<td></td>
<td>W: 10</td>
<td>C: 0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo: 9</td>
<td>B: 0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu: 4</td>
<td>Ni: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr3C2–37WC 18NiCoCrFe</td>
<td>C: 8.11</td>
<td>Fe: 0.23</td>
<td>30/10–45/15</td>
<td>&lt; 700</td>
<td>Agglomerated and sintered (TS)</td>
</tr>
<tr>
<td></td>
<td>Ni: 11.63</td>
<td>Cr: 40.74</td>
<td>1.6/0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co: 3.63</td>
<td>WC: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85WC–15(FeCrAl)</td>
<td>Fe: 10.79</td>
<td>C: 5.58</td>
<td>45/15</td>
<td></td>
<td>Agglomerated and sintered (TS)</td>
</tr>
<tr>
<td></td>
<td>Cr: 5.58</td>
<td>O: 0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al: 1.02</td>
<td>W: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-FeNiCrMoCu</td>
<td>Fe: 5.1</td>
<td>Mo: 1.0</td>
<td>45/15</td>
<td></td>
<td>Agglomerated and sintered (TS)</td>
</tr>
<tr>
<td></td>
<td>Ni: 4.6</td>
<td>Cu: 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr: 4.3</td>
<td>WC: Bal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-10, 20FeNi</td>
<td>Fe: 9, 18</td>
<td>WC: Bal.</td>
<td></td>
<td>...</td>
<td>Hardmetal (PM)</td>
</tr>
<tr>
<td></td>
<td>Ni: 1, 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-15FeCoNi</td>
<td>Fe: 9.75</td>
<td>Ni: 2.25</td>
<td></td>
<td>...</td>
<td>Hardmetal (PM)</td>
</tr>
<tr>
<td></td>
<td>Co: 3</td>
<td>WC: Bal.</td>
<td>0.21 ± 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-10FeMn</td>
<td>Fe: 9.84, 9.69, 9.38, 8.4</td>
<td>WC: Bal.</td>
<td></td>
<td>...</td>
<td>Hardmetal (PM)</td>
</tr>
<tr>
<td></td>
<td>Mn: 0.16, 0.31, 0.62, 1, 1.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Processing Routes

An Overview of Thermal Spray Deposition of WC-Based Coatings

Nowadays, cermet coatings can be deposited through a variety of thermal spray routes. Plasma spraying, including APS (Ref 79, 93), vacuum plasma spray (VPS) (Ref 79), low-pressure plasma spray (LPPS) (Ref 94) and high-power plasma spray (HPPS) (Ref 95), most recent emerging suspension plasma spraying (SPS) (Ref 96, 97), cold spray (CS) (Ref 98, 99) and high-velocity spraying; including HVOF (Ref 101), HVAF (Ref 101) and denotation gun process (Ref 102, 103) are the techniques applicable for fabrication of this class of materials.

Generally, the main difference between these spraying techniques is the variable flame parameters, particularly the temperature and velocity of the flame. Torches with different prevailing gas temperature and velocity substantially influence the kinetic and thermal energy transfer to the injected powder particles. As explained earlier particles experiencing diverse driving forces for heat-up and acceleration in-flight end up with very distinct temperature and velocity at impact and result in coatings with different microstructure characteristics, which in turn govern coating properties.

In plasma spray techniques, the flame velocity is relatively low and the temperature is significantly high (up to 15000 °C). So, feedstock particles with the velocity of around 50-100 (m/s) are exposed to a gas stream with a high level of heat energy and because of the velocity being low, the dwell time is relatively long (Ref 15, 104). This situation leads to an excessive level of material degradation in form of oxidation, decomposition and decarburization which would affect the wear performance of the resulting coating (Ref 20, 79). It has been reported that a large portion of the WC phase can transform into W_2C phase during the plasma spray process (Ref 12, 105). Results from a study by Al-Mutairi et al. (Ref 106) show that excessive phase transformation and cobalt evaporation occur during APS as compared to HVOF, which causes the wear performance of WC-based coatings processed by APS to be inferior compared to those sprayed using HVOF (Ref 107-110).

Suspension plasma and suspension HVOF spraying methods have also been explored as processing routes to deposit WC-based feedstock materials. In these methods, typically submicron sized feedstock particles in forms of suspension are directly injected into the plasma or HVOF plume, thus preventing powder agglomeration in the spraying nozzle (Ref 18, 111, 112). The particle’s velocity can reach up to 800 m/s and the particle’s temperature up to 2500 °C in SPS technique (Ref 111). Although the feedstock particle temperature and as a result degradation of carbide grains is reduced in this method compared to APS technique, excessive carbon loss is still reported in literature (Ref 113-115) making it not the most desirable technique for spraying WC-based wear-resistant coatings.

Cold spraying is another technique used to deposit WC-based feedstock materials which relies on high-pressure compressed air/gas accelerated by a de Laval type nozzle to impart sufficient momentum to the injected powder particles. The powder particles are accelerated to supersonic velocities and propelled onto the part to be coated. With the thermal energy content being absent/negligible, the process can potentially prevent excessive material degradation resulting from high temperature in a plasma flame and, to a reduced extent, in a combustion flame in HVOF. Having a low gas temperature and high kinetic energy makes this method well suited for depositing materials that are predominantly comprised of a ductile constituent. Therefore, deposition of WC-based feedstocks, comprising hard carbide grains, using cold spraying faces several challenges including low deposition efficiency. More than a few investigations have been carried out to study the deposition behavior and characteristics of WC-based coatings by cold spraying technique (Ref 116-118). While the much colder process temperature in this technique suppresses formation of brittle phases like W_2C, shattering of WC grains because of their brittle nature (Ref 119, 120), erosion of the surface because of the impact of hard particles during spraying, and high levels of porosity (Ref 99, 116, 119) remain the main challenges yet to be addressed.

Therefore, plasma spray, suspension spray and cold spray methods do not seem to be the most promising routes to apply WC-based feedstock materials. Hence, this paper would mostly focus on high-velocity spray methods of HVOF and HVAF, which have shown great capability in processing cermet materials. Detailed discussion of these two techniques is provided in “High-Velocity Spraying Methods” section.

High-Velocity Spraying Methods

In high-velocity techniques, the attempt is to enhance the particle impact velocities by increasing flame velocity, which further reduces particle dwell times. Moreover, in these processes, the energy source is derived from combustion which intrinsically gives much lower temperatures as compared to the plasma arc. Having a flame with these conditions would result in softened or partially molten particles highly accelerated toward the substrate. This high amount of kinetic energy transforms into heat as a result of impact with the substrate. The amount of generated heat...
has a direct relation with the velocity to the power of two which makes it more pronounced when the velocity is higher than 400 m/s (Ref 104). Because of high kinetic energy, the particles deform plastically (Ref 121, 122) as a result of impact with the substrate or underlying coating layers which yields nearly fully dense coating with better mechanical and tribological properties (Ref 1, 123, 124). So, the high-velocity route seems to be a promising approach to develop durable wear-resistant coatings. However, depending on the selected technique and process parameters, results can vary substantially. In this section, the high-velocity techniques (HVOF and HVAF) and the effect of process parameters on the quality of the coating are reviewed.

HVOF Method

The high-velocity oxy-fuel (HVOF) method can be identified as the most popular route employed to apply WC-based coatings since the early 1980s (Ref 15, 26). In this method, a mixture of fuel (gaseous: hydrogen, propane, propylene, or liquid: kerosene) and oxygen is introduced into the combustion chamber. The resulting flame issuing from the nozzle can heat the particles from 1500 up to 3000°C. Also, the transferred kinetic energy from the stream of combustion gases can accelerate the particles to a velocity of up to 1000 m/s (Ref 1, 15, 125). In the first generation of HVOF systems, a gaseous fuel is used for combustion and the nozzle is straight and parallel sided with a length of around 120 mm. In the second-generation HVOF systems, a converging-diverging throat was added between the combustion chamber and the nozzle leading to a substantial increase in the flame velocity. Also, in some of the second-generation systems, liquid fuel can be employed. The flame velocity is higher in the second-generation and it generates lower flame temperature which can be specifically beneficial for diminishing material degradation (Ref 14, 34, 126, 127). All these make the HVOF technique a particularly suitable candidate for applying cermet materials. Although the extent of material degradation, resulting in the formation of undesirable phases such as W2C, is much lower with the HVOF method than with the plasma spray technique, HVOF-sprayed WC-based coatings still can suffer from this phenomenon (Ref 15, 128). However, it is still possible to deposit cermet coatings with promising performance employing this technique by fine-tuning the process parameters.

Role of Process Parameters in the HVOF Technique

Having several process parameters, some even interrelated, makes the HVOF method an operation dependent technique affecting coating microstructure significantly with varying process parameters, requiring mastery on the process-microstructure relationships. These parameters can be connected to hardware system, e.g., nozzle configuration, injection system and its location, or related to plasma thermodynamics such as fuel type, fuel/oxygen pressure. Also, there are other parameters associated with particle/flame interaction, e.g., feedstock particle size distribution, the pressure of carrier gas, powder feeding rate or connected to the substrate, e.g., standoff distance, spraying angle and substrate roughness and/or temperature. A list of popular HVOF guns, classified with respect to fuel type and manufacturer, is provided in Table 2.

Some studies have tried to establish a correlation between the in-flight state (temperature and velocity) of particles, microstructure and properties of HVOF-sprayed WC-based coatings (Ref 121, 133-135). Wang et al. (Ref 136) conducted an optimization study to evaluate the effect of HVOF process parameters for spraying WC-Co powder. The process parameters showed a significant influence on the performance and mechanical properties of the fabricated coatings such as hardness and fracture toughness. It was found that hardness of the coating increased with fuel (kerosene) and oxygen flux, but decreased with powder feeding rate and standoff distance, while the fracture toughness values tended to show an opposite trend.

Another way of achieving desired velocity and temperature for the feedstock particles and, as a result, after coating’s properties is to regulate oxygen-fuel ratio to a suitable stoichiometry. In a study by Picas et al. (Ref 137), it was shown that by increasing the total oxygen flow rate, while kerosene flow is constant, the initial temperature of the feedstock particles increased and after reaching a certain point it started to decrease. This was because, after a certain value for the oxygen/fuel ratio, when the amount of oxygen goes beyond the amount needed for complete combustion of kerosene, it can act as a cooling gas and as a result promotes the decrease in flame temperature. This was while the velocity of particles continuously increased by increasing oxygen flow. This increase in particles velocity can yield a considerable improvement in density of the resultant coating. Stoichiometric combustion ratio, \((O/F)_{\text{stoich}}\), can be theoretically estimated, however, to reach highest possible temperature, for a given volume flow rate, an optimum fuel rich combustion is required. For this, normalized \(O/F\) can be defined as:

\[
\lambda = \frac{(O/F)_{\text{act}}}{(O/F)_{\text{stoich}}} \tag{Eq 1}
\]

where \(\lambda\) is normalized \(O/F\), \((O/F)_{\text{act}}\) is the actual ratio of oxygen and fuel and \((O/F)_{\text{stoich}}\) is the calculated stoichiometric ratio of oxygen and fuel. \((O/F)_{\text{stoich}}\), by mass, are calculated to be 7.14, 6.97 and 3.28 for hydrogen, propylene and kerosene, respectively. In case of the hydrogen
gas-fueled DJ 2600 gun, it was shown that for various total volume flows between 1100 SLPM and 1250 SLPM, the maximum temperature occurs at the $\dot{\lambda}$ of around 0.77 (Ref 17) and 0.74 in another study (Ref 137). Employing numerical simulation, it has been revealed that for a propylene gas-fueled HVOF gun a fuel rich $\dot{\lambda}$ between 0.83 and 0.96 can generate the peak temperature inside the nozzle. In the fuel rich combustion there is an additional unburnt fuel in the nozzle and as a result of its combustion with the ambient air along the spray plume, a higher maximum temperature occurs in the stream outside of the nozzle. It was also suggested that a lean mixture with the $\dot{\lambda}$ of 1.16 can provide the maximum temperature at the nozzle exit (Ref 138). For the liquid-fueled WokaJet-400 gun, a $\dot{\lambda}$ of 0.88-0.92 can provide the maximum flame temperature in case of employing kerosene as the fuel (Ref 137, 139). The intrinsic properties of the fuel type are another factor influencing flame temperature and velocity. It is known that, at a given temperature (of feedstock particles), kerosene can generate higher particle velocities compared to hydrogen and propylene due to its intrinsic properties. On the other hand, when keeping the velocities the same, kerosene produces lower temperature of feedstock particles as compared to hydrogen and propylene (Ref 125, 140, 141). In addition, gas-fueled torches exhibit a wider range of processing parameters as compared to liquid-fueled guns (Ref 142). This results in cermet coatings with more extensive range of performance and mechanical characteristics when deposited by a gas-fueled gun. After discovering appropriate SCR, change in the total volume flow can deliver different temperature values of the flame. An increase in backpressure and as a result total volume flow from 5.22 bar to 5.51 bar can increase particles temperature from around 1630 to 1870 °C and velocity from 570 to 610 m/s (Ref 17). However, in the case of WC-based coatings, reaching the maximum temperature is not always desirable since it can result in an increase in the molten fraction of feedstock particles which leads to an increase in the extent of phase change such as the formation of brittle W$_2$C phase which is discussed in “Phase Change During HVOF Spraying” section.

Deposition efficiency is another factor that can be influenced depending on the employed process parameters. It has been shown that, for a CJS liquid fuel HVOF gun, by keeping particles velocity the same (by reaching the same combustion chamber pressure), but increasing the particle temperature (by increasing the O/F$_{act}$ ratio from 5 to 3.45), deposition efficiency can be improved by about 5%, from 41.6 to 46.7%. Also, it was shown that with the same temperature ($\sim$ 1780 °C), an increase in particles velocity from 780 to 850 m/s can lead to a drop in deposition efficiency from 46.7 to 39.4% (Ref 100). For an internal diameter HVOF (HVOF-ID) system it has been found that a change in the fuel/oxygen ratio can dramatically affect the deposition efficiency within the range of 27–52%. Also, spraying angle can considerably influence deposition efficiency of feedstock powders. It is well-known that the highest deposition efficiency can be obtained by spraying at 90° angle in a way that large deviations from this angle can lead to a significant drop in deposition efficiency (Ref 143–145). For instance, it has been shown by Houdkova et al. (Ref 146) that by decreasing spraying angle from 90° to 30° deposition efficiency can be halved (from 40 to 20%). Powder characteristics are other factors which can greatly influence the deposition efficiency (discussed in “Role of Feedstock Characteristics” section). The deposition behavior of feedstock particles can directly influence the chemical composition of resultant coatings since the hard carbide grains are more susceptible to rebound and as a result a loss in carbide content can occur. This is explained in “Phase Change During HVAF Spraying” and “Phase Change During HVAF Spraying: A Comparison with APS and HVOF” sections. A list of the deposition efficiency values obtained by various HVOF equipment is provided in Table 4.

**Phase Change During HVOF Spraying** As explained in the previous section, exposing the feedstock powder to high temperatures can lead to the formation of brittle phases such as W$_2$C which is a result of WC transformation due to decarburization during spraying. Although the amount of decarburization reported for HVOF coatings is significantly lower than that of plasma spray coatings, it is still documented as one of the shortcomings of this method (Ref 1, 13, 147). The process of dissolution of WC grains in the molten metallic binder (Co) and, ultimately,

---

**Table 2** HVOF spray guns (Ref 129-132)

<table>
<thead>
<tr>
<th>Spray gun</th>
<th>Fuel type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet Kote or JK (e.g., Jet Kote II and III)</td>
<td>Gas</td>
<td>Deloro Stellite</td>
</tr>
<tr>
<td>Diamond Jet (e.g., DJ 2600 and 2700)</td>
<td>Gas</td>
<td>Oerlikon Metco</td>
</tr>
<tr>
<td>HV-2000</td>
<td>Gas</td>
<td>TFA Praxair</td>
</tr>
<tr>
<td>JP 5000/8000</td>
<td>Liquid</td>
<td>TFA Praxair</td>
</tr>
<tr>
<td>CJS (e.g., CJS 4.2 and 5.2)</td>
<td>Liquid</td>
<td>Thermico</td>
</tr>
<tr>
<td>WokaJet and WokaStar</td>
<td>Liquid</td>
<td>Oerlikon Metco</td>
</tr>
</tbody>
</table>
decarburization initiates at temperatures above the eutectic temperature (~1350 °C for WC-CoCr) (Ref 148, 149). During this process, carbon diffuses through the liquid binder and oxidizes at the surface in form of CO and/or CO2, leading to a reduction in the C and WC contents in the coating (Ref 150-152). By subsequent cooling down of the liquid binder, it becomes supersaturated, leading to the formation of W2C and W phases, depending upon the extent of carbon loss (Ref 148, 151). By further cooling down below the eutectic temperature, due to a reduction in solubility, precipitation of η-carbide phases of Co-W-C (M6C; e.g., Co9W3C or M12C; e.g., Co3W6C), in the form of solid solution, may occur (Ref 148, 150). WO, WO2, WO3, W2O6 and W3O9 are other possible gaseous products as a result of reaction with oxygen (Ref 153). Another mechanism of carbon loss can be direct oxidation of WC grains in reaction with other combustion products such as water vapor and carbon dioxide. W2C and W can be considered as the main products of these reactions (Ref 19, 153). It is broadly reported that thermal dissolution and decarburization of feedstock powder can significantly affect the wear performance of thermally sprayed WC-based coatings (Ref 1, 80, 154, 155). This influence can be attributed to various factors such as decohesion of the carbide grains (Ref 155), increase in brittleness of the coating and decrease in the carbide content (Ref 156). While the ratio of W2C/WC (using x-ray diffraction technique) is a common criterion to judge the extent of decarburization (see Table 5), it may not provide a fair view of the amount of WC loss since it might partially occur due to carbide rebounding during the process. Although very few investigations (Ref 157-159) have employed direct measurement of elemental content through LECO technique, it can potentially provide a good insight in this regard. In a study by Agüero et al. (Ref 160), employing a LECO GDS analyzer, it was shown that during HVOF spraying of WC-CoCr, the content of W and C is decreased from 80 and 5.5% to 64.2 and 4.63%, respectively. This was attributed to rebounding of the hard WC grains during the spraying.

Thermal degradation of WC grains becomes even more pronounced when the attempt is to fabricate a fine-structured coating using finer (submicron) carbide grains and/or feedstock powder, due to higher specific surface area of the finer carbide grains or feedstock particles (Ref 25, 161). This is where the HVAF method has the potential to provide a considerable advantage by mitigating the extent of material degradation.

HVAF Method

HVAF not only has the potential to produce high-quality coatings but also is economically attractive and demands more attention to be well established in industry. In this method, by using compressed air (instead of pure oxygen as compared to the HVOF technique), the idea is to reduce the flame temperature and compensate for it by increasing the stream’s velocity. The velocity of feedstock particles in HVAF can reach up to 1200 m/s while the temperature is typically under 1500 °C, just under the melting temperature of most of the metals used as binder in WC-based coatings (Ref 162-164). Propane, propylene and natural gas are usually used as fuel in this method (Ref 165). In this technique, oxidation and material degradation due to high-temperature reactions are significantly reduced (Ref 157, 166-168). Figure 7(a) and (b) shows SEM images of HVOF-sprayed WC-12Co and HVAF-sprayed WC-10Co4Cr coatings, respectively. Light gray areas in Fig. 7(a) demonstrate tungsten-rich phases (shown by arrows) as a result of thermal dissolution reactions. It can be identified that in some areas the carbide grains are completely vanished as a result of these reactions. The HVAF coating, on the other hand, does not show any sign of formation of tungsten-rich phases in a way that the carbide grains retain their original shape, homogeneously distributed throughout the coating (Ref 2, 152, 167). Like HVOF technique, there are various process parameters that need to be fine-tuned in HVAF method.

Role of Process Parameters in the HVAF Technique

It has been reported that, because of the limited temperature range in the HVAF method, the properties of the resultant coatings are not extremely affected as a result of changes in processing parameters (Ref 104, 163, 169). Although the HVAF technique does not seem to be as sensitive as HVOF is, this method still is a process parameter dependent technique and demands extensive expertise. Hence, most of the process parameters highlighted for the HVOF method in the previous section, are the case here as well. However, the difference here is that in the HVAF method, gun configuration is another parameter of high importance. The particle temperature and dwell time can be altered using nozzles with different total length and varying convergent-divergent section designs. A list of popular HVAF guns and corresponding powder size range is provided in Table 3.

There have been investigations exploring the effect of processing parameters in the HVAF method. Consistently noting compressive stresses in WC-based coatings is a feature of HVAF spraying and this results from the peening effect associated with high-velocity impact of feedstock particles inherent in this method (Ref 7, 21, 173). Having high kinetic energy coupled with low temperature allows the particles to induce peening effect on the impacting surface. Lyphout et al. (Ref 174) investigated the correlation between coatings characteristics and process variables...
including nozzle design, standoff distance, the pressure of fuel 1, fuel 2 and carrier gas, and powder feeding rate, employing design of experiment methods. It was shown that increasing the length of nozzle can improve the microhardness of the resultant coating as well as its abrasion wear resistance. Also, higher powder feed rate and shorter standoff distance resulted in higher deposition efficiency. Increase in fuel 1 and fuel 2 pressure did not have a significant influence either on the quality of coating (i.e., porosity, decarburization), or on the abrasive wear performance of the coating. The average hardness value reportedly increased by increasing length and/or exit diameter of the nozzle, when spraying WC-CoCr feedstock of 5-20, 5-30 and 15-45 μm size distribution using the M3 HVAF gun. Also, the specific wear rate experienced a threefold improvement (from $23 \times 10^{-9}$ to $8 \times 10^{-9} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) when using longer nozzle with larger exit diameter to spray WC-CoCr feedstock with 5-20 μm particle size. Using the same two nozzles, negligible deviations were observed for processing the same feedstock with 5-30 μm particle size (Ref 169). Although other studies (Ref 172, 175) can be found suggesting the possibility of improving the properties of the coating by engineering the configuration of the HVAF gun, the extent of variation in the achieved properties is not well understood yet.

Lower temperature of in-flight particles in the HVAF technique can potentially raise some concerns around the deposition efficiency and the relevant determining factors in this technique which can be considered as a research gap in the field. Nevertheless, comparable or even higher deposition efficiencies than are obtained with the HVOF process, namely 46-62% for the M3-HVAF gun (Ref 170) and 36-70% for the AK-HVAF gun (Ref 171), were claimed by the respective manufacturers when spraying WC-based coatings. A change in gas type from propane to propylene can produce an improvement in deposition efficiency from 52 to 63% when spraying WC-CoCr by a HVAF gun. In a study by Myalska et al. the deposition efficiency of WC-Co and 5 wt.% of TiC was similar when spraying by HVAF and HVOF (Ref 176). In a direct comparison between HVOF and HVAF technique, it was shown that for a WC-based feedstock, a deposition efficiency of around 60% is obtained when using DJ2700 HVOF gun while the value is only around 42% when employing the K2 HVOF gun or M3 HVAF gun. The characteristics of the feedstock powder constitute another important parameter given the fact that different production procedures can result in powders with varying densities. For feedstock powders with the same particle size, deposition efficiencies of 43, 60 and 64% have been reported for fused/crushed, sintered/crushed and agglomerated/sintered powders, respectively (Ref 165). Deposition efficiency values reported in literature for the HVAF technique along with values achieved from the HVOF method are listed in Table 4.
Phase Change During HVAF Spraying: A Comparison with APS and HVOF

Studies show that HVAF has the possibility to dramatically reduce decarburization to near zero. It has been shown that carbon retention of WC-CoCr coatings can increase from 0.84 when processing by HVOF to 0.96 when HVAF technique is used for spraying (Ref 180). Wang et al. (Ref 156) using x-ray diffraction analysis showed that ratio of W2C to WC can decrease from 0.7 in HVOF to nearly 0 in HVAF method. These results confirm the findings of a similar study from the same authors (Ref 181). However, carbon loss can also occur due to rebounding of carbides upon impact. This can be especially more pronounced in the HVAF technique depending on the size of carbide grains and content of metallic matrix. However, not many studies have been conducted on this for WC-based coatings. Although the flame temperature of the HVAF process is lower than that characteristic of the HVOF technique, carbon loss can still occur during HVAF spraying due to oxidation, because of the typically longer dwell time (longer nozzle) as well as the finer particle size of powders typically deployed in this method. 24.6% loss in carbon content is reported when spraying Cr3C2-based feedstock using HVAF technique (Ref 182). However, contradictory findings can be observed in the literature. In a study by Jacobs et al. (Ref 157), no change in carbon content, measured using the LECO method, was observed when spraying WC-Co and WC-CoCr employing the HVAF technique.

In Table 5 the W2C/WC ratio is listed for different deposition techniques based on prior studies. In the APS method this ratio can reach 1. The amount of decarburization in the HVOF method is highly dependent on the type of HVOF torch as well as the employed process parameters. The W2C/WC ratio, for the HVOF technique, can vary from 0.1 to up to 0.7. In contrast, negligible decarburization is reported in the literature for HVAF processed coatings which can be considered as a great advantage of this technique. Also, spraying feedstock with smaller carbide size, with the aim of producing refined microstructures, seems feasible by employing the HVAF route and needs more attention in future studies. By having an improved coating’s properties, it may be possible to reduce the coating thickness which can have some technical and economic benefits. Promising capabilities of HVAF technique can make all these possible. However, there are not enough investigations around this and hence it demands much more attention of the community.

Role of Feedstock Characteristics

Employing different powder manufacturing methods such as agglomeration and sintering; sintering and crushing; casting, crushing and fusing, can affect the principal features of the powders such as size distribution, morphology, apparent density, etc., and consequently the microstructure and performance of coatings (Ref 104, 187-190). It should be noted that the influence of powder characteristics can considerably differ when employing different processing routes. In the rubber wheel abrasion test, HVOF (JP 5000) coatings produced using cast-crushed powders showed inferior resistance compared to those manufactured by sintered-crushed and agglomerated-densified powders (Ref 189). However, in a comprehensive study by Schwetzke et al. (Ref 191) on coatings fabricated from feedstock produced by four different manufacturing routes, it was shown that no major difference in performance can be seen by employing powders with different morphologies. Employing feedstock powder with finer particle size during HVAF spraying, can result in higher in-flight temperature and velocity which in turn can improve microstructural characteristics of the coatings by resulting in higher density and better homogeneity. The in-flight velocity of WC-CoCr powders, sprayed by M3 HVAF gun, can be increased from 780 to 1050 m/s when decreasing the size from 15-45 to 5-20 µm. Also, the Vickers hardness of the coating experienced an improvement from 1300 to 1575 HV0.3 when employing finer powder. All these led to about a fourfold decrease in the specific wear rate from 33 $\times 10^{-9}$ to 8$\times 10^{-9}$ mm$^3$ N$^{-1}$ m$^{-1}$ (Ref 192).
The characteristics of the feedstock powder can influence deposition behavior of particles. Increase in size (Ref 193) and content (Ref 192) of WC grains can result in a reduction of the deposition efficiency because of higher chance of particles rebounding when spraying by HVOF technique. Also, particles with higher density tend to resist more against deformation and, ultimately, exhibit lower flattening and higher chance of rebounding off the surface upon impact. It has been shown that with the same particle size, an increase in apparent density from 4.43 to $5.02 \, \text{g cm}^{-3}$ can result in a drop in deposition efficiency from 43.6 to 38.7%, when using CJS HVOF gun (Ref 100).

It has been shown that a decrease in feedstock particle size range (between 5 and 45 $\mu$m) can result in a significant decrease in deposition rate when employing the M3 HVAF gun. The deposition rate of WC-CoCr feedstock sprayed by M3 HVAF gun has been reported to drop from around 25 $\mu$m/pass to 14 $\mu$m/pass when decreasing the particle size range from 15-45 to 5-20 $\mu$m (Ref 169). The influence of powder characteristics is also observed for the cold spray technique, in a way that an increase in the WC content (Ref 194), WC size (Ref 99) and feedstock particle density (Ref 195) can result in a drop in deposition efficiency. Rebounding of carbides can especially occur more frequently when the content of the carbide is high and/or the size of carbide grains is large ($>2\, \mu$m) (Ref 159, 180, 182).

The relative size of feedstock particles and carbide grains (equation 2) governs the flattening ability of the particles upon impact (Ref 159, 169).

$$\delta = \frac{dp}{dc} \quad \text{(Eq } 2)$$

Table 5 Decarburization ratio in WC-based coatings reported for APS, HVOF and HVAF processing routes

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Decarburization ratio (W2C/WC)</th>
<th>Chemistry</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS</td>
<td>0.2</td>
<td>WC-17Co</td>
<td>(Ref 105)</td>
</tr>
<tr>
<td>APS</td>
<td>$\approx$ 1</td>
<td>WC-17Co</td>
<td>(Ref 110)</td>
</tr>
<tr>
<td>APS</td>
<td>0.46</td>
<td>WC-Ni</td>
<td>(Ref 183)</td>
</tr>
<tr>
<td>HVOF (JK)</td>
<td>0.7</td>
<td>WC-10Co4Cr</td>
<td>(Ref 156)</td>
</tr>
<tr>
<td>HVOF (JP 8000)</td>
<td>0.12</td>
<td>WC-10Co4Cr</td>
<td>(Ref 156)</td>
</tr>
<tr>
<td>HVOF (JP 5000)</td>
<td>0.055</td>
<td>WC-10Co4Cr</td>
<td>(Ref 184)</td>
</tr>
<tr>
<td>HVOF (DJ)</td>
<td>0.14-0.16</td>
<td>WC-10Co4Cr</td>
<td>(Ref 185)</td>
</tr>
<tr>
<td>HVOF (JP 5000)</td>
<td>0.114</td>
<td>WC-12Co</td>
<td>(Ref 184)</td>
</tr>
<tr>
<td>HVOF (DJ 2700)</td>
<td>$\approx$ 0.6</td>
<td>WC-12Co</td>
<td>(Ref 186)</td>
</tr>
<tr>
<td>HVOF (DJ 2700)</td>
<td>0.13</td>
<td>WC-12Co</td>
<td>(Ref 167)</td>
</tr>
<tr>
<td>HVOF (HV-2000)</td>
<td>0.25</td>
<td>WC-12Co</td>
<td>(Ref 167)</td>
</tr>
<tr>
<td>HVAF (AK)</td>
<td>$\approx$ 0</td>
<td>WC-10Co4Cr</td>
<td>(Ref 156)</td>
</tr>
<tr>
<td>HVAF (M2)</td>
<td>$\approx$ 0</td>
<td>WC-10Co4Cr</td>
<td>(Ref 80)</td>
</tr>
<tr>
<td>HVAF (M3)</td>
<td>$\approx$ 0</td>
<td>WC-12Co</td>
<td>(Ref 186)</td>
</tr>
<tr>
<td>HVAF(Aerospray)</td>
<td>0</td>
<td>WC-12Co</td>
<td>(Ref 167)</td>
</tr>
</tbody>
</table>

where $dp$ and $dc$ are particle and carbide size, respectively. As this relative size approaches 1 (smaller feedstock particle and bigger carbide grains), the flattening behavior is more governed by hard carbide grains which increases the chance of rebounding. The role of carbide size, as one of the key characteristics of the feedstock powders, is the main focus in this section.

A reduction in carbide size can potentially improve the mechanical properties such as hardness and toughness as well as the tribological performance of the coatings (Ref 1, 16, 196). Wang et al. (Ref 197) studied the microstructure and mechanical properties of HVOF-sprayed cermet coatings from WC-Co feedstock powder with the mean carbide size of 80 nm. The idea of using nanosize carbides was to replace some of the WC/binder interfaces by WC/WC interface. They suggested that a clustered structure which comprises of small carbide grains (increasing the number of carbide/carbide interfaces) can enhance the wear performance of the coating compared to the regular coatings containing singular large carbides. In the case of a coating with regular carbide size once the binder (Co) is removed, the single carbide grain is very likely to be pulled out while in a clustered structure, there are plenty of hard WC grains bonded together embedded in the binder beneath, making the material difficult to be removed. However, it has been reported in some studies that a decrease in carbide size can result in a decrease in the value of fracture toughness (Ref 32, 198). Also, there are contradictory reports on the correlation between carbide size and wear performance of a WC-based coating. While some studies show that employing feedstocks with smaller carbide size range result in superior wear resistance (Ref 16, 193, 199-202), other investigations report either no
In cermet coatings, besides the intrinsic properties of reinforcing grains and metallic binders, the mean free path (MFP) is the other parameter that governs the properties of the coating. For a given volume fraction of carbides, the MFP value depends on the size of carbides. The parameter MFP or mean free interparticle distance is defined as (Ref 206, 207):

$$\lambda = \frac{1 - V_p}{N_L}$$  \hspace{1cm} (Eq 3)

where $\lambda$ is MFP, $V_p$ is the volume fraction of the WC grains, $N_L$ is the number of carbide grains that intercept per unit length a random test line. For a given carbide-binder volume fraction, the MFP value decreases with a decrease in the size of employed carbides.

In a study by Kumari et al. (Ref 3) it is shown that a reduction in MFP can considerably improve the abrasion wear performance of the coating with a linear correlation. In this study the extend of decarburization, during HVOF spraying of powders with finer carbides, was controlled by keeping flame temperature to be as low as possible. Also, similar linear relationship is suggested between relative abrasive wear rate and relative carbide size by other studies (Ref 16, 208, 209) confirming the improvement in abrasive performance by decrease in carbide size. It has been reaffirmed for sliding wear conditions (Ref 198, 208), that when the decarburization ratio is negligible, a decrease in carbide size can lead to a substantial decline in specific wear rate by a factor of two, which is attributed to an increase in hardness and toughness of the coating.

In general, considering the decarburization ratio to be negligible, larger MFP (bigger carbide size) means higher local surface exposure of the binder and this results in a tougher and softer composite system. So, by having a composite system that has higher toughness, it is easier to absorb more energy through plastic deformation, leading to an improvement in resistance against fracture. If MFP is considered to be representative of the binder width (Ref 210), in the configurations with larger carbide grains, the thickness of the binder is bigger (more available space between the carbide grains). As a result, under loading, the configuration can accommodate the deformation within the tough binder. On the other hand, by decreasing the MFP, accommodation for deformation within the binder is limited (greater constraint against deformation). So, for further deformation, such configuration requires more stresses to be applied, resulting in improvement in strength. Also, in the configurations with finer carbide grains, the carbides will be more uniformly and homogeneously distributed throughout the matrix. This can prevent the coatings from being deeply penetrated in the case of two and three-body abrasion wear and the resulting grooves would have shorter length (higher number of hard carbide grains are in the way). The other benefit is that by reducing particle size, a lower surface roughness on the coatings will be achieved, leading to improvement in wear performance and reduction in finishing costs.

**Tribological Behavior**

After the selection of the proper deposition technique and setting the desired spray parameters and assessing the coating properties in terms of microstructure and mechanical properties, the performance of the coating when exposed to different application-relevant wear modes needs to be evaluated. Wear-resistant coatings are supposed to perform well under various tribological conditions. There are several standard tests to examine the behavior of a coating under these conditions, including sliding wear (Ref 211), dry and wet abrasion (Ref 212, 213), erosion and slurry erosion (Ref 214, 215) conditions. Each of these tests is distinct and subjects the coating to entirely different wear environments, which result in different mechanisms of material removal from the coatings. In this section, the focus is on reviewing the performance of HVAF- and HVOF-sprayed WC-based coatings and also the mechanisms that are responsible for coating degradation when exposed to different modes of wear.

**Performance Comparison of HVAF and HVOF Coatings**

As mentioned in “Phase Change During HVOF Spraying” section, material degradation can occur in the case of using HVOF as the deposition method. This leads to brittleness of the coating resulting in rapid propagation of surface and subsurface cracks, which can affect wear mechanisms and tribological performance of the coating (Ref 205, 216, 217). On the other hand, material degradation is
minimized in coatings applied using the HVAF route. However, since the temperature is relatively low and particles are scarcely heated, the method can lead to weak inter-lamellar cohesion.

Since both methods are significantly influenced by feedstock characteristics and spraying parameters, an equitable comparison of the two processes in terms of properties and performance is challenging. Still, results ensuing from comparative studies involving HVOF and HVAF can give a good picture of advantages and disadvantages of each. Making this comparison for various coatings deposited using distinct feedstocks and employing different spray parameters can make it more comprehensive. In a comprehensive study by Bolelli et al. (Ref 2), the wear performance of HVAF- and HVOF-sprayed WC-CoCr coating was compared by conducting abrasion and sliding wear tests. The selection of feedstocks with two different particle sizes of 5/30 μm (W1) and 15/45 μm (W2) for both HVAF and HVOF method provides a well-grounded comparison. Employing two different guns for each technique, JP5000 (P2) and DJ2700 (P3) for HVOF and M3 (P1) and M2 (P4) for the HVAF method, covers diverse coating properties resulting from intrinsic differences in the employed equipment. Figure 8 shows the specific wear rate and volume loss obtained from testing samples in different wear environments.

According to Fig. 8(a), with the exception of coatings deposited by HVOF DJ2700 (P3) and tested at high temperature, the sliding wear performance of all the thermal spray coatings is roughly the same with negligible difference in specific wear rates. In the two cases P3W1 and P3W2, networks of through-thickness macrocracks were reportedly visible to the naked eye across the surface of the samples before starting the ball-on-disk test. The case with electrolytic hard chromium (EHC) was provided as a reference. Also, dry sand rubber wheel tests were conducted to compare the abrasion resistance of the coatings fabricated by the two high-velocity techniques. Although according to Fig. 8(b), all the samples show comparable wear performance under dry sand rubber wheel test, it can be noticed that the feedstock powder particle size was a more influencing factor in abrasive wear environment rather than the process route. The coatings generated with the powder with coarser particle size (W2-series) showed larger volume losses than those of the finer powder cut size (W1-series). The authors also confirmed similar behavior for HVOF and HVAF coatings in the other study (Ref 80).

To compare the wear performance of the coatings from the two methods at higher temperatures, a combination of Fe-based feedstock of FeCrNiSiBC with 0, 20 and 40 wt.% addition of WC–Co composite powder were examined. Performing ball-on-disk tests at higher temperatures revealed that an increase in temperature can lead to an increase in wear rate for both HVOF and HVAF coatings by roughly the same magnitude. For a given composition and test temperature, the specific wear rate values of the coatings deposited by the two processing techniques were in the same range (Fig. 9). It can be seen in Fig. 9 that the coatings with addition of Fe-based binder show a comparable performance at higher temperatures as compared to the reference WC-Co.

Comparable performance was suggested by other researchers under sliding wear test (Ref 218, 219) as well as under jet erosion test at 30°, 60° and 90° as well as slurry erosion (Ref 220). However, other reports can be found with contradictory conclusions which are discussed below.

Wang et al. (Ref 221) compared the slurry erosion behavior of HVOF- and HVAF-sprayed WC-CoCr coatings of two different particles sizes, 5/30 μm (W1) and 15/45 μm (W2), processed by various spraying techniques, JP5000 (P2) and DJ2700 (P3) for HVOF and M3 (P1) and M2 (P4) for HVAF (Ref 2).
coatings, AK 07 HVAF and DJ2700 HVOF gun were employed to fabricate the coatings. The slurry erosion test was performed by mixing 40-70 mesh SiO\textsubscript{2} sand in water. The feed rate of sand was 150 g/min and the test was performed at 30° and 60° impact angles. According to Fig. 10, the erosion resistance of HVAF samples is slightly superior compared to that of HVOF samples. This superior performance can be attributed to the lower porosity, higher hardness and fracture toughness for HVAF samples compared to those deposited by HVOF method.

Hulka et al. (Ref 222) showed that HVAF-sprayed WC-based coatings exhibit similar or better wear performance compared to the coatings deposited by HVOF process, under sliding and abrasive conditions. Weight loss under abrasion wear for HVOF coatings was slightly higher than that of HVAF coatings (65 mg for HVOF coatings vs. 57 mg for HVAF coatings). Also, the specific wear rate under ball-on-disk test conditions for HVOF coatings with 2.62 × 10^{-5} (mm\textsuperscript{3} N\textsuperscript{-1} m\textsuperscript{-1}) was higher than that of HVAF coatings with 2.26 × 10^{-5} (mm\textsuperscript{3} N\textsuperscript{-1} m\textsuperscript{-1}). In another study, Wang et al. (Ref 156) by conducting sliding and abrasion tests concluded that HVAF coatings exhibited better performance compared to HVOF-sprayed layers. For the same abrasive test conditions, the average abrasive wear rate for the HVAF samples sprayed using the AK 07 gun was 3.76 × 10^{-6} g/m while the wear rate values for the other two HVOF coatings sprayed using JP8000 and Jet Kote III were 6.05 and 18.72 g/m, respectively. They attributed such results to lower decarburization in HVAF coatings compared to that of HVOF, leading to higher hardness and fracture toughness for the coating.

Recently, there have been some studies focused on the wear behavior of high-velocity sprayed WC-based coatings under erosive environments (Ref 223-226). Matikainen et al. (Ref 180) conducted a comprehensive comparative investigation to evaluate the wear performance of WC-CoCr sprayed using HVOF and HVAF techniques under various erosive environments, including dry, slurry and cavitation erosion. The most substantial difference was found in cavitation erosion rate for HVAF-sprayed samples (0.4 \mu m/h) compared to HVOF coatings (1.5-3.7 \mu m/h). There are other studies claiming that the process route can have great influence on the performance of the resulting coating (Ref 157, 167, 218, 227).

In general, as discussed in “High-Velocity Spraying Methods” section, the quality of deposited coatings using HVOF and HVAF methods in terms of mechanical properties and tribological performance can be highly influenced by the process parameters as well as feedstock characteristics. Sometimes, this can lead to contradictory results when it comes to comparing coatings sprayed using HVOF and HVAF methods (Ref 80, 156, 167, 228). It can be found in the literature that HVAF WC-based coatings in some cases show inferior and in some other cases superior wear performance compared to HVOF-sprayed WC-based coatings. For instance, in Fig. 11 it can be seen that HVAF.
WC-FeCrAl is ranked between two HVOF coatings sprayed with different guns in terms of abrasive wear performance.

**Mechanisms of Material Removal Under Different Wear Conditions**

Wear is a complicated phenomenon and there is no unified classification of wear mechanisms. This is not only because it is intrinsically a complex process, but also because it is greatly dependent on the material being worn, its properties and the environment that it experiences. There are a great number of studies devoted to description and classification of wear mechanisms from various perspectives. The delamination theory of wear was introduced by Suh in 1973 (Ref 230). This theory was established based on the formation of subsurface microcracks and voids and their propagation toward surface and detachment of material. Wear mechanisms are mostly classified in four major groups as adhesive, abrasive, fatigue and corrosive by Furey (Ref 231), Rabinowicz (Ref 232) and Budinski (Ref 233). Budinski later considered four main modes of wear considering material removal mechanisms including abrasion, nano-abrasive, rolling contact fatigue and impact. Based on the type of wear test and test conditions a combination of these modes can play a role. Also, the process of material removal is greatly dependent on the material texture and properties. In literature, the process of material removal during different forms of wear is known by terms like failure modes, degradation mechanisms, damage mechanisms, etc. It includes post facto analysis of the worn surface and corresponding subsurface microstructure. In this paper the wear mechanisms are categorized based on different types of wear conditions, so the prominent material removal mechanisms in play during sliding, abrasive and erosive forms of wear are briefly discussed below for thermal spray coatings.

**Sliding Wear**

Several investigations can be found putting forward a failure scenario for thermal spray WC-based coatings under sliding wear conditions using ball-on-disk test according to the standard ASTM G99 (Ref 211). Based on literature studies (Ref 156, 234-236), the proposed failure mechanisms fall mostly into one or a combination of these categories: complete delamination, micro-chipping, crack propagation along the carbide/binder interface, extrusion of matrix and, as a result, carbide pulling out due to weak binder support. Test conditions such as temperature, characteristic of mating counterpart, load and duration can highly affect the wear process and mechanism in the sliding wear. Besides, characteristics of the feedstock such as employed production route, size distribution of the particles or of individual carbide grains, and intrinsic properties of the binder can influence the process of material removal (Ref 6, 14, 25, 169). According to several reports, it has been revealed that performing tests at higher temperatures expedites material removal and the formation of oxides (Ref 80, 237, 238). Wesmann et al. (Ref 237) in their study showed that the amount of WC measured on the surface after a sliding test decreases from 92 to 47.8 at.% as a result of increasing test temperature from room temperature to 200 °C. This led to an increase in the average value of the specific wear rate from \(0.4 \times 10^{-7}\) to \(2.0 \times 10^{-7}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\). Generally, increasing the applied load can lead to higher material removal. Generally, increasing the applied load can lead to higher material removal. This can be due to more severe damage of the coating accompanied with more complex removal mechanisms governed, among other factors, by correspondingly higher tangential force (Ref 236, 237, 239). In (Ref 236) it is shown that specific wear rate can increase from \(0.17 \times 10^{-5}\) to \(3.53 \times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) at 30 N to 90 N. They found that the rate of material removal increases significantly once the load surpasses 45 N. The dominant wear mode in the case of 15 N was individual carbide pullouts (Fig. 12a). Removal of material in forms of carbide pull-outs is reported to be a very common mechanism in WC-based coatings (Ref 241-243). Carbide pull-out can occur through various mechanisms; in some cases, the carbide grains get fractured as a result of contact with the counterpart and fragments get pulled out during the test (Ref 169). Also, it can happen because of binder removal around the carbide grain or even because of weak cohesion with the binder. Increasing the load to 30 N created several plowed grooves (Fig. 12b) and with further increase to 45 N, macro-scale cracks emerged on the scar region (Fig. 12c). Under 60 N of normal load, severe fatigue delamination occurred due to plastic deformation leading to a sharp increase in the removal rate (Fig. 12d). For the cases 75 and 90 N, extensive material exfoliation can be observed (labeled as massive exfoliation in Fig. 12e) in the form of pits.

Therefore, the following scenario according to Fig. 13 was proposed as the mechanism of material removal in case of sliding wear condition. First, small cracks nucleate within the binder phase and the carbide/binder interface, followed by plastic deformation, removal of small fragments, and fatigue delamination as a result of large-scale
cracks, and finally large scale of material removal and formation of pits.

Excessive material removal in the form of pits happens either because of very harsh test conditions (e.g., high load) or when the coating does not have a great cohesion (Ref 167, 169, 244). Along with the intrinsic behavior of the binder which provides the cohesion in WC-based coatings, the spraying process seems to have a profound influence on the microstructure characteristics and property retention of the feedstock properties and, as a result, on cohesion. In a study by Shipway et al. (Ref 205) on the performance of HVOF-sprayed WC-Co coatings in the ball-on-disk test, it was shown how degradation of feedstock material during deposition can influence the wear process. The loss of ductility in the Co-rich binder phase, because of carbide dissolution during spraying, can result in subsurface fracture, leading to excessive material removal. Using a cross-sectional analysis of the wear scar, deep subsurface cracks parallel to the surface, across W2C-rich areas (bright regions), were observed (Fig. 14). These cracks can propagate through the binder phase and lead to material loss once they reach the free surface.

In a study by Wang et al. (Ref 156), the influence of the processing technique on wear mechanisms under sliding conditions was evaluated. The wear behavior of three different WC-CoCr coatings applied by HVAF (using AK gun) and HVOF (using JP and JK guns) methods was investigated. It was concluded that the dominant wear mechanism is different for coatings with various degrees of decarburization. The HVAF coating exhibited the

Fig. 12 High-magnification SEM micrographs of the HVOF WC–Co–Cr coating tested at different loads of (a) 15 N, (b) 30 N, (c) 45 N, (d) 60 N, (e) 75 N and (f) 90 N (Ref 236)
The smoothest worn surface and the smallest scar width among all the three. As shown in Fig. 15(a), no apparent cracks or deep plows can be found in the AK coating which is attributed to the coating’s high hardness and toughness. On the other hand, significant amount of brittle phases (resulting from decarburization) led to the nucleation and propagation of a large number of cracks and pits on the surface of the JK coating without any apparent plows. A small number of cracks, pits and plows were visible within the wear track of the JP coating compared to the JK coating. This was attributed to the hardness and toughness of the JK coating being low, resulting in the worst sliding wear resistance of this coating.

The following three steps were proposed as wear mechanism in the coatings: (1) severe deformation and extrusion of binder, (2) formation and propagation of fatigue cracks, leading to pull-out of carbides, spallation of splats and as a result formation of wear debris, and (3) entrapping of some debris between the two surfaces acting as a third-body abrasive.

Generally, the wear process of thermal spray WC-based coatings in sliding wear conditions is dependent on two main factors: test conditions and inherent tribological properties of the coating. It is expected that, by making the test conditions harsher, the mechanism of material removal changes from carbide pull-out to plowed grooves, cracking, pitting and finally extensive separation of material. Besides, having brittle phases in the coating can affect the mechanism of wear as the brittle phases can facilitate the initiation and propagation of cracks. Due to the tendency of these phases to cracking, the removal mechanism in the coatings with brittle phases initiates from the surface and/or subsurface cracking through the brittle phase and, as a result, material is detached. This brittleness can be due to excessive decarburization during spraying. On the other hand, decreasing the flame temperature by employing the HVAF technique can resolve the brittleness problem. Lacking the brittle phases can potentially limit the removal process to carbide pull-outs, plowing and grooving, which can substantially improve the performance of the coating.

Fig. 13 Evolution of material removal stages by increasing loading in sliding test (Ref 236)

Fig. 14 Horizontal subsurface cracks (indicated by arrows) across the W_2C rich regions as a result of ball-on-disk test (Ref 205)

Fig. 15 SEM images of the surface subjected to sliding wear test of the (a) AK, (b) JP and (c) JK coatings (Ref 156)
Abrasive Wear

Another testing method which simulates a vast variety of application conditions is abrasion wear. There are several relevant standards such as abrasion resistance of hard materials, ASTM B611 (Ref 245) and dry sand rubber wheel test, ASTM G65 (Ref 212) for the evaluation of the performance of the WC-based coatings under three-body wear conditions. The analysis of the wear mechanism under various three-body abrasive conditions is crucial since it can be employed to have a good understanding of how the amount of wear can vary as the wear conditions change. Having third-body particles in this condition can induce high levels of shear stresses to the surface and as a result expedite the wear process. There are several test parameters that need to be set depending on the standard on which the wear test is based. The characteristics of the abrasive media, temperature, load, speed and test duration are among the determining test conditions (Ref 10, 246, 247). In general, the abrasive wear mechanism of a given WC-based coating is dominated by the following steps (Ref 136, 197, 248-250): (1) removal of soft matrix phase, (2) partial or complete fragmentation of unsupported WC grains and (3) removal of fragments (Ref 248).

Depending on the characteristics of the coatings, which are determined based on the process technique and the corresponding parameters, the first two steps can be skipped or occur very quickly in a way that the step three is the prominent occurrence. This was affirmed in a study on the abrasion behavior of HVAF (using AK gun) and HVOF (using JP and JK guns) WC-CoCr coatings with diverse mechanical properties (Ref 156). Typical SEM images of abraded surfaces of the three coatings are provided in Fig. 16. A large number of grooves and pits are visible on the surface of the JK coating leading to a rougher surface of this coating compared to JP and AK coatings. Also, the degree of binder scratching and the number of fractured carbides (yellow arrows) in the JK coating is higher than the other two. Based on the morphology of the worn surfaces, it can be concluded that the “micro-cutting” was the dominant wear mechanism of the JK coating accompanied by spallation of the splats. This behavior was attributed to the amount of brittle phases (W2C and W) being higher in this coating as a result of decarburization. It can be seen how the degree of decarburization can affect the dominant wear mechanism.

The effect of decarburization can be further pronounced and lead to crack formation throughout the coating. In a study conducted by Stewart et al. (Ref 161), through a dry sand rubber wheel test with alumina and silica sands and through post wear analysis, they described the material removal process of HVOF-sprayed WC-Co coatings. In the case of using alumina as abrasive sand, besides horizontal cracks (parallel to the surface) mentioned in the case of “Sliding Wear” section, several vertical cracks were formed as it can be seen in Fig. 17. These vertical cracks were not observed in the case of using silica sand (with more rounded morphology) leading to a wear rate ten times lower than that with the alumina sand.

It was suggested that the vertical cracks initiated from indentations of the abrasive particles into the surface of the coating. They grow vertically through the coatings until they reach W2C rich areas and continue to propagate across a W-rich path until finding their way back to the surface. For cases like these, involving a severely decarburized coating, the first step out of the three (removal of soft matrix phase) constituting the material removal mechanisms during abrasion does not occur because of the very brittle structure. Having extremely brittle phases (in decarburized coatings) facilitates the propagation of cracks through the whole system. Therefore, before any matrix extrusion happens, degradation of the coating already occurs. On the other hand, in coatings whose toughness is not significantly altered as a result of decarburization, the propagation of cracks occurs in a more controlled manner and only to a limited extent. In this case all the three mentioned steps occur in sequence and the coating exhibits a superior performance.

![Fig. 16 SEM images of abraded surface of the (a) AK, (b) JP and (c) JK coatings (Ref 156)](image_url)
As mentioned earlier, the properties and morphology of the abradant sand can affect the material removal mechanism. Ghabchi (Ref 17) studied the influence of abradant sand on the wear mechanism of HVOF-sprayed WC-CoCr using dry and wet abrasion test with fine and coarse sand particles. A mix of 10 wt.% titania sand in water was used for soft slurry abrasion test. In this case, besides the removal of carbides and splats, it was revealed that another fracture mechanism contributed to the interaction of sand particles with WC grains (Fig. 18).

Employing an image analysis method, the effect of the relative size of the abradant sand (220 nm) and WC grains was investigated and the following material removal mechanism were suggested: when the ratio of carbide grain size to the abrasive particle is; (1) less than 0.5, the removal of the binder containing carbide grains occurs (Fig. 19a), and (2) between 0.7 and 1.3, fragmentation of WC grains happens (Fig. 19b). In the latter case, when the ratio is close to 0.7, complete fracture of WC grains happens and when it is close to the upper limit (1.3), partial fracture happens. For the cases higher than 1.4, no segmentation of carbides was observed. In another study, fracture of carbides was reported as the dominant mechanism, by increase in abradant size (Ref 246). The influence of the abrasive particle size on the wear mechanism of thermally sprayed WC-CoCr coatings was investigated. SiC abrasive media was employed with three different particle sizes of 4.5, 17.5 and 180 μm in a rubber wheel abrasion test. They observed a sharp increase from an average value of around $1 \times 10^{-13}$ (SWR/m$^3$ N$^{-1}$ m$^{-1}$) for the two smaller particle sizes to around $3.3 \times 10^{-13}$ (SWR/m$^3$ N$^{-1}$ m$^{-1}$) for the abrasive with the particle size of 180 μm. They attributed this rapid increase to change in wear mechanism from plastic deformation to a more fracture-dominated removal mechanism.

To study the material removal mechanism in dry abrasion testing, coarse SiO$_2$ and SiC were used as soft and hard abrasive particles, respectively. The test was stopped at the very early stage and the surface was analyzed. For the case with SiO$_2$, as it can be seen in Fig. 20, it was found that the scratches initiated from surface open porosities and continued along the direction of rotation of the rubber wheel. In this case, the penetration of the abrasive particles into the hard surface of the coatings is very limited.

In the case of using hard SiC abrasive sand, according to Fig. 21, a penetration of particles into the hard surface of the coating occurs. As can be seen unlike SiO$_2$, the scratch groove is not initiated from open porosity regions. It is originated from the location that contact pressure is high enough to trigger the penetration of abrasive particles to the
material. The scratch continues until the pressure is enough and particles are not damaged and result in chipping of material.

As it can be observed in Fig. 20 and 21, the abrasive process can be considered as a combination of multiple scratch tests (Ref 251). So, understanding the material removal mechanism in a single scratch test can give a good picture of the removal process in the abrasion test. Ghabchi et al. (Ref 252) tried to draw a clear mechanism for the damage process of WC-CoCr coatings employing controlled scratch testing. The test was performed by using a conical diamond indenter applying a progressive load from 5 N preload increasing to 100 N. According to Fig. 22, they described the damage evolution to occur in four steps (1) local material removal, (2) formation of angular cracks, (3) formation of semi-circular cracks and (4) delamination of splats.

In another study, Younis et al. (Ref 253) by performing scratch tests, found similar removal mechanisms as those shown in Fig. 22. In this study, two grade sizes of WC-Co coatings, fine and coarse, were applied using the HVOF method. Generally, in the scratch test performed on coatings with fine feedstock particle size, higher load is required to induce fracture on the surface. This is while the wear mechanism in both coatings exhibits similar material removal processes.
In the abrasive wear environment, there are various parameters affecting the process of material removal. The characteristics of abradant particles as well as test conditions and the intrinsic properties of the coating can influence the mechanisms of material removal. In general, abrasion wear can be considered as a superposition of numerous micro-scratching of the abradant particles on the surface. It can lead to fracture of the carbides and/or grooving of the surface resulting in the removal of material. Also, depending on the brittleness of the coating, cracking can happen and as a result expedite the removal of the material.

**Erosive Wear**

There are several standard tests including ASTM G76 and G73 to study the erosion behavior under dry and wet conditions (Ref 214, 215). In erosive environments, depending on abradant characteristics, mechanical properties of the target and test parameters, different material removal mechanisms can be expected. One of the determining factors is the hardness ratio of abradive sand and the target. If the hardness of abradive particles is higher than that of the target, the dominant mechanisms are plastic deformation, surface fatigue and micro-cutting. If the target’s hardness is higher than the erosive particles, in addition to surface fatigue, direct fracture is the main removal mechanism (Ref 254, 255). The other important parameter is the toughness of the coating. In brittle materials, surface fatigue and direct fracture are the dominant mechanisms, while in ductile materials, deformation with micro-cutting is the case (Ref 255-257). For WC-based coatings, the erosion mode is a combination of ductile and brittle mechanisms. For the matrix, micro-cutting and extrusion of the material are the dominant erosive wear processes. This results in isolated uplift of carbide grains that are prone to fracture due to excessive impacts of the erosive particles (Ref 256, 257).

This different ductile and brittle removal mechanisms can be seen in the paper by Ramesh et al. (Ref 258). Performing erosion tests on HVOF-sprayed WC-based coatings using silica sand with the size of 125-180 μm impacted at 40 m/s, they found a combination of ductile and brittle modes of erosion. Based on surface morphology analysis, several grooves in the binder region and lips on the surface were found which indicate plowing and cutting mechanisms. The grooves in the matrix caused dislocation of carbide grains such that small WC grains were pulled out without any damage to individual carbide grains, while the dominant failure mechanism for large grains is chipping. Similar mechanisms of material removal were reported by Kulu et al. (Ref 259) and Thakur et al. (Ref 260). Also, a similar mechanism was proposed by Ding et al. (Ref 135) investigating the failure mechanism of HVOF-sprayed (gas and liquid fuel) WC-CoCr coatings under erosion tests performed at 30° and 60° impact angles on coatings with different WC sizes, Conventional WC-CoCr coatings with a WC size of 1.5 μm and multimodal WC-CoCr coatings comprising micrometric carbides of 2.5 μm size and 80-200 nm size were used as feedstock. Formation of micro-damages followed by propagation of micro-cracks, resulting in material removal from the surface, were proposed as the dominant wear mechanism in all the samples. Figure 23 shows schematic diagram of the erosion wear mechanism at 30° for conventional and multimodal coatings.

First, as a result of the collision of erodent particles on their sharp corner, the binder phase with low hardness is prone to be removed. The presence of hard WC grains can prevent further removal of the binder phase (Fig. 23a). Once the large WC grains fall off due to pull-out or fracture, the erodent particles continue to exfoliate the matrix phase and submicron WC grains, Fig. 23(b) and (c). The presence of the nanosized carbide grains can slow the process of material removal such that the binder in the conventional coating is eroded more easily as shown in Fig. 23(d).

In addition to the former mechanisms which are mainly attributed to surface evolution of the coating, the formation and interlinking of subsurface cracks resulting in material removal is the other scenario for erosion wear proposed by Li et al. (Ref 261). They performed erosion tests at different impact angles on conventional WC-CoCr coatings with different porosities deposited using HVOF and HVAF methods. Micro-cutting and coating spallation were proposed to be the dominant mechanisms for material removal under these test conditions. Figure 24 shows schematic diagrams of the formation and growth of subsurface microcracks in porous and dense coatings.

Crack nucleation and propagation behavior were suggested to be different in porous and dense coatings. In porous microstructures, cracks nucleate at pores and propagate between the carbides while in dense coatings, the cracks form in the weak areas and stress concentration regions like sput boundaries. As a result of interlinking of these cracks and propagation toward the surface, material removal can occur. Small, flat plateaus and a rough surface were formed in the case of dense and porous coatings, respectively (see Fig. 24). A similar mechanism for material removal is proposed by others (Ref 262-264). Despite the comprehensive analysis on wear mechanisms in these studies, the difference in removal mechanisms of HVAF and HVOF coatings were not studied.

Feedstock characteristics like carbide size are a key factor in determining the removal mechanism of WC-based coatings under erosion conditions. Matikainen et al. (Ref
showed this by employing feedstock powders with two different carbide sizes of 0.8 μm (H1W1) and 0.4 μm (H1W2) deposited by the HVAF method. Finer carbide size resulted in carbide-rich areas in the H1W2 coating (red circles) which naturally made it more resistant against erosive wear, while more binder-rich areas were visible in the H1W1 coating. Larger carbides led to higher amount of carbide removal and as a result rougher surface (Fig. 25a), while very limited fractures of carbides happened in the case of the coating with fine carbide size. Hence, a reduction in carbide size can significantly enhance the wear performance under erosion conditions. This is reaffirmed by several other reports (Ref 208, 265).

The material removal mechanism of WC-based coatings under erosive environment generally starts from the removal of binder and consequently, the fracture and/or pull-out of the carbide grains on the surface. In addition to surface removal, as the porosity of the coating increases the possibility of formation of subsurface cracking networks increases under the impact of erodent particles, resulting in excessive separation of material. Employing finer carbide size, which is plausible employing HVAF technique, can have a great influence on improving the erosion wear performance by the microstructure more homogeneous, along with less tendency to fracture as a result impact of erodent particles.

Overview

As evident from the preceding discussion in the above three parts ("Sliding Wear", "Abrasive Wear" and "Erosive Wear" sections), the wear mechanism can differ depending on the wear condition. For the sliding conditions, it is dominated by the propagation of fatigue cracks and carbide pull-outs and fragmentations in form of pits. For abrasion conditions, due to high stresses induced on the surface, a severe fragmentation occurs as a result of either extensive cracks propagation in the system or binder removal and fragmentation of unsupported carbides. The wear mechanism in erosion is even more different, it comprises various mechanisms ranging from plastic deformation, crack formation, fatigue and fracture to...
micro-cutting. Therefore, it is challenging to make a direct comparison or to draw a valid comparison between mechanisms and the extent of material loss in the three wear conditions especially since the wear performance is mostly reported in terms of wear rate which is in different units for each test (i.e., mm$^3$ N$^{-1}$ m$^{-1}$ for sliding, mm$^3$ g$^{-1}$ for erosion and usually mass loss or volume loss in case of abrasion). In general, in the cases where decarburization of carbide increases the brittleness of the coating (which is the case for some of the HVOF methods) the removal process is faster as a result of accelerated crack propagation. It has been reported by Testa et al. (Ref 75) that the binder composition of HVOF WC-based coatings, when changing from CoCr to NiMoCrFeCo or FeNiCr-MoCu, does not greatly influence the wear mechanisms under sliding and abrasive wear. However, in a very recent study by Heinrichs et al. (Ref 266), performed on sintered cemented carbide samples, it was shown that binder chemistry can significantly influence wear initiation. Conventional Co-based binder composition exhibited much more resistance against damage initiation compared to Ni and Fe binders. Although this is not a thermal spray example, it indicates potential contradictions that demand closer scrutiny. To the best of the authors’ knowledge, there are rare comprehensive investigations studying the effect of binder composition on the removal mechanisms of thermal spray WC-based coatings.

Summary and Conclusions

In this paper, a comprehensive review on thermal spray WC-based coatings has been presented with specific emphasis on alternative binders, processing techniques and tribological behavior of these coatings.

- The need for moving away from Co as a conventional binder, due to several environmental and supply risk concerns, seems obvious and there are several alternatives studied in the literature in terms of mechanical and tribological performance. Ni-based and Fe-based compositions such as NiMoCrFeCo and FeCrAl, deposited using HVOF method, have been shown to be promising alternatives. However, their tribological behavior deserves further comprehensive assessment. There are various other promising alternative Fe-based matrix compositions such as FeCoNi that are processed by means of powder metallurgy and it is plausible that they can be tried employing thermal spray methods.
- While HVOF is currently the most widely employed process for applying WC-based coatings, HVAF has emerged as a promising technique to tackle some of the shortcomings of the HVOF method such as decarburization. In terms of wear performance, HVAF WC-based coatings tend to exhibit promising results. Under sliding and abrasive wear environments, the absence of brittle phases (mainly W$_2$C) can mitigate surface and subsurface cracking, resulting in an improvement of the wear performance. The HVAF technique appears to be a more robust method in terms of the quality of the deposited coating using different spraying parameters compared to HVOF. Also, it can make the fabrication of coatings with refined microstructures possible, by employing smaller carbides, while this is not possible by HVOF due to excessive decarburization.
- There are several investigations on the wear behavior of WC-based coatings trying to present a scenario on the material removal under different environments including sliding, abrasive and erosive wear conditions: plowed grooves, cracking, pitting and finally extensive separation of material. Plowing and grooving leading to cracking and pitting of coating materials and subsequently extensive separation of the coating are found to be the most common removal mechanism process under sliding wear conditions. Under abrasion conditions, the coating degradation usually starts with the removal of the soft matrix phase and results in the partial or complete fragmentation of weakened WC grains and, subsequently, material removal. Under erosive conditions, the wear process is a combination of plastic deformation, subsurface crack initiation/propagation and chipping, all of which subsequently contribute to material removal. Although there have been a number of good investigations on the material removal mechanisms...
removal process for WC-based coatings applied by the HVOF process, very limited studies deal with the removal mechanisms of coatings applied using the HVAF method. The removal mechanisms can differ for HVAF and HVOF coatings, since the coatings applied using HVAF method do not contain many brittle phases, resulting in a possible change in removal mechanisms.

Employing the experiences from powder metallurgy to the thermal spray field regarding the use of alternative binders should be considered in future studies. There are few investigations on fabricating HVAF WC-based coatings with refined structures by using fine carbides and this demands more attention in future studies. Moreover, the influence of feedstock characteristics such as carbide size on the wear mechanism is not fully understood yet and this also demands more attention in future studies. The material removal behavior and mechanisms in coatings with alternative binders (to Co) are not well explored yet. Since in most of the wear mechanisms the material removal initiates from the binder, having different chemistries with distinct material properties can potentially affect the process of wear. Hence, future future works in these areas would be beneficial to the thermal spray community.

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Influence of Test Conditions on Sliding Wear Performance of High Velocity Air Fuel-Sprayed WC–CoCr Coatings

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Abstract: Sliding wear performance of thermal spray WB-based coatings has been widely studied. However, there is no systematic investigation on the influence of test conditions on wear behaviour of these coatings. In order to have a good understanding of the effect of test parameters on sliding wear test performance of HVAF-sprayed WC–CoCr coatings, ball-on-disc tests were conducted under varying test conditions, including different angular velocities, loads and sliding distances. Under normal load of 20 N and sliding distance of 5 km (used as ‘reference’ conditions), it was shown that, despite changes in angular velocity (from 1333 rpm up to 2400 rpm), specific wear rate values experienced no major variation. No major change was observed in specific wear rate values even upon increasing the load from 20 N to 40 N and sliding distance from 5 km to 10 km, and no significant change was noted in the prevailing wear mechanism, either. Results suggest that no dramatic changes in applicable wear regime occur over the window of test parameters investigated. Consequently, the findings of this study inspire confidence in utilizing test conditions within the above range to rank different WB-based coatings.

Keywords: tests conditions; sliding wear; HVAF; WC–CoCr; ball-on-disk; wear mechanism

1. Introduction

WC-based cermets sprayed using high velocity thermal spray techniques are one of the most common protective layers employed in industry for wear applications [1,2]. They are expected to resist various wear environments, namely erosive wear, abrasive wear, fretting wear, fatigue and sliding wear [1,3]. There are several standardized test procedures to simulate different wear environments, including ASTM G76 [4] for erosive, ASTM G65 [5] for abrasive and ASTM G99 [6] for sliding wear conditions. Ball-on-disk is one of the most commonly employed tests to assess sliding wear performance of WB-based coatings [7,8]. In this test, however, there are several parameters that can potentially affect the results. It is known that a minor change in the contact conditions can influence the process of material removal in a tribosystem [9]. Bayer [10] remarks that “Wear is not a material property. It is a system response”, and this clearly highlights the importance of test conditions in a wear experiment. A sliding ball-on-disk test can result in different contact conditions depending on applied load, the material of the mating surfaces, hardness and size of the produced debris, which can potentially lead to changes in material removal mechanisms and, consequently, test results [11,12]. Occasionally, laboratory testing also compels conduct of multiple tests on a single specimen by varying the wear track radii [13,14]. For a given sliding distance, such tests inevitably lead to varying linear sliding velocities as well as different number of contact incidents at a specific location. The influence of the above on the test outcome also needs to be well understood. Further, it is pertinent to mention that the influence of test conditions on results could be material-specific. This is expected, since the threshold for a dramatic change in wear regime is expected to be intimately related to the materials being tested.
Performing ball-on-disc tests on thermally sprayed WC-based coatings typically results in a very shallow volume loss and, as a result, extremely low specific wear rate (in order of $10^{-8}$–$10^{-9}$ mm$^3$·N$^{-1}$·m$^{-1}$) [15,16]. This extremely low material removal introduces potential sensitivities to selection of test conditions as well as measurement procedure. As stated in the standard [6], chosen test parameters can influence precision of measurement as well as repeatability of test results. Particularly, great precision is required when volume loss is extremely low, as typically in the case of WC-based coatings. According to the standard ASTM G99, linear measures of wear scar should at least have a sensitivity of 2.5 µm. However, the depth of a typical wear track in a ball-on-disc test can be below 1 µm [17,18], which demands a higher measurement sensitivity than that stated in the standard. Generally, in a ball-on-disk test, applied load, test duration and sliding speed are the three main parameters that can potentially influence test results, particularly in terms of material loss and coefficient of friction. Some studies can be found in literature studying influence of these test parameters [19–22]. Based on the selected test parameters, two main regimes can be achieved during sliding wear test, namely mild wear and severe wear [1,23]. A transition is known to happen in wear regime from mild to severe by increasing load and/or sliding speed or running the test for longer distances. For instance, it has been shown in some studies [24,25] that a full transition in wear regime can occur in the case of HVOF-sprayed WC–Co samples when increasing the normal load from 19 to 35 N, resulting in a substantial increase in specific wear rate. Moreover, Wang et al. [26] performed ball-on-disk tests on high velocity oxy-fuel (HVOF)-sprayed WC–CoCr coatings at many different loads in the range 15 N–90 N for same test duration, sliding speed and ball material. They concluded that, despite a huge change in the applied load, the friction coefficient during the steady state period fluctuated in a small range of 0.3–0.4. However, their results showed that the mechanism of material removal can greatly change from carbide pull-outs to massive material exfoliation, depending on the applied load. Moreover, specific wear rate experienced a substantial increase by a factor of $10^2$ (from $3.6 \times 10^{-8}$ to $3.5 \times 10^{-5}$ mm$^3$·N$^{-1}$·m$^{-1}$). Karaoglanli et al. [27] studied wear behaviour of HVOF WC–Co coatings, employing the ball-on-disk test under loads of 5 N and 15 N and sliding speeds of 10 and 20 cm/s for the same test duration and ball material. It was shown that an increase in sliding speed resulted in higher specific wear rate, while the wear rate decreased on increasing the normal load from 5 N to 15 N. Although these studies provide an understanding of the influence of test conditions on wear behaviour of WC–CoCr coatings, there is no published report systematically investigating the effect of all the aforementioned parameters on wear performance of WC-based coatings. In this study, we tried to fill this research gap by conducting a systematic study on wear behaviour of WC-based coatings under various wear conditions.

In order to have a good understanding of the role-playing factors and their effects on the sliding wear behaviour of WC-based coatings, conducting a comprehensive investigation is vital. This helps to establish a reliable testing routine for HVAF-sprayed WC–CoCr coatings. In this study, the effects of potential influencing parameters including angular velocity, load and sliding distance on wear behaviour of WC-based coatings, fabricated using high velocity air fuel (HVAF) spraying, are systematically evaluated and discussed.

2. Experimental Procedure

2.1. Deposition of Coating

Commercially available 86WC–10Co–4Cr powder manufactured employing agglomeration and sintering technique (trade name: Amperit® 558.059, Höganäs GmbH, Goslar, Germany) was used as feedstock. Characteristics of the used powder are provided in Table 1. Domex 355 coupons of 25.4 mm diameter and 6 mm thickness were used as substrate. All the samples were degreased and mounted on a fixture rotating with a 1.66 m/s linear speed. The samples were grit blasted with alumina particles of average size 220 µm sprayed with the HVAF gun, resulting in a surface roughness (Ra) of approximately 4 µm. The grit-blasted substrates were then coated using a 5L2 convergent-divergent nozzle with
an M3 HVAF torch (Uniquecoat Technologies LLC, Oilville, VA, USA). Spray parameters for grit-blasting and coating, both carried out using the above torch, are listed in Table 2.

Table 1. Characteristics of WC–CoCr feedstock powder.

<table>
<thead>
<tr>
<th>Composition (% Mass)</th>
<th>Particle Size Range (µm)</th>
<th>Carbide Size</th>
<th>Service Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co: 8.5–11.5</td>
<td>C: 5.0–6.0</td>
<td>W: Bal.</td>
<td></td>
</tr>
<tr>
<td>Cr: 3.0–5.0</td>
<td>5/30 fine</td>
<td>fine</td>
<td>&lt;500</td>
</tr>
</tbody>
</table>

Table 2. Grit-blasting and spraying parameters employed.

<table>
<thead>
<tr>
<th>Gun/Nozzle</th>
<th>Air (psi)</th>
<th>Fuel 1 (psi)</th>
<th>Fuel 2 (psi)</th>
<th>Carrier (L/min)</th>
<th>Feed (g/min)</th>
<th>SoD (mm)</th>
<th>Number of Strokes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grit-blasting</td>
<td>M3/SL2</td>
<td>110</td>
<td>100</td>
<td>80</td>
<td>60</td>
<td>≈100</td>
<td>350</td>
</tr>
<tr>
<td>WC–CoCr</td>
<td>M3/SL2</td>
<td>118</td>
<td>105</td>
<td>115</td>
<td>50</td>
<td>200</td>
<td>300</td>
</tr>
</tbody>
</table>

2.2. Coating Characterization

Coated samples were ground and polished for microstructural characterization of coating cross-sections and hardness measurements. Surfaces of coated samples were also polished prior to wear testing. Following grinding using a 45 µm diamond disk, three steps of polishing were performed successively with 9 µm and then 3 µm Kemet liquid diamond media, followed by MasterMet 2 dispense to reach a mirror-polished state corresponding to Ra value less than 0.01 µm. General microstructure analysis of the coatings as well as post-wear analysis on wear scars were performed by scanning electron microscopy (SEM) (HITACHI TM3000 microscope, Krefeld, Germany, and ZEISS GeminiSEM 450, Oberkochen, Germany).

Vickers hardness measurement of the coating was conducted employing Struers Duramin-40 microhardness tester. Following the standard ASTM E384 [28], a total of fifteen indentations were performed on coating specimens.

2.3. Ball-on-Disk Sliding Tests

Samples were exposed to sliding wear employing a ball-on-disk testing rig (Tribometer TRB3, Anton-Paar, Buchs, Switzerland) following the procedure of the standard ASTM G99. The tests were conducted on mirror-polished samples. Three parameters, namely angular velocity, load and sliding distance, were varied (see Table 3). A test run conducted at 20 N of normal load for 5000 m of sliding distance with a linear speed of 0.2 m/s was selected as the reference. All the test runs were performed at a constant linear speed of 0.2 m/s, which resulted in various angular velocities corresponding to 2400, 2000, 1700, 1500 and 1333 rpm when the radii of the wear tracks, made by the sliding ball on the coating surface, were set to 5, 6, 7, 8 and 9 mm, respectively. That Alumina ball of radius 6 mm was used as the mating material in all cases.

For each set of tests to assess parametric impact on ensuing results, the parameter of interest was systematically varied compared to the reference run mentioned above. The angular velocity was changed by varying the wear track radius and keeping the linear speed constant during the tests. All the tests conducted to assess influence of angular velocity (Figure 1a) were repeated three times at each wear track radius on three different samples (S1, S2 and S3). Figure 1b shows a typical sample after testing on radii of 5, 7 and 9 mm. For the set of tests using the load as variable parameter, the normal applied load was varied between 20 N and 40 N. Due to limitation in the testing rig, it was not plausible to increase the load beyond 40 N. In yet another, the sliding distance was increased to 10 km from 5 km. Finally, in one particular run, both load and distance were simultaneously increased to 30 N and 10 km, respectively. The tests with load and distance as variables were conducted on radii of 7 and 8 mm. This was done since the outcome of the tests of different radii (see Section 3.2) has already established that the wear track radius does not influence the specific wear rate.
Table 3. Test parameters employed during sliding wear tests.

<table>
<thead>
<tr>
<th>Variable Parameter</th>
<th>Code</th>
<th>Radius (mm)</th>
<th>Load (N)</th>
<th>Distance (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular velocity</td>
<td>R5 (S1/S2/S3)</td>
<td>5</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>R6 (S1/S2/S3)</td>
<td>6</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>R7 (S1/S2/S3)</td>
<td>7</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>R8 (S1/S2/S3)</td>
<td>8</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>R9 (S1/S2/S3)</td>
<td>9</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Load</td>
<td>L20D5</td>
<td>7 and 8</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>L30D5</td>
<td>7 and 8</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>L35D5</td>
<td>7 and 8</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>L40D5</td>
<td>7 and 8</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>Distance</td>
<td>L20D10</td>
<td>7 and 8</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Load and distance</td>
<td>L30D10</td>
<td>7 and 8</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 1. (a) Schematic diagram of different radii and distinct locations for volume loss measurements on the testing samples, and (b) a typical sample after ball-on-disk test.

Sliding data such as friction force and friction coefficient were continuously monitored during the tests. After each test, the samples were ultrasonically cleaned and the volume loss measured employing white light interferometry (WLI) method (Profilm 3D, Filmetrics, Unterhaching, Germany). The measurement was performed at four different locations on the wear track, as shown in Figure 1a. The cross-sectional area of the wear track at each location was determined by dividing measured volume loss by length of wear track at each segment measurement. Approximate arc length of each segment is 1.75 mm. From the four measured values, an average value for the cross-section area of the whole wear track was calculated along with standard deviation of the four measurements. Having total length of the wear track and the average value of cross-section area, the total volume loss from the wear track (Equation (1)), and therefore, the specific wear rate, can be obtained according to Equation (2).

\[
V_{\text{loss}} = \frac{1}{2} \pi R \cdot \left( \frac{V_1}{l_1} + \frac{V_2}{l_2} + \frac{V_3}{l_3} + \frac{V_4}{l_4} \right)
\]

(1)

\[
W = \frac{V_{\text{loss}}}{L \cdot d}
\]

(2)

where in Equation (1) \( V_1, V_2, V_3 \) and \( V_4 \) are volume losses at the four locations shown in Figure 1a; \( l_1, l_2, l_3 \) and \( l_4 \) are the corresponding arc length of the segments; and \( R \) is radius of the wear track. \( L \) and \( d \) in Equation (2) are the applied normal load and total sliding distance, respectively.
3. Results and Discussion

3.1. Coatings Characterization

Figure 2 shows low and high magnification images of the WC–CoCr coating used throughout this study. It can be seen that a uniform and dense WC–CoCr coating is achieved by the HVAF method. Although there are some submicron pores (as indicated in Figure 2) noted in the coating, the overall porosity content is less than 1 percent and comparable with literature [7,8]. Vickers hardness value for the coating measured to be 1410 ± 27 HV0.3. All the coating specimens utilized for subsequent ball-on-disk wear tests were simultaneously HVAF sprayed to ensure minimal variation, and the influence of each test parameter on ensuing results is individually discussed below.

Figure 2. SEM images of cross-sections of deposited coatings at (a) low magnification and (b) high magnification.

3.2. Influence of Angular Velocity on Wear Behaviour

3.2.1. Local Variations within a Wear Track

According to Table 3, identical coating specimens were subjected to ball-on-disk tests, with the track radius being the only variable. As mentioned in Section 2.3, specific wear rates are calculated based on four local measurements using WLI method. Therefore, depending on variation in volume loss from the four different locations, a standard deviation can be defined for specific wear rate measurement corresponding to each wear track. This deviation is a measure of uncertainty associated with specific wear rate determination due to local variations within the wear track. The standard deviation values (Sm) for all the radii are reported as error bars in Figure 3. It can be seen that a standard deviation as high as 4.18 mm$^3$·N$^{-1}$·m$^{-1}$ can occur in specific wear rates corresponding to the same wear track, calculated based on four local measurements. It is also noticeable that no trend is evident in magnitude of Sm by changing angular velocity, which means the number of revolutions on the same wear track as well as angular velocity does not significantly influence uniformity of the wear track for the radii between 5 and 9 mm and angular velocity corresponding to 1333 rpm to 2400 rpm. This indicates that the effect on uniformity of wear track due to change in angular velocity can be considered negligible within this window.

3.2.2. Variation in Specific Wear Rate

Figure 3 shows specific wear rate value for all the 15 test runs (3 each for the five track radii tested), and the error bars indicate standard deviation (Sm) of the four measurements on each wear track.

Barring S2R5, S1R7 and S3R8, at least two out of the three tests performed at each radius on the three samples were found to result in similar specific wear rate values. Regardless of the different wear track radii, a clear overlap in error bars can also be
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recognized. Therefore, the three conditions above (S2R5, S1R7 and S3R8) may be considered to be outliers. Thus, the ball-on-disk tests are observed to yield consistent specific wear rate results regardless of the angular velocity being varied over a wide range, as demonstrated by the present experiments. This is due to the fact that no change in wear mechanisms and wear regime happened in this window of tests conditions. More detailed discussion is provided in Section 3.5.

Figure 3. Specific wear rates from all fifteen ball-on-disc tests conducted at various wear track radii.

To further highlight the consistency of the specific wear rate results regardless of angular velocity, omitting the three above mentioned outlier values, the calculated average value of the specific wear rate and the maximum standard deviation that can occur from measurement are depicted in Figure 4.

It can be seen that all the average values of each radius fall in a range of around 11—18.6 mm$^3 \cdot$N$^{-1} \cdot$m$^{-1}$. This deviation in average specific wear rate is smaller than the maximum standard deviation from measurement (Max. $Sm = \pm 4.18$ mm$^3 \cdot$N$^{-1} \cdot$m$^{-1}$). Therefore, it can be concluded that maximum deviation from changing the wear track radius (and, hence, angular velocity) is smaller than the maximum standard deviation from the measurement method itself. Moreover, standard deviation of the specific wear rates of all the twelve measurements is 2.9 units, which is still much less than maximum $Sm$. Therefore, results from the tests performed on the same sample with various track radii (between 5 and 9 mm in the present study and corresponding to substantially varying angular velocity) can be consistent and deemed to be representative of wear behaviour of the coating.

3.2.3. Variation in Coefficient of Friction and Wear Mechanism

The coefficient of friction (CoF) for all the samples reached steady state after around initial 5000 s of sliding. Figure 5 shows average steady state CoF values for all the 15 test repetitions performed on the 3 samples at different radii, along with the standard deviation (as error bars) showing fluctuation of CoF values. It can be seen that a majority of CoF values fall into a narrow range of 0.3 to 0.4. However, looking at S1R6 and S1R8, the average CoF value can deviate from 0.16 to 0.58 units without any considerable change in the specific wear rate (see Figure 3). Comparing specific wear rate figures with CoF values (Figures 3 and 5), no direct correlation can be clearly made between specific wear rate and its corresponding friction coefficient value. Unlike two studies conducted by
Wesmann et al. [29,30] attributing higher coefficient of friction to formation of surface oxides and tribofilm, no obvious correlation was identified between CoF values and surface morphology during post-wear analysis. In other words, some wear tracks were found to be similar, while the corresponding CoF values were different by a factor of 2 or 3. Hence, the CoF value in the WC–CoCr coating studied in this paper appears to vary without a clear trend within the aforementioned range. Similar large variation in CoF without any clear trend was found in a study by Wilkowski et al. [31].

![Figure 4. Average specific wear rate value of different wear track radii.](image)

![Figure 5. Average CoF value for all the fifteen tests.](image)
Although the specific wear rate values appear consistent regardless of angular velocity as discussed above, it is also important to ensure that this observation is not coincidental and there is no change in wear regime over the test parameter window under consideration. Therefore, in order to investigate the wear mechanisms responsible for material removal, wear tracks were studied under SEM. Figure 6 shows SEM images of wear scars of various radii of R5, R7 and R9 on the two samples, S2 and S3. Ploughing is the dominant wear mechanism regardless of the angular velocity of the test. In addition, some signs of shallow grooving can be detected (shown by double sided arrows). These two mechanisms are...
also reported in other studies to be the common wear mechanisms in case of WC-based coatings under sliding wear conditions [26,32]. SEM image on wear scar of the sample S2R5 shows that the number and depth of the ploughs are extremely higher than the rest of the test runs, which is the reason for its specific wear rate being too high (see Figure 3). Moreover, as shown by arrows, there are regions with significant material removals within this wear track, while no such large-scale removal (in form of pitting wear) was detected in other wear tracks. The reason for this unique behaviour was not clear. By comparing SEM images of the wear tracks with various radii (various angular velocities), it is clear that the quantity and depth of ploughs and grooves are differing randomly from a case to the other, without any direct correlation with the radius (angular velocity). For instance, number of ploughs on the sample S2R7 are clearly higher than the sample S2R9, but this trend is completely reversed in the case of sample 3 (compared S3R7 with S3R9). All things considered, it is clear that for none of the samples major wear mechanisms changed, and it is dominated by ploughing and minor grooving.

3.3. Influence of Load on Wear Behaviour

3.3.1. Variation in Specific Wear Rate

Wear behaviour of the HVAF-sprayed WC–CoCr coating was also evaluated at different loads applied during ball-on-disk testing. Specific wear rate values corresponding to various loads are reported in Figure 7. No major change in specific wear rate was detected, and it is also clear that no major variation in the range of error bars is noted. This means that increase in load over the range investigated (20 N to 40 N) has no influence on consistency of the sliding wear test results.

![Figure 7](image-url)  
**Figure 7.** Specific wear rates from ball-on-disc tests conducted under different loads.

3.3.2. Variation in Coefficient of Friction and Wear Mechanism

Figure 8 shows evolution of friction coefficient of the samples during the tests performed at radius of 7 mm. The height of the CoF plateau is observed to clearly decrease with increasing normal load. A gradual decrease in the average values can be seen when increasing the load from 20 N to 30 N, 35 N and 40 N. This indicates that, in spite of increase in normal load, friction load does not experience any considerable change. Although some studies can be found reporting a similar trend [33], this trend can also exhibit random behaviour depending on contact conditions [26] or may even be completely reversed [34] based on the number of third-body particles involved in the contact region. In general, when fewer third-body particles are involved in the test, i.e., when the test condition is close to two-body wear, with increase in load, the CoF value decreases.
To investigate any possible change in mechanism of wear as a result of increase in load, SEM analysis was performed on wear tracks. Figure 9 shows SEM images of wear scars of the L30D5 and L40D5 samples. The number of ploughs has clearly experienced a noticeable increase by increasing the load from 30 N to 40 N. Comparing Figures 6 and 9, it is clear that, in spite of the increase in load from 20 N to 40 N, ploughing is still the dominant wear mechanism. This suggests that no significant changes occurred in the mechanism of material removal [1,26,35].

![Figure 8. CoF evolution for the coating tested under different normal loads.](image)

Running the test for longer time (longer sliding distance) is another way to investigate any changes in wear rate. Three tests were conducted for this matter: two with the same load of 20 N and different sliding distance of 5 km and 10 km (L20D5 and L20D10) and one with normal load of 30 N and distance of 10 km (L30D10). Figure 10 shows specific wear rate of the three samples. Increasing sliding distance of the test from 5 km to 10 km (under normal load of 20 N) resulted in neither a substantial difference in specific wear rate nor any improvement in repeatability of result (bigger error bar for L20D10 compared to L20D5). As presented later in Figure 12, all the three values are still within the window of maximum $Sm$ and thus do not differ significantly.

![Figure 9. SEM images of wear tracks at different normal loads of 30 N and 40 N. (a) L30D5 and (b) L40D5.](image)

3.4. Influence of Sliding Distance on Wear Rate

Running the test for longer time (longer sliding distance) is another way to investigate any changes in wear rate. Three tests were conducted for this matter: two with the same load of 20 N and different sliding distance of 5 km and 10 km (L20D5 and L20D10) and one with normal load of 30 N and distance of 10 km (L30D10). Figure 10 shows specific wear rate of the three samples. Increasing sliding distance of the test from 5 km to 10 km (under normal load of 20 N) resulted in neither a substantial difference in specific wear rate nor any improvement in repeatability of result (bigger error bar for L20D10 compared to L20D5). As presented later in Figure 12, all the three values are still within the window of maximum $Sm$ and thus do not differ significantly.
Figure 9. SEM images of wear tracks at different normal loads of 30 N and 40 N. (Figure 11a,b) SEM images of wear tracks performed under 20 N (a) and 30 N load (b).

Figure 10. Specific wear rate values from ball-on-disc tests conducted for different sliding distance and load.

Figure 11a,b show SEM images on wear tracks of the two L20D10 and L30D10 samples. First, by comparing Figure 11a and SEM images in Figure 6, it is clear that no major changes are detectable by increasing the sliding distance from 5 km to 10 km under the same normal load of 20 N. However, a noticeable change is evident when comparing SEM images of Figure 11a,b, which is rooted from an increase in applied normal load from 20 N to 30 N when running for the same distance of 10 km. One clear change is that quantity and depth of the ploughs experienced an obvious increase, and the number and size of pits (dark regions) also considerably increased. The pits, which are filled up with wear products, indicate material removal [18]. Therefore, by a simultaneous increase in the normal load (from 20 N to 30 N) and sliding distance (from 5 km to 10 km), some signs of material removal in form of pits is added to ploughing as dominant wear mechanisms. However, as far as the pits are isolated and therefore possible to be filled up with wear products such as oxides of alumina, tungsten, cobalt and chromium, they are not taken into account in volume loss measured by WLI technique and, consequently, not in specific wear rate. This explains no major change in specific wear rate value reported in Figure 10 in spite of minor change in removal mechanisms and, therefore, no changes in wear regime. As shown in the study by Wang et al. [26], connection of these pits can cause a dramatic change in removal mechanism and result in the magnitude of specific wear rate.
3.5. Wear Regime

When the specific wear rate is low and does not substantially change (i.e., remains of same order of magnitude) by changing test conditions, the wear regime can be termed as mild [1,26,35]. Moreover, in case of WC-based coatings, it is known that, after a certain increase in normal load, the specific wear rate experiences a substantial increase by orders of magnitude [26]. The specific wear rate values for various angular velocities, loads and sliding distances (from a large matrix of ball-on-disk tests conducted, as listed in Table 3) previously presented in Figures 4, 7 and 10 reveal that the average specific wear rate values vary from 11 to 18.6 mm³·N⁻¹·m⁻¹, which are small enough to be categorized as mild wear regime. All the specific wear rate values from ball-on-disc testing under different angular velocities, different loads and/or sliding distances along with the corresponding average value are depicted in Figure 12. It can be seen that deviation of all the specific wear rate values (with the only exception of S3R9) from average value is still within the window of maximum Sm. It should be mentioned that the conclusions in this paper are specific to sliding wear rate behaviour of HVAF-sprayed WC–CoCr coatings, and the results may differ for other coatings. Additionally, no significant difference in wear mechanisms was evident from post-wear analysis, confirming that no transition from mild to severe wear regime occurs over the investigated test parameter window. Therefore, as shown in Figure 13, by individually increasing either normal load up to 40 N, angular velocity up to 2400 rpm, or sliding distance up to 10 km from the ‘reference’ test parameters of 20 N, 2400 rpm and 5 km, no changes in wear regime occur during ball-on-disk testing of HVAF-sprayed WC–Co-Cr coatings.

![Figure 12](image12.png)  
**Figure 12.** Specific wear rate from various ball-on-disc tests conducted under different conditions according to Table 3.

![Figure 13](image13.png)  
**Figure 13.** Schematic diagram of the mild and severe wear regimes adapted from [1].

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Author Contributions:

Investigation, K.T. and V.K.S.; data curation, K.T. and V.K.S.; writing—original draft preparation, K.T.; review and editing, S.J. and M.G.; funding acquisition, S.J. All authors have read and agreed to the published version of the manuscript.

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The authors declare no conflict of interest.
A comprehensive investigation was conducted in order to understand sliding wear behaviour of HVAF-sprayed WC–CoCr coatings under a variety of different test conditions, and the following conclusions were drawn: No significant difference was observed in specific wear rate when changing angular velocity from 1333 rpm up to 2400 rpm in a way that the difference in smaller than precision of measurement method. Increase in load up to 40 N did not make any major change in either specific wear rate or deviation of values from different repetitions. Increase in sliding distance up to 10 km while the normal load was fixed at 20 N changed neither specific wear rate nor repeatability deviation. All these roots from no major change in dominant wear mechanisms or wear regime. Therefore, conducting ball-on-disc test on WC–CoCr coatings under test conditions within the range conducted by this study could be considered as a reliable testing routine.

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Paper C

Influence of nozzle configuration and particle size on characteristics and sliding wear behaviour of HVAF-sprayed WC-CoCr coatings

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Influence of nozzle configuration and particle size on characteristics and sliding wear behaviour of HVAF-sprayed WC-CoCr coatings

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ABSTRACT

In this study, effect of feedstock particle size and nozzle configuration on deposition, microstructural features, hardness and sliding wear behaviour of high velocity air fuel (HVAF)-sprayed WC-CoCr coatings was evaluated. Three different WC-CoCr powders with nominal particle sizes of 5/20 μm (fine), 5/30 μm (medium) and 15/45 μm (coarse) were sprayed employing a HVAF gun with four distinct DeLaval nozzle configurations involving different lengths and/or exit diameters. Microstructure, phase constitution and mechanical characteristics of the coatings were evaluated using SEM, EDS, XRD and micro indentation testing. Specific wear rate for all the samples was determined under sliding conditions and a comprehensive post wear analysis was conducted. X-ray diffraction analysis showed negligible decarburization in all the HVAF-sprayed coatings. It was shown that decrease in particle size of employed feedstock results in discernible changes in microstructural features of the coatings as well as considerable improvement in their performance. Also, notable changes in wear mechanisms were identified on reducing particle size from coarse to medium or fine. Fine and coarse feedstock powders were found to be sensitive to the type of nozzle used while no major difference was observed in coatings from powders with medium cut size sprayed with different nozzles.

1. Introduction

High velocity air-fuel (HVAF) spraying method has been considered increasingly attractive for spraying WC-based wear resistant coatings and attracting significant research attention. This is largely by virtue of its capability to produce high quality coatings and overcoming some of the existing problems such as decarburization [1–3]. HVAF spraying method typically generates higher particle velocities leading to higher kinetic energy and, due to the lower flame temperature, the particle temperatures are also lower compared to other spraying techniques like high velocity oxy-fuel (HVOF). The latter is a key factor responsible for diminishing decarburization [4,5]. Moreover, in the HVAF method, substituting air in place of oxygen not only results in lower spraying costs, but can also effectively mitigate oxidation of the feedstock. Consequently, a finer powder cut size can be used as feedstock [6–8]. However, different hardware configurations in the HVAF method result in varied particle temperatures and velocities. Different torch configurations can be achieved particularly through variations in length and the convergent-divergent design of the nozzles. Therefore, selecting a proper configuration demands a deep understanding of its effect on properties of the resultant coating. Feedstock characteristics such as morphology, density, and particles size also significantly influence the resultant coating properties. Among these, the particle size distribution can be considered a prominent feedstock characteristic for a given chemistry in case of HVAF spraying. Some investigations have been previously conducted to study the effect of HVAF process parameters on characteristics and performance of WC-based coatings. Matikainen et al. [11] studied the effect of nozzle configuration on tribological properties of HVAF-sprayed WC-CoCr coatings deposited using feedstock powder of 10–30 μm size range. They employed a M3 gun (Uniquecoat Technologies LLC, USA) and utilized three nozzles of the same length but with different exit diameters: one cylindrical (named 4L0) and two convergent-divergent configurations.
which a few have investigated the influence of particle size \[20,21\]. Bolelli
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from 780 m\(\mu\) (named 4L2 and 4L4) with increasing exit diameter as the nozzle
coating. In another study by Kumar et al. [10], it was shown that the
der, studied mechanical and wear properties of WC-CoCr coatings. Their
and 15
logical performance of HVAF WC-based coatings \[10\] have been performed to investigate mechanical properties and tribo-
LLC, USA). Their results showed that coatings deposited from powders
spraying WC-CoCr feedstock powder of the same particle size (20
improvement in microhardness and abrasion wear resistance of the
AK06 HVAF gun (Kermetico, USA) with three different nozzle designa-
tions 5O, 5E and 5L, of varying geometrical design, can result in average
particle velocities of 1010, 960 and 895 m\(\cdot\)s\(^{-1}\), respectively, when
spraying WC-CoCr feedstock powder of the same particle size (20–45
μm). However, the above investigations were conducted on powders
with an identical particle size and, as a result, do not provide a broad
view of how the nozzle geometry-particle size combinations can influence
the properties and performance of the resultant coatings. Besides, given the fact that HVAF parameters are primarily hardware dependent
[12] as compared to other spraying techniques like HVOF and plasma
spraying, where other spraying variables, such as particle velocity \(v\),
changing nozzles covers a wide-ranging process window in HVAF
spraying and is of considerable practical relevance. Consequently,
considering the rapid progress of the HVAF technology and commercial
availability of different spray equipment, the influence of nozzle configuration needs to be well established for different powder particle
types to be sprayed.

During the spraying process, particles attain different temperatures and velocities depending on their size. Another key factor is the duration of high temperature exposure, which itself is dependent on the size
(mass) of the particles [15,16] since the in-flight residence time is
governed by the particle velocity. Through a modeling simulation, it has
been shown that WC-CoCr particles are fully molten during HVOF
spraying when their size is smaller than 15 μm [13,14]. Several studies
have been performed to investigate mechanical properties and tribolo-
tical performance of HVAF WC-based coatings \[10–12,18–21\], among
which a few have investigated influence of particle size \[20,21\]. Bolelli
et al. [21] studied sliding and abrasive wear performance of HVAF-
sprayed WC-CoCr with two different particle size ranges of 5–30 μm
and 15–45 μm employing M3 and M2 guns (Uniquecoat Technologies
LLC, USA). Their results showed that coatings deposited from powders
with finer particle size yield superior wear performance. The main
objective of this study was to compare the tribological properties of
HVOF and HVAF WC-10Co4Cr coatings and this was conducted by
employing powders of two particle sizes without considering influence
of nozzle configuration. Matikainen et al. [20] deposited two different
powders with particle size ranges of 10–30 and 5–25 μm using an
identical HVAF M3 gun configuration. Average measured temperature of
in-flight particles was 50 ºC higher for coarser cut size (1410 °C vs.
1360 °C) while the particle velocity for the finer powder was around 30
m\(\cdot\)s\(^{-1}\) higher than that for the coarser powder (957 m\(\cdot\)s\(^{-1}\) vs. 929 m\(\cdot\)s\(^{-1}\)).
Average Vickers hardness was slightly higher for coatings sprayed with
the coarser powder, with a value of 1458 HV0.3 as compared to 1344
HV0.3 for coatings sprayed with a finer cut size. The main focus of this
effort was to evaluate cavitation, slurry and dry particle erosion of WC-
10Co4Cr and Cr3C2-5Si3N4 coatings sprayed by HVOF and HVAF and
two different size ranges for the powders were used without considering
influence of nozzle configuration. Different nozzle configurations can potentially affect the quality of deposited coating and need to be properly selected based on particle size
used as feedstock. The studies mentioned above indicate that selection of
an appropriate feedstock particle with a suitable nozzle configuration
could result in an enhanced wear performance. Notwithstanding the
above, none of the existing studies have undertaken a dedicated effort
focused on investigating the effects of particle size and nozzle configu-
raton when spraying WC-based coatings using HVAF. Hence, con-
ducting a comprehensive study, involving a wide range of particle size
distributions and a host of different nozzle configurations, to assess how
each can influence microstructural, mechanical and tribological proper-
ties of HVAF sprayed WC-CoCr coatings is deemed crucial and pro-
vides the motivation for this work. Accordingly, a comprehensive
investigation is conducted on three powders with different particle size
ranges sprayed with four different nozzles with varying length and/or
convergent-divergent design to investigate the influence of nozzle
configuration and particle size on characteristics and sliding wear per-
formance of HVAF-sprayed WC-CoCr coatings.

### 2. Experiment procedure

#### 2.1. Spraying process

Three commercially available WC-10Co4Cr powders with different particle size ranges produced by Hoganas GmbH employing the
agglomeration and sintering technique (see Table 1), were used as
feedstock material. Domes 355 coupons of diameter 25 mm and thick-
ness 6 mm were used as substrates.

An M3 HVAF torch (Uniquecoat Technologies LLC, Oilville, VA, USA) was used and four different DeLaval nozzles (Fig. 1) were
employed to spray the feedstock powders. All three powders were
sprayed with each nozzle configuration in this study, except PF which
was not sprayed with nozzle N3.

Cleaned samples were mounted on a rotating fixture and grit-blasted
employing alumina powder. Then the three powders were sprayed with
the process parameters mentioned in Table 2 with a targeted thickness of
250 μm for all the coatings. The carrier gas was Nitrogen. It is relevant to

![Fig. 1. Different nozzle configurations used for spraying.](image-url)
mention that the HVAF torch technology is critically based on the orifice design inside the torch. Moreover, the fuel and air supply are pressure controlled, not flow controlled. Therefore, an appropriate way to describe torch parameters in a M3 MVAF torch would be to indicate the nozzle dimensions (as done in Fig. 1) and the supply pressures for Air, Fuel 1 and Fuel 2 (provided in Table 2). Nonetheless, it may be added for completeness that, the air and fuel pressures stated in Table 2 for nozzle 9000 l/min for Air and 200 l/min for Fuel 1 and 2.

Table 2
HVAF spraying parameters used for coating deposition.

<table>
<thead>
<tr>
<th></th>
<th>Pc (N)</th>
<th>Pm (N)</th>
<th>Pf (N)</th>
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<tbody>
<tr>
<td>N1</td>
<td>111</td>
<td>100</td>
<td>105</td>
</tr>
<tr>
<td>N2</td>
<td>114</td>
<td>105</td>
<td>115</td>
</tr>
<tr>
<td>N3</td>
<td>113</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>N4</td>
<td>114</td>
<td>115</td>
<td>115</td>
</tr>
</tbody>
</table>

Accuraspray – G3C (Tecnar, Quebec, Canada) was employed to measure temperature and velocity of in-flight particles at impact. In order to assess repeatability of measured data, the measurement was repeated three times for Pf sprayed using N1 and N2 nozzles several days apart.

2.2. Characterisation of powders/coatings

Scanning electron microscopy (SEM) analysis was performed on all powders to examine their morphology and cross-sections. Powders were collected on carbon tapes and observed under SEM (Hitachi TM3000 microscope, Krefeld, Germany, and Zeiss GeminiSEM 450, Oberkochen, Germany). In order to perform cross-sectional observations, powders were mixed with epoxy, cold mounted, ground and polished (employing the same procedure explained in next paragraph) before being studied in the SEM.

Employing a surface roughness tester (SurfTest 301, Mitutoyo, Japan), roughness values of as-deposited coatings ($R_a$) were measured as per ASME B46.1 standard. Three measurements were performed on each coating and average values and standard deviations have been reported herein.

After sectioning and hot mounting, the samples were ground and polished. Grinding was performed by employing a 45 μm diamond disk, while polishing was carried out successively using 9 μm and 3 μm Kemet liquid diamond solution. Finally, the specimens were mirror-polished employing MasterMet 2 dispense. General microstructure analysis of the samples was performed using SEM analysis.

Vickers hardness of the samples was measured employing Struers Duramin-40 microhardness tester (Cleveland, United States). Fifteen indentations were performed on each sample according to the standard ASTM E384 [22].

Identification of the crystalline phases was performed by X-ray diffraction analysis (XRD), with a Philips XPert device (PANalytical B. V., The Netherlands) on as-coated surfaces. XRD measurements were carried out at 40 kV and 40 mA, with Cu Kα radiation ($\lambda_{Kα1} = 1.540598 Å, \lambda_{Kα2} = 1.544426 Å$), with a scan range of 20°–80° (20), step size 0.02°, and an acquisition time of 2 s/step.

2.3. Ball-on-disk test

Sliding wear tests were performed on samples with a mirror-polished surface (ground and polished in the same manner as described in the Section 2.2), following the procedure prescribed in ASTM G99 standard [23]. The test was conducted using a tribometer rig (Tribometer TRB3, Anton-Paar, Switzerland) which monitors friction coefficient during the test. Alumina balls with radius of 6 mm were employed as the mating counterpart. The ball-on-disk tests were conducted under a constant normal load of 20 N, with a constant linear speed of 0.2 m s$^{-1}$ and for a total sliding distance of 5000 m. At least two repetitions were performed for each test on radius 7 and 9 mm of wear trace. All the tests were done at room temperature with relative humidity of around 30%. After each test, wear products were collected from the surface of the sample in the form of debris, and then the samples were cleaned ultrasonically prior to surface analysis. The top-surface of the wear tracks as well as the wear debris were characterized using SEM/EDX analysis.

Volume loss in the samples as a result of sliding wear was measured employing white light interferometry (WLI) technique (Profilm 3D, Filmetrics, Unterhaching, Germany). Using WLI, it was not possible to capture the whole wear track. Therefore, volume loss in four different regions across the wear track was measured (Fig. 2(a)), based on which an average cross-sectional area was obtained for the wear track at once. Hence, four different wear track locations, approximately 90 degrees apart were scanned on each circular wear track. The overall volume loss was calculated by multiplying the average cross-sectional area by the total length of the wear track (Eq. (1)). Also, specific wear rate for balls...
corresponding to wear track radius of 7 mm was measured. For this, the worn surface area of balls (see Fig. 16) was measured using image analysis [24], then the corresponding radius ($r$) and volume loss determined as shown in Fig. 2(b). Consequently, using Eq. (3), the specific wear rates for both the ball and the coating were obtained by dividing volume loss over the normal load ($L$) and sliding distance.

$$V_{\text{loss-coating}} = \frac{1}{2} \left( \pi R \left( V_1 \frac{l_1}{h_1} + V_2 \frac{l_2}{h_2} + V_3 \frac{l_3}{h_3} + V_4 \frac{l_4}{h_4} \right) \right)$$  \hspace{1cm} (1)

$$V_{\text{loss-ball}} = \frac{1}{6} \left( \pi h \left( 3r^2 + h^2 \right) \right)$$  \hspace{1cm} (2)

$$W = \frac{V}{Ld}$$  \hspace{1cm} (3)

where in Eq. (1) $V_{1-4}$ are volume losses at the four scanned locations, $l_{1-4}$ are the lengths of the corresponding wear track segments at these locations and $R$ is radius of the wear track. In Eq. (2), $h$ and $r$ are the height and radius of the removed spherical cap, respectively. Finally, in Eq. (3), $W$ is specific wear rate, $V$ is volume loss, $L$ is load and $d$ is total sliding distance.

3. Results

3.1. Powder characteristics

Morphologies of the three used powders are shown in Fig. 3(a), (b) and (c). Most of the powder particles of Pc and Pm exhibit a spherical shape while most of the Pf particles were irregular in shape. Fig. 3(d), (e) and (f) shows cross-sectional images of Pc, Pm and Pf, respectively. From the SEM visualization, it is clear that by decreasing the particle size, the number and dimension of the pores within the particles decreases because the smaller the dimension the limited number and size of comprising defects [25]. In other words, the density of individual particles seemed to increase with decrease in particle size, which can potentially have an influence on density of the resultant coating.

3.2. Deposition rate

Fig. 4 shows the measured in-flight temperatures and velocities of particles, in case of different powders used and nozzle configurations employed. Indicative standard deviation values are drawn as error bars in the corresponding data points, based on repeat measurements.

Fig. 3. SEM images of (a-c) particle surface morphologies and (d-f) particle cross-sections of the three powders used (coarse: Pc, medium: Pm and fine: Pf).

Fig. 4. Measured in-flight a) temperature and b) velocity, for the three feedstock powders sprayed using four different nozzles.
conducted on Pf sprayed using nozzles N1 and N2 to show reliability of data. The particle temperature was not significantly influenced by the particle size, varying over a window of 105 °C or less when using the same nozzle. Increasing the exit diameter of the nozzle from N1 to N2, led to a drop in particle temperature by around 150 \( °C \) for Pc and Pm and by about 100 \( °C \) for Pc. The particle velocity was found to increase with reducing particle size in case of each of the nozzles. However, for a given powder, no significant differences in particle velocity were discernible with change in type of nozzle, with the noted variation being limited to a maximum of around 100 m s\(^{-1}\).

An average targeted thickness of around 250 \( μm \) was achieved for all the coatings. From the measured coating thickness and the total number of strokes for each coating (see Table 2), the thickness built up per pass (deposition rate) can be determined, which is a fair measure of deposition efficiency. The deposition rates for all the coatings are provided in Fig. 5.

In general, a substantial decrease in deposition rate can be observed with decrease in particle size from Pc to Pm and from Pm to Pf. This trend was consistent and more clearly evident when comparing the deposition rates for each nozzle used for spraying the three powders with varying particle size ranges. The reason for this must be related to the intrinsic properties of particles associated to their dimension and is further discussed in Section 4.1.

Reduction in deposition efficiency may raise concerns around costs. However, it is worth mentioning that deposition efficiency is not the only determining factor governing the choice of feedstock. For example, a finer feedstock particle size makes it possible to fabricate thinner coatings which involve less powder being used in a shorter spraying time and can, in turn, reduce total coating costs. Also, a finer particle size makes it possible to achieve smoother coatings, which can potentially reduce the demand for subsequent machining leading to significant savings in post-processing costs. On the other hand, in this study, powders of all particle sizes were sprayed with a fixed set of parameters. Therefore, the “optimum” spray conditions in terms of deposition efficiency, which could vary with particle size, may not have been encompassed in the process parameter window that has been investigated herein in case of all powders.

### 3.3. Coating microstructure

Fig. 6 shows SEM images of surfaces of the Pc, Pm and Pf coatings sprayed with the nozzle N2. It is clearly noticeable that, with decrease in particle size, the surface of the coatings attains a finer morphology, resulting in a lower average roughness. Average \( Ra \) value decreases from around 4.5 \( μm \) for Pc coating to around 2.5 \( μm \) and 2 \( μm \) for Pm and Pf, respectively. No significant difference was observed in surface morphology and roughness of the coatings of the same particle size sprayed with different nozzles.

Fig. 7 shows SEM images of all the eleven coatings. No significant differences in microstructure were detected by changing the nozzle configuration for the same powder. However, with decrease in particle size, the homogeneity of the coatings seemed to experience a substantial improvement. The number and size of the dark regions, which correspond to either pores or binder accumulation (see Fig. 17), considerably decrease with reduced feedstock particle size. In order to differentiate pores, SE SEM images were taken from the polished surfaces of coatings from the three different powders (Fig. 8). It was clear that the size and number of pores dramatically reduced with decrease in particle size from Pc to Pm or Pf. The Pf coating exhibited the highest density among all, with minimal detectable pores observable in the coating at 5000× magnification (shown by arrows). There could be two main reasons for this: first, as discussed before, porosity within the particles decreases with size and consequently yields a denser coating. Besides, as shown in Table 2, the number of passes needed to reach the targeted thickness substantially increased with decrease in feedstock particle size despite the same powder feed rate, which leads to a greater peening effect [26]. This effect can be even more pronounced considering the higher in-flight particle velocity for smaller cut size powders (see Fig. 4), and consequently result in an improvement in the final density of the corresponding coating.

### 3.4. X-ray analysis

Since all powders were of identical chemistry, X-ray diffraction analysis was performed on one of the powders (Pc) as well as two of the coatings deposited using the coarsest and the finest powders (Pc and Pf) employing N1 and N4 nozzles. As shown in Fig. 9, no deviation in phase constitution is recognizable when comparing all the coatings with the starting powder. This implies that negligible decarburization or phase change occurs when spraying WC-CoCr feedstock powder through HVAF within the process parameter window used in this study. This reaffirms findings from other studies employing the HVAF technique [27].
3.5. Microindentation test

Results from indentation testing show that the Vickers hardness values experience a considerable increase with decrease in particle size, increasing from around 1100–1300 HV0.3 for Pc coatings, to 1350–1450 HV0.3 for Pm coatings, and to 1500–1600 HV0.3 for Pf coatings (see Fig. 10). This is attributable to the denser coatings being formed by decrease in particle size, combined with the stronger peening effect resulting from higher velocity for finer particles as well as the higher number of strokes required due to the lower deposition rate to achieve the targeted thickness [28,29]. Average hardness value of the coatings manufactured from Pc slightly increases with increasing length of the nozzle and/or increasing degree of divergence (larger exit diameter) of the nozzle (N3/N4 vs. N1/N2). The reason for this could be the slight increase in particle velocity as seen in Fig. 4 and the corresponding increase in peening effect. This effect of velocity on peening effect has also been confirmed by other studies [20,25]. For each particle size (Pc, Pm and Pf), average hardness values are highest for coatings sprayed by nozzle N4 as evident from Fig. 10.

3.6. Sliding wear

By calculating specific wear rates of each coating and corresponding mating ball, as well as monitoring coefficient of friction (CoF) values
throughout the duration of the wear test, an effort was made to compare all the coatings in terms of their sliding wear performance. Also, a comprehensive post wear analysis was performed to shed light on prevailing material removal mechanisms.

Fig. 11(a) shows average values of friction coefficient for all the coatings after the initial running-in period (after 10,000 s). Error bars show standards deviation in the CoF values calculated based on the test repetitions. It can be seen that, with the sole exception PfN2, the average value for all the other coatings decreases with decrease in powder cut size. For Pc and Pm, the average value of friction coefficient was not found to be dependent on the employed nozzle. Pf sprayed by N2, on the other hand, had an average coefficient of friction that was about double as that of PfN1 and PfN4. The reason for this is not clear, but it could be just an outlier value in CoF which is usual to happen in these coatings, as it was shown in our other study [30]. It was also shown in the above study that there was no correlation between the CoF value and the specific wear rate.

In Fig. 11(b), evolution of friction coefficient of the three coatings from Pc, Pm and Pf powders sprayed using nozzle N1 is shown. It can be seen that all the coatings follow the same generic trend, with the CoF attaining a steady state after around 10,000 s. Also, it is clear that the CoF value decreases with decrease in particle size. Notably less fluctuation in CoF values (during steady state period) can be observed for Pf when compared to Pm and Pc, as well as for Pm when compared to Pc. It is discussed later in Section 4.2 that the reason for reduction in CoF value as well as its fluctuation can be related to the initial powder particle size and consequently the size range of the ensuing debris. Coatings fabricated from smaller feedstock particle size led to production of finer wear debris, resulting in lower CoF and less fluctuation.

Fig. 12(a) shows specific wear rates of all the coatings. Specific wear rate was extremely low and of the order of magnitude of $10^{-8}$ mm$^3$ N$^{-1}$ m$^{-1}$ in all cases. Moving to finer powder cut size from Pc to Pm, regardless of the nozzle type, the average value of specific wear rate of the coatings was found to decrease. Further decreasing particle size (Pm to Pf) leads to further decrease in specific wear rate of the coatings sprayed employing nozzles N2 and N4. The coatings deposited with medium and fine sized powders performed similarly, one of the reasons being that the difference in particle sizes between the two powders was not as large as that between medium and coarse powders (see Table 1). Among all the three powder cut sizes, Pm showed the least sensitivity to the type of nozzle, with the average specific wear rates of all the four coatings deposited with different nozzles being in the narrow range of $14 \times 10^{-8}$ mm$^3$ N$^{-1}$ m$^{-1}$ to $21 \times 10^{-8}$ mm$^3$ N$^{-1}$ m$^{-1}$. Pc and Pf sprayed by nozzle N1 exhibited the least resistance against wear while Pf sprayed using nozzle N4 accounted for the best performance among all coatings.
Comparing specific wear rates of the alumina balls used as counter body in each of the wear tests (Fig. 12(b)), it was difficult to establish a clear correlation. However, a general trend can be observed that higher specific wear rate in the coating leads to a higher specific wear rate in the corresponding ball. Powder Pc sprayed with nozzle N3 was the only exception in this regard, showing comparable specific wear rate as PcN1 but the counterpart ball exhibiting much lower wear than that of PcN1 counter body.

Lower specific wear rates and consequently smaller contact surface areas of the corresponding balls (see Fig. 16) in case of coatings fabricated from finer powder cut size, could be correlated with the noted lower coefficient of friction values. This is consistent with other studies reporting that smaller frictional surface can result in lower friction coefficient [31,32].
4. Discussion

4.1. Deposition behaviour

The consistent decrease observed in deposition efficiency for each nozzle when particle size is decreased can be discussed from various points of view. According to the literature, it is already known that for WC-based feedstock sprayed by cold spray and HVOF, the size and content of WC particles [33–36], powder porosity [29,37] as well as substrate hardness and roughness [38,39] can all significantly influence the flattening ability of powder particles impacting the substrate and its deposition rate. Presence of an intimate conformal contact surface occurring as a result of particle flattening is essential for good bonding, and can also be beneficial for enhancing deposition efficiency [36,37]. Porous particles show better deformation ability or flattening upon impact compared to dense particles [37] and, as a result, have lesser chance of being rebounded. As discussed in Section 3.1, in case of the feedstocks used in the present study, increase in particle size corresponds to higher porosity content within powder particle and as a result improves flattening ability. This is in line with the studies conducted by Gao et al. [37] on cold-sprayed WC-Co coatings, Varis et al. [29] on HVOF-sprayed WC-CoCr coatings and Chivavibul et al. [40] on warm-sprayed WC-Co coatings. So, better deformability can be one of the reasons for higher deposition rates noted when powder particle size is increased (Fig. 5).

However, besides the porosity effect, the size of particles is another key factor determining flattening behaviour. For homogeneous particles, it has already been shown by experiment and modeling that smaller particles tend to exhibit greater resistance against deformation upon impact [41]. Several studies have been conducted with the aim of understanding the effect of carbide dimensions on flattening behaviour of WC-based coatings [33–35,42]. If the particle is assumed to be spherical, the flattening ratio can be defined as [41,43]:

$$\varepsilon = 1 - \frac{h}{d_p}$$  \hspace{1cm} (4)

where $d_p$ and $h$ are particle size and the height of flattened particle, respectively.

Depending on the relative size of powder particle ($d_p$) and carbide particle ($d_c$), the flattening behaviour can be categorized as follows:

Case I:

$$\delta = \frac{d_c}{d_p} \gg 1, \varepsilon > 0$$  \hspace{1cm} (5)

For Case I, where the particle size is much larger than the carbide size ($\delta \gg 1$), flattening ratio increases with the ratio $d_c/d_p$ and can be calculated theoretically [44]. In this case, the deformability of the particle is governed by equivalent properties of both binder and carbide particles. However, with decrease in size of powder particle ($d_p$) when the carbide size is constant ($d_c$), the flattening ratio progressively decreases to the point where the powder particle theoretically comprises only one carbide particle (Case II) and the flattening ratio approaches zero. As the ratio $d_p/d_c$ approaches 1, solid carbide particles dominate the flattening behaviour. Hence, because of low flattening ratio, the chance of the particle being rebounded off increases. This trend is observed when reducing particle size from $P_c$ to $P_m$ and $P_f$ (Fig. 13(a, b and c)), with decrease in particle size resulting in decrease in $\delta$ value and consequently a decrease in flattening ratio ($\varepsilon$) of the particles. This can explain how more particles tend to bounce off and result in lower deposition rate for powders with smaller particles, when carbide size is the same. High chance of particles corresponding to smaller $\delta$ values being bounced off after impacting the surface is consistent with other studies [35,42].

Surface roughness is another factor influencing flattening behaviour of particles and, as a result, the deposition rate [45]. It was shown in Section 3.3, Fig. 6, that the three coatings $P_c$, $P_m$ and $P_f$ are characterized by different progressively decreasing surface roughness values. During spraying, every deposited layer can be considered as the ‘substrate’ for the next pass. Higher roughness can result in higher induced shear stress on the particle upon impact, which leads to better flattening and, consequently, improved deposition rate [38,45].

According to Accuraspray data (see Fig. 4), decrease in particle size leads to a substantial increase in particles velocity. This can be another key parameter influencing deposition behaviour of powders with varying particle size. In case of cold spray, it has been reported that there exists a critical velocity which the particles must overcome in order to get deposited successfully onto a substrate [46,47]. Similarly, there have also been studies on metallic powders which reveal that, for velocities beyond a certain value, no major difference is noted in deposition efficiency [48,49]. In some cases, it has indeed been shown that increase in velocity can lead to increase in rebounding of particles [35]. Therefore, increase in velocity of powder feedstock containing hard WC particles may not improve deposition rate.
4.2. Wear behaviour

Fig. 14 shows low and high magnification SEM images taken on wear tracks with the same track radii \( r = 7 \text{ mm} \) on tested coating specimens fabricated from the three feedstocks Pc, Pm and Pf, sprayed with nozzle N1. Comparing the low magnification images with specific wear rate values (Fig. 12(a)), it can be inferred that samples with deeper and higher number of grooves account for higher specific wear rate values. Another clear difference between the three images is the presence of pits within the wear track of the sample PcN1, which are negligible in the other two samples. These pits could have been formed as a result of breakage of group of carbides resulting in massive exfoliation. It is plausible that the segregated carbides get stuck between sliding ball and sample surface leading to chipping of coating and consequently formation of narrow deep grooves. The other two samples do not exhibit presence of such grooves, and wide shallow ploughing tracks are detectable instead. The tracks are deeper and higher in number for the sample PfN1 compared to sample PmN1. The ploughing tracks could...
have formed as a result of the alumina ball sliding over the surface leading to coating material being pushed aside as well as beneath [50,51]. Using nozzle N4 for spraying Pf resulted in the best sliding wear performance among all the eleven samples. From SEM images of its wear track (Fig. 14), extremely shallow ploughing tracks are detectable without any sign of grooving and carbide fragmentation.

One feature that was observed in some of the wear tracks (e.g. PcN1 in Fig. 14) was the formation of a thin, narrow and smooth tribolayer similar to that reported in a previous study [52]. In some cases, the tribolayer seemed to be thicker and could be distinguished as a distinct layer which is perfectly bonded to the surface. Fig. 15 shows a typical tribolayer within the wear track of sample CfN1. The EDS analysis on the tribolayer reveals presence of W, Co, Cr, Al and O elements, with O being the predominant element and W, Co and Cr showing similar patterns. Hence, the formed tribolayer is essentially a mixture of oxidized elements from the coating as well as alumina from the ball counterpart. Formation of such oxide rich layers has been reported by others, and referred to as tribolayer or tribofilm [52–54]. Presence of a tribolayer can effectively separate the coatings surface from the counterpart ball and, therefore, change the governing tribological behaviour of the
It has been reported that the presence of such a tribolayer covering the surface of a wear track can significantly decrease the specific wear rate \cite{53-56}. However, the presence or absence of this tribolayer did not seem to significantly influence the specific wear rate or coefficient of friction of the corresponding samples in this study. The reason could be that in none of the samples a continuous and wide tribolayer covering a significant fraction of the wear track could be distinguished.

Fig. 16 shows the wear debris accumulated around the leading edge of the contacting region of the balls. Presence of the wear debris can potentially act as third body particles and facilitate the process of material removal \cite{57,58}. Parallel ploughs on the balls are detectable along the sliding direction and can be attributed to such third body action of particles present in the debris.

It was observed that ploughing was the common mechanism in all the three (Pc, Pm and Pf) coatings. It was also seen that, for coatings fabricated from the coarse powder (Pc), several narrow shallow grooves are visible on the wear track apart from some pits. The presence of these pits was the main identifiable difference between the Pc coatings and the other two (Pm and Pf). These pits could have initiated from small pores and accumulated binder areas (Fig. 17) where there was lack of support for material around the pit. Fig. 17(a) shows high magnification SEM images on shallow and deep pores on the surface of the coating, taken in areas outside of the wear track regions. Fig. 17(b) additionally shows regions of accumulation of binder (in form of pits) outside of the wear track. EDS analysis on the pits shows accumulation of binder rich in Cr in these regions. Similar EDS map was performed for Co and no accumulation of the element was identified. Similar analysis was also performed on pits within the wear track (Fig. 18). It is clear that, unlike the ones outside the wear track (Fig. 17(b)), the pit within the wear track was filled with material transferred during wear testing, which was mostly aluminum oxide from the ball counterbody.

SEM analysis at higher magnifications was performed on the wear tracks to explore breakage mechanism around the pits in more detail. Fig. 19(a) and (b) shows breakage of coating in the form of batches of carbides. In Fig. 19(a), breakage of a fragment was observable and transformed along the sliding direction. It may be pointed out that similar behaviour was observed for coatings with WC-CoCr feedstock of identical chemistry sprayed with another HVAF spray gun (Kermetico, Inc.) \cite{19}. Also, a groove can be detected continuing over the fractured fragment and being closed within the pit (shown by arrow). Existence of the grooves facilitates breakage of fragments because of high amount...
of stressed induced to the coating due to presence of a third body particle. In Fig. 19(b), breakage of several fragments was observable being separated both along the sliding direction and in the opposite direction as shown by arrows. These fragments were possibly fractured in absence of any major third body particle since there was no grooving detectable over these fractured fragments. These pits can introduce some stress concentrated locations leading to crack propagation (shown by the square in Fig. 19(b)) and further breakage into fragments. Fig. 19(c) shows a high magnification image of the crack indicated in Fig. 14(b). It can be seen that an intergranular crack was formed regardless of the carbide’s presence towards the next pore. The fractured carbides are identified with red marks.

As discussed, the presence of these pits can facilitate the process of material removal. However, the pits are not reflected as removed material when measuring volume loss, since they are already filled up with wear products. Besides ploughing and grooving as the two common removal mechanisms for Pc coatings, crack initiation and propagation around pits leading to breakage of batches or groups of carbides was the other main wear mechanism. These batches of carbides can be further fragmented into individual carbides as a result of further sliding and removed from the surface. The described mechanisms were similar for the coarse powder sprayed with all the four nozzles (PcN1, PcN2, PcN3 and PcN4). However, in case of Pm and Pf coatings, there was no detectable fragmentation of carbides as a batch.
In both Pm and Pf coatings, there were no signs of pits filled up with wear products. Instead, as shown in Fig. 20, in the first step, binder around carbides seems to be removed resulting in lack of support around the carbides. Then due to load applied from slider, the individual carbides could get fractured, leading to production of submicron sized carbides (shown by arrows in Fig. 20). The last step would be removal of these nano size wear products. SEM investigation of wear debris confirms these differences in wear mechanism between Pc coatings and Pm/ Pf coatings.

As shown in Fig. 21, size of debris particles in case of Pc coatings was much coarser and irregular shaped than that observed in Pm and Pf coatings. Fig. 21(a) shows debris produced from Pc coatings, which are mostly in size range of initial carbide particles (1–3 μm). Presence of these micro size carbides acting as third body particles explains higher coefficient of friction during the ball-on-disc tests as shown in Fig. 11. For Pm and Pf coatings (Fig. 21(b) and (c)), very few micro size particles are found in the debris, with a majority of them being in the nanometric size range and spherical in shape.

Comparing dimensions of the wear debris with friction coefficient values (Fig. 11(b)), it is clear that CoF value is reduced with reduction in debris size. For Pm and Pf, the presence of nano-sized spherical shaped debris particles can result in reduction in friction coefficient [31,59,60]. Also, it can be seen that by reduction in debris size, friction coefficient value as well as its fluctuation was reduced.

Semi-quantitative EDS analysis was conducted on debris from PcN1 samples shown in Fig. 22. Elements of O, W, Al, Co and Cr were detectable in debris. The EDS analysis conducted on wear debris from Pm and Pc coatings showed similar result for all.

Fig. 22. EDS analysis on wear debris from PcN1 coating.

5. Summary and conclusions

Sliding wear tests were conducted on different HVAF-sprayed WC-CoCr coatings with the aim of evaluating effect of feedstock particle size and spray nozzle configuration on tribological performance of the coatings. Moreover, their influence on coatings’ hardness and their microstructural characteristics were assessed by conducting micro indentation test, SEM, EDS and XRD analyses. The main conclusions are listed as following.

- For a given nozzle, reduction in particle size leads to increased density, better homogeneity and higher hardness in the coating. At the same time, the reduction in particle size is accompanied by a reduction in deposition efficiency. Despite the decrease in particle size, negligible decarburization was detected in all the coatings. All these result in better wear performance of the coatings by decreasing the feedstock particle size.
- Fine feedstock powder sprayed with nozzle 5L4 exhibited the best wear performance among all the coatings. Therefore, nozzle 5L4 is recommended for spraying fine powder. However, the specific wear rates of coatings with the medium sized feedstock were independent of nozzle type.
- Although no major change was observed in microstructure of the coatings deposited from the same feedstock particle size but with different nozzle configurations, the average hardness value increased by increasing length of the nozzle and/or its exit diameter (from 4L4/4L2 to 5L4) for all the three particle sizes.
- While shallow and wide ploughing was found to be the common wear mechanism in all the coatings, decrease in feedstock particle size led to a major change in material removal mechanism in the corresponding coating. Wear mechanism for coarse feedstock coatings involved crack propagation around pores and binder accumulation areas leading to breakage of batches of carbides with binder into the pit areas. Further sliding of the ball possibly caused further fragmentation and removal of these batches of carbides, with the debris acting as third body particles to leave narrow deep grooves on the coating surface. In medium and fine feedstock coatings, no pits were observed. In these two coatings, the wear process seems to start with removal of binder and subsequent fracture and fragmentation of loosely bound individual carbides resulting in removal of fine-sized carbides. SEM analysis of debris particles confirmed this difference,
with debris for coarse feedstock coatings being much coarser as compared to the medium and fine feedstock coating debris.

CRediT authorship contribution statement

Kaveh Torkashvand: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft. Mohit Gupta: Conceptualization, Methodology, Supervision, Writing – review & editing. Stefan Björklund: Investigation, Conceptualization. Francesco Marra: Investigation, Data curation. Lidia Baiamonte: Investigation, Data curation. Shirinoshirin Jafari: Conceptualization, Methodology, Supervision, Writing – review & editing. Funding acquisition.

Declaration of competing interest

No conflict of interest.

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References


Paper D

Tribological behaviour of HVAF-sprayed WC-based coatings with alternative binders

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ABSTRACT

The tribological performance of High Velocity Air-Fuel (HVAF) sprayed WC-based cermet coatings with binders containing no or very limited amount of cobalt was evaluated under dry sliding, erosion, and abrasion wear conditions. The wear and corrosion behaviors of WC-NiMoCrFeCo, WC-FeNiCrMoCu and WC-FeCrAl HVAF sprayed coatings were investigated and compared to standard WC-CoCr coatings as benchmark. Microstructure characterization along with XRD analysis was conducted on all powders as well as the corresponding coatings. Comprehensive post wear analysis was conducted on all coatings subjected to ball-on-disk, gas jet erosion and dry sand-rubber wheel abrasion tests. Moreover, all coatings were exposed to 3.5% (wt./vol.) NaCl aqueous solution to evaluate their corrosion performance through electrochemical testing. XRD results showed negligible phase transformation between the powders and the deposited coatings. The WC-NiMoCrFeCo coating exhibited the best sliding wear and electrochemical corrosion performance, with an average specific wear rate value of 3.1 × 10^{-8} (mm^3 N^{-1} m^{-1}) and a corrosion current density of 1.9 μA/cm^2. This coating also showed comparable abrasive wear resistance to the WC-CoCr coating. Under erosive wear conditions, too, the WC-FeNiCrMoCu and WC-FeCrAl coatings showed a comparable performance to the benchmark. Dominant wear mechanisms for the reference WC-CoCr coating, under sliding wear conditions, were abrasion (deep grooving) and surface fatigue (crack propagation and pitting). On the contrary, no pitting was observed in WC-NiMoCrFeCo and WC-FeCrAl coatings during the sliding wear test. No considerable difference was identified in the wear mechanisms of the different coatings under abrasion and erosion wear conditions. The results highlight the promise of some of the environment friendly binders studied to replace Co.

1. Introduction

Hard tungsten carbide (WC) particles embedded in a metallic binder in the form of hard-metal thermal sprayed coatings show excellent properties in several applications in different tribological conditions, including abrasive, erosive, sliding wear [1–4]. The components protected by such coatings belong to very different industrial fields [5,6]. The attractive performance of these coatings relies on the optimized combination of high hardness, provided by the carbide hard phase, and good toughness, ensured by the metallic binder. The metallic binder plays a crucial role, acting as a glue, both in sintered hardmetals [7,8] and in their equivalent thermal sprayed coating compositions [9,10]. The thermophysical properties of the binder are a key factor in determining processing routes suitable for coating deposition. Considering the relatively low melting temperature of the typical metallic binders (Co, Ni or Fe-based alloys) suitable for WC-based coatings, and the need
for these coatings to be deposited dense and with minimal in-flight oxidation, lower temperature and higher kinetic energy deposition processes are usually preferred. Thus, High Velocity Oxy Fuel (HVOF) and High Velocity Air Fuel (HVAF) are the state of the art technologies to manufacture dense and highly cohesive WC-based coatings with superior wear performance and adhesion to the substrate [11–13].

In binder selection for WC-based hard-metal coatings, several major requirements must be fulfilled. Foremost, the potential binder candidate must exhibit excellent technical performance and environmental sustainability, without raising any health concerns. Cobalt has been the most popularly used commercial binder for WC particles [4,14,15]. The solubility of WC in the liquid cobalt binder is a major advantage for processing WC-Co-based compositions by thermal spraying [15]. Cobalt, however, poses several environmental, health and supply concerns. It is known to be toxic and is listed as a human carcinogen [16–18]. Besides, because of limited and locally concentrated reserves [19], there are significant supply and cost worries associated with this element, enough for it to be listed as a Critical Raw Material by the EU Commission [19–21]. To address the above-mentioned issues, research investigations on mechanical, tribological and corrosion resistance properties of Co-free hard-metal coatings with alternative metallic binders have been carried out. As in the case of sintered hard-metals [22–24], Fe-based and Ni-based compositions have been selected as candidates. A study conducted by Testa et al. [25] could be the most recent investigation on WC-based coatings with alternative binders sprayed by HVOF technique. The authors compared the wear and corrosion performance of three HVAF-sprayed hard-metal coatings with alternative binders, NiMoCrFeCo, FeNiCrMoCo and FeCrAl, with the behavior of state-of-the-art WC-CoCr coatings. WC-NiMoCrFeCo and WC-FeNiCrMoCo coatings, in particular, showed sliding and abrasive wear resistance comparable to the reference coating. WC-FeCrAl coatings exhibited a lower wear resistance in both sliding and abrasive conditions, but other studies with such a binder [26,27] reported a sliding wear resistance comparable to the WC-CoCr reference. FeCrAl could represent a very safe and sustainable binder, but WC-FeCrAl coatings produced from the available commercial feedstock seem to suffer from oxide inclusions caused by the HVOF deposition process, which lower their fracture toughness. HVOF sprayed WC-NiMoCrFeCo has also been studied and showed promising results [26,28].

The literature on sintered hard-metals includes interesting results about some more alternative binders, such as FeMn, FeNi, NiCoCrFe [29–31], thermal spray grade powder compositions available commercially are much more limited. As mentioned in [25], the literature seems to be richer in replacement attempts concerning the whole WC-Co system, i.e. TiC-based compositions, rather than focusing on binder replacement alone.

Since powders in “high velocity” thermal spray techniques are accelerated to very high velocity and processed at temperatures much lower than in Atmospheric Plasma Spraying (APS), the deposited coatings are usually very dense and display very limited dissolution/decarburization, thereby minimizing the formation of brittle W2C and solid solution η-phases and even metallic WC [11,32]. Although HVOF can presently be considered as the most common technique to spray hard-metal coatings, it can nevertheless cause some degree of decarburization in the coatings [33–35]. HVAF has the potential to overcome the abovementioned shortcoming with HVOF, since the use of compressed air in place of pure oxygen lowers the flame and the particle temperatures (−1500 °C). Besides, the kinetic energy contribution in HVAF is usually even higher than in a HVOF process, since the particle velocities can reach up to 1000 m/s, allowing the deposition of very dense coatings [3,36,37] with excellent bond-strength. At the present time, Co-free compositions have been sprayed and tested only by HVOF with very few attempts to deposit them by HVAF, due to the relatively recent development of an effective HVAF technology thanks to breakthrough patents [38]. Therefore, a systematic study on HVAF sprayed WC-based coatings with alternative binders when subjected to corrosive environments or to different wear processes including sliding, erosive and abrasive wear has not been carried out yet and could be a useful addition to the existing thermal spray literature.

2. Materials and methods

2.1. Feedstock materials and coatings’ deposition

According to Table 1, three different commercially available WC-based feedstock powders with alternative binders produced by Horganas GmbH (Laufenburg, Germany), manufactured following the agglomeration and sintering route, were used. A standard WC-10Co4Cr composition completed the list of deposited and tested coatings. The volume fraction of the binder and WC grains is expected to be similar in all the four feedstock powders. Domex 355 HSLA steel, in the form of disk-shaped samples (diameter, 25.4 mm; thickness, 6 mm) and plates (50 × 25 × 6 mm), was used as the substrate.

After degreasing, the substrates were mounted on a rotating fixture, with a linear speed of 1.66 m/s, and grit-blasted using alumina grits with an average size of 220 μm. All powders were then sprayed on to the samples employing an M3 HVOF gun (Uniquecoat Technologies LLC, Oilville, USA) equipped with a SL2 convergent-divergent nozzle. The spray parameters are summarized in Table 2. The torch was fueled with propane and nitrogen was used as the carrier gas. It should be noted that grit-blasting was done using the same M3 gun.

2.2. Characterization of powders and as-sprayed coatings

SEM studies were carried out both on the powder surfaces by laying them on adhesive carbon tapes as well as on their cross-section. To perform cross-sectional studies, the powders were cold mounted, and then ground and polished employing the same procedure described below for metallographic preparation of coating cross-sections. For cross-sectional analysis, the coatings were first sectioned using a diamond blade, then they were hot-mounted and ground/polished till mirror finish. The metallographic procedure was carried out by successively grinding the samples using a 45 μm diamond disk, then polishing them using 9 μm and 3 μm Kemet diamond slurries, with a final polishing step using a colloidal silica MasterMet 2 suspension. The microstructural analysis of the coatings was performed using scanning electron microscopy (Hitachi TM3000 tabletop microscope and Nova NanoSEM-450 FEI) and energy-dispersive spectroscopy (X-ray microanalysis system Quantax-200, Bruker Nano GmbH).

Table 1
Specifications of the feedstock materials (manufactured by Horganas GmbH).

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>WC size</th>
<th>Particle size (μm)</th>
<th>Type</th>
<th>Trade name</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-10Co4Cr</td>
<td>Fine</td>
<td>45/15</td>
<td>Aggl. &amp; Sint.</td>
<td>Amperit®</td>
</tr>
<tr>
<td>WC-18</td>
<td>Medium</td>
<td>45/15</td>
<td>Aggl. &amp; Sint.</td>
<td>Amperit®</td>
</tr>
<tr>
<td>WC-15</td>
<td>Fine</td>
<td>45/15</td>
<td>Aggl. &amp; Sint.</td>
<td>Amperit®</td>
</tr>
<tr>
<td>WC-15</td>
<td>Fine</td>
<td>45/15</td>
<td>Aggl. &amp; Sint.</td>
<td>Amperit®</td>
</tr>
</tbody>
</table>

| Specifications of the feedstock materials manufactured by Horganas GmbH. |
To assess possible phase transformation during the deposition process, phase analysis was carried out on polished coatings by X-ray diffraction using a diffractometer (X'Pert PRO, PANalytical, Almelo, NL) equipped with a conventional Cu-Kα source operated at 40 kV, 40 mA and a 1 D array of solid-state detectors (X'Celerator, PANalytical). An angular range of 30° ≤ 95° was scanned with a step of 0.0167° and a counting time of 120 s/step. The XRD patterns of the feedstock powder had already been acquired by the authors [25] and are employed here as a term of comparison.

The Vickers micro-hardness of the coatings was measured using Struers Duramin-40 on mirror polished cross sections under a load of 300 gf and with a dwell time of 10 s in accordance with the ASTM E384 standard [39]. Fifteen indentations were performed on each coating.

2.3. Tribological tests under various wear environments

Sliding ball-on-disk, jet erosion and dry abrasion tests were performed to evaluate the tribological behavior of various coatings under different wear conditions.

2.3.1. Ball-on-disk sliding test

Ball-on-disk tests (Tribometer TRB®, Anton-Paar, Switzerland) were conducted on the coating surface of mirror polished (polishing procedure described in Section 2.2) disk-shaped samples according to ASTM G99 standard [40]. The typical as-sprayed Ra roughness values of the coatings were about 4.5 μm and an Ra less than 0.1 μm was ensured prior to conducting the ball-on-disk tests. All tests were performed at the same environmental temperature (25 ± 2°C) and humidity (30%) against 6 mm grit-blasting substrate, and a 1D array of solid-state detectors (X'Celerator, PANalytical). An angular range of 30° ≤ 95° was scanned with a step of 0.0167° and a counting time of 120 s/step. The XRD patterns of the feedstock powder had already been acquired by the authors [25] and are employed here as a term of comparison.

The Vickers micro-hardness of the coatings was measured using Struers Duramin-40 on mirror polished cross sections under a load of 300 gf and with a dwell time of 10 s in accordance with the ASTM E384 standard [39]. Fifteen indentations were performed on each coating.

2.3.2. Jet erosion testing

Dry jet erosion testing (using the AIR JET EROSION TR-470 test rig, DUCOM, India) was performed on mirror-polished disk-shaped samples with two different test conditions. The samples were fixed on a holding fixture during the test using a magnet and were exposed to a jet of alumina particles with an average size of 50 μm. Three test repetitions were conducted for each test condition on every sample. In condition A, the test was performed with eroded particle speed of 30 m/s for 10 min, whilst in condition B the speed of eroded particles was increased to 70 m/s whilst the test duration was decreased to 4 min. For both test conditions, eroded feed rate of 2 g/min, impingement angle of 90° and standoff distance of 10 mm were used. Samples were ultrasonically cleaned before and after each test.

Mass loss was measured by weighing the samples before and after the test using a laboratory weighing scale (PCE Deutschland GmbH) with a resolution of ±0.1 mg. In addition, volume loss for the test condition B was measured using white light interferometry by dividing every erosion crater into four regions, scanning them, and then merging them together to generate the 3D topography. Under test condition A, the craters were too wide and shallow to be clearly discernible on 3D topographical maps and, therefore, separate volume loss measurements were not possible in this case.

The eroded areas were investigated both on their top surface and in cross-section to investigate the erosion mechanisms. The cross-section metallographic preparation followed the procedure described in Section 2.2.

2.3.3. Dry sand-rubber wheel abrasion testing

Plate samples were subjected to dry sand rubber wheel abrasion test (Abrasion tester, DUCOM, India) according to the ASTM G-65 standard [41] to evaluate the performance of the alternative binders under three-body abrasion wear conditions. The samples were subjected to the test in their as-sprayed state since coatings which must protect from coarse abrasive are often employed in unfinished conditions. SiO2 quartz-based sand (DUCOM, India) with particle size range of 100–500 μm was utilized as abrasive medium with a feeding rate of 315 g/min. A concentration of 5–10 wt% of aluminum in the sand was measured by EDS indicating significant alumina presence in the procured sand. A normal force of 130 N was applied on the samples, pressing them against a wheel (227 mm diameter, and 13 mm width) rotating at a speed of 200 rev/min. Each test lasted 30 min, but the samples were weighed every 10 min using the same scale described in Section 2.3.2. 10-minute tests were performed on a second coating sample to verify the repeatability of the results. The wear scars were investigated both on their top surface and in cross-section to study the abrasion mechanisms. The metallographic preparation for the cross-section analysis included cold-mounting in a transparent epoxy resin before metallographic cutting and polishing, to minimize any cutting-induced artefact. All samples were then polished using SiC papers (down to P2500 abrasive size), polished with 3 μm polycrystalline diamond slurry and then ±60 nm-sized colloidal silica.

2.4. Corrosion testing

Corrosion resistance was measured by electrochemical polarization testing in 3.5% (wt./vol.) NaCl aqueous solution according to ASTM G5-14. The equipment consisted of a three-electrode cell connected with a potentiostat (Flat Cell, Princeton Applied Research, Princeton, UK), a platinum grid used as counter electrode, an Ag/AgCl/3 M KCl electrode.

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Table 2

<table>
<thead>
<tr>
<th>HVAF spraying parameters employed for coating deposition.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (psi)</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Grit-blasting substrate</td>
</tr>
<tr>
<td>WC-CoCr</td>
</tr>
<tr>
<td>WC-NiMoFeCo</td>
</tr>
<tr>
<td>WC-FeNiMoCoCu</td>
</tr>
<tr>
<td>WC-FeCoAl</td>
</tr>
</tbody>
</table>

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as the reference. The samples were pressed on a PTFE gasket, leaving a surface area of 1 cm² exposed to the solution. Sample surfaces were previously mirror finished with the same steps described in Section 2.3.3. To stabilize the open circuit potential (OCP) of the system and assure full impregnation of any open pores, the sample was left in contact with the electrolyte for 1 h without a potential scan. Subsequently, an overpotential range was applied, at 0.5 mV/s rate, in two steps: from 400 mV vs OCP to OCP (cathodic scan) and from OCP to 1400 mV vs OCP (anodic scan). Corrosion potential and corrosion current density were obtained by the Tafel method [42], by linear fitting of two suitable portions of the cathodic and anodic polarization curves (plotted on a log (I) vs. potential diagram) and extrapolation of their point of intersection. The current density corresponding to this point is directly proportional to the spontaneous corrosion reaction rate when no external overpotential is applied to the system. At least two samples were tested for each coating. Cross-sections of the tested coatings, prepared by cold mounting in resin and finished with same steps described in Section 2.3.3, and coating surfaces were analyzed by SEM/EDX to assess the prevailing corrosion mechanisms.

3. Results and discussion

3.1. Microstructural characterization of powders and coatings

SEM images of the free standing powders (Fig. 1(a)) and their cross-section (Fig. 1(b)) show a similar, spherical shaped morphology as well as a noticeable internal porosity in all cases. Both features are consistent with the agglomeration and sintering manufacturing route. Looking at the cross-sectional micrographs, there are several locations where binder material is accumulated in the form of clusters. The number and extent of the clusters are higher in the WC-NiMoCrFeCo powder. The reference WC-CoCr shows fewer binder clusters. As shown in Fig. 2, a very dense microstructure has been achieved in all coatings. The thickness of all the four coatings is around 250 μm. There are no visible pores/cracks within the coating or at the interface with the substrate. In the lower magnification images (column a) alumina grit residues can be identified (black spots shown by arrows). Relatively larger carbides (up to few microns) are easily distinguishable in high-magnification SEM images of WC-NiMoCrFeCo (column c), as it could be expected from the nominal carbide size (see Table 1). Carbide size in the other three coatings is usually below 1–2 μm. Some clusters of binder material can be detected in all the coatings, but their size is larger in WC-NiMoCrFeCo as indicated in Fig. 2 columns b and c. Intermediate-gray areas (shown by arrows in high-magnification image) can be seen in the WC-NiMoCrFeCo coating which are regions rich in Mo (spectra 3 in Fig. 3, II), retained from the feedstock powder.

Indeed, HVAF is a deposition process where the original microstructure of the powder feedstock could be retained much more than in HVOF, because the lower flame temperatures limit the phase transformations [11]. Even the finest carbide particles still exist in all the coatings. Moreover, binder clusters were also fully carried over from the powders into the corresponding coatings. For example, spectra 2, 4 and 5 in Fig. 3, III show the presence of Cr-rich clusters in the WC-FeNiCrMoCu coating and spectrum 2 in Fig. 3, IV shows a Cr-rich cluster in the WC-FeCrAl coating. This trend was not true with the HVOF technique because of the higher process temperature and the resulting dissolution and decarburization [25]. However, some areas of the matrix in the WC-CoCr coating (Fig. 3, I, spectra 2 and 3) exhibit brighter contrast and are richer in W (compared to spectrum 1), which suggest minor dissolution of WC in the matrix, even during HVAF.

Almost all the pores that existed in the feedstock powders are eliminated after deposition of the coatings (compare Figs. 1(b) and 2(c)). This shows that the HVAF technique provides enough thermal and kinetic energy to flatten the particles and build up a dense structure. Except for WC-FeCrAl, no or negligible oxide inclusions can be detected in the HVAF coatings. On the contrary, when using HVOF as the processing technique for spraying the same feedstock materials, oxide inclusions could be detected in the WC-NiMoCrFeCo and WC-FeNiGrMoCu coatings [25]. In the HVAF-sprayed WC-FeCrAl coating, spectrum 4 (Fig. 3, IV) exhibits a strong oxygen peak, indicating an oxide inclusion rich in aluminum. Even more of these inclusions were present in the WC-FeCrAl coatings deposited by HVOF technique [25,27].

3.2. XRD analysis

The coatings largely retained the phase composition of the corresponding feedstock powders (Fig. 4), which had already been characterized in [25]. No new phases appear except for the formation of a slightly greater amount of W₆C in the WC-FeNiGrMoCu and WC-NiMoCrFeCo coatings (Fig. 4-Ib, IIa). The diffraction peaks of the matrix phases, including e.g., M₁₂C and M₃C carbides, f.c.c.-Co (in the WC-CoCr powder), γ-Ni (in the WC-NiMoCrFeCo powder) or α-Fe (in the WC-FeCrAl powder) were retained, albeit weakened in their intensity, in the patterns of the coatings. This testifies to the very limited degree of...
decarburization and dissolution of the WC phase during the HVAF process, and the limited extent of matrix melting. This behavior can be contrasted with that of the HVOF coatings reported in [25], where W₂C was formed in greater amounts whilst the matrix phase was largely turned into an amorphous/nanocrystalline phase (loss of diffraction peaks). The main difference between the patterns of the feedstock powders and the corresponding HVAF coatings lies in the broadening of the diffraction peaks in the latter, which is likely a consequence of plastic deformation upon solid-state impact.

3.3. Hardness measurement

The reference WC-CoCr coating exhibits the highest average Vickers microhardness value of 1260 ± 40 HV₀.₃ (Fig. 5). The hardness values of all the four coatings were anyway comprised in a relatively narrow range between 1100 HV₀.₃ and 1300 HV₀.₃. The hardness of HVAF-sprayed WC-CoCr and WC-FeCrAl coatings was higher compared to the corresponding HVOF coatings [25] by around 200 HV₀.₃ and 100 HV₀.₃, respectively. Also the hardness values of HVAF WC-NiMoCrFeCo and WC-FeNiCrMoCu coatings are similar or superior to the HVOF-sprayed coatings [25]. We also noted that no cracks within and around the indentation marks were visible under the applied load of 300 gf (Fig. 6).

It should be noted that, among the HVOF-sprayed coatings characterized in [25], those with coarser carbides exhibited systematically higher microhardness than those obtained with finer carbides, which was attributed to the fact that large carbide particles might carry the contact with the indenter and shield the surrounding, softer matrix. This, however, is not as apparent among the present samples, where coarse-grained WC-NiMoCrFeCo is indeed harder than fine-grained WC-FeNiCrMoCu and WC-FeCrAl but softer than the equally fine-grained WC-CoCr reference. With the assumption of having very limited extent of decarburization, some literature studies showed that an increase in carbide size would, in fact, lead to a decline in the hardness value and/or wear performance, because of increase in binder mean free path [43–45]. However, other studies suggest an opposite trend, i.e. an
A significant increase in carbide size would, instead, improve the hardness of the coatings [25,37]. Therefore, it is not straightforward to suggest a direct relation between carbide size and mechanical properties and/or wear performance [46]. Hence, simply drawing a conclusion on how carbide size could have affected the hardness of this coating could be arguable.

WC content can be another influencing factor. However, the higher mass fraction of binder in the WC-NiMoCrFeCo coating compared to the reference WC-CoCr (18 vs. 14 wt%) is at least partly due to the presence of heavier elements such as Mo and Ni, thus the volume fraction of the binder is expected to be quite similar, and it should not affect much the hardness value.

Fig. 3. High magnification SEM micrographs (a) and EDX analyses (b) acquired on the cross sections of all samples.
3.4. Sliding wear performance

Average specific wear rates (along with the standard deviation) of the four coatings after the sliding wear test are plotted in Fig. 7. Since it is already shown that performing tests at different radii between 5 mm and 9 mm has hardly an effect on the specific wear rate values of hardmetal coatings [47], the average is calculated based on specific wear rate values from tests performed on radii of 5, 7 and 9 mm. The order of magnitude of the specific wear rate for all the four coatings is in the range of $10^{-7}$–$10^{-8}$ (mm$^3$ N$^{-1}$ m$^{-1}$), which is extremely low.

The specific wear rate of the reference chemistry (WC-CoCr) is of the same order of magnitude as reported in the literature for coatings with the same carbide size distribution and deposited with the same spraying technique [11,37,47,48]. However, the difference in specific wear rate among the coatings with alternative binders sprayed by HVAF technique in this study is higher when compared with the same powder.
compositions sprayed with HVOF technique and tested at 10 N normal load with the same sliding distance as in the current study [25]. Especially the HVAF WC-FeCrAl coating shows significantly lower sliding wear resistance when compared with the other HVAF coatings in a way that, unlike the HVOF coatings in [25], no overlap can be identified in the error bars. On the other hand, The WC-NiMoCrFeCo coating is clearly more resistant against sliding wear conditions.

Fig. 8(a) shows the evolution of the friction coefficient during the tests performed with a radius of 7 mm. The coefficient of friction (CoF) for all the four coatings fell in the range of 0.3–0.5. WC-NiMoCrFeCo and WC-FeCrAl showed the lowest and highest friction coefficient values during the steady state situation, respectively. As shown in Fig. 8(b), in some of the test runs on WC-CoCr and WC-FeNiCrMoCu coatings, the CoF evolution experienced mid-test a sudden increase before stabilizing at a higher plateau value. It occurred twice for the WC-CoCr coating and once for the WC-FeNiCrMoCu coating among all the repetitions.

SEM micrographs with three different magnifications (200×, 2000×, 10,000×) were acquired on wear tracks with the same radius r = 7 mm (Fig. 9). Looking at the 200× SEM images in Fig. 9 (column a), the wear track on the WC-NiMoCrFeCo coating is the narrowest among the investigated samples. Pits (dark areas) were found on the worn surfaces of all coatings but WC-NiMoCrFeCo: pits indicate local delamination of coating material (shown by circles), which is confirmed by cross-section views (Fig. 10). Delamination pits signal a surface fatigue mechanism and they were formed by the propagation of cracks, mainly in a brittle manner. This is confirmed by the occurrence of microcracks perpendicular to the sliding direction, as indicated by short arrows on the WC-CoCr and WC-FeNiCrMoCu coatings (Fig. 10-b, I-c, III-b, III-c). On the other hand, there are no visible microcracks in the WC-NiMoCrFeCo coating, which probably explains its lower wear rate. The WC-FeCrAl

![Fig. 6. Optical micrographs of Vickers microindentation marks on all coatings: Ia) WC-CoCr; Ib) WC-NiMoCrFeCo; IIa) WC-FeNiCrMoCu; IIb) WC-FeCrAl.](image)

![Fig. 7. Specific wear rates of the four coatings determined from ball-on-disk testing.](image)
Fig. 8. CoF evolution during ball-on-disk test a) stable value for all the four coatings b) sudden transitions in some tests involving the WC-CoCr and WC-FeNiCrMoCu coatings.

Fig. 9. SEM micrographs of worn surfaces of the four coatings: (I) WC-CoCr, (II) WC-NiMoCrFeCo, (III) WC-FeNiCrMoCu and (IV) WC-FeCrAl; with three different magnifications (a: 200×, b: 2000×, and c: 10000×).
coating also exhibits fewer pits than do the WC-CoCr and WC-
FeNiCrMoCu ones, despite its higher wear rate, which, in this case, is
probably due to deeper abrasive grooving as this is the softest among all
coatings. This finding is also consistent with the more severe abrasion
seen on HVOF-sprayed WC-FeCrAl compared to all other HVOF-sprayed
coatings in [25].

Due to the low level of decarburization and dissolution of WC in the
matrices, it is unlikely that cracks and delamination are driven by
brittleness of the matrix itself. As the only coating that does not exhibit
this behavior is the coarse-grained WC-NiMoCrFeCo one, it is likely that
this behavior is associated to carbide size. The lower matrix mean free
path in fine-grained coatings might not allow for sufficient plastic
deformability, hence inducing a more brittle behavior under sliding
wear conditions.

The presence of grooves in the WC-CoCr and WC-FeNiCrMoCu
coatings can explain the jumps in the CoF value (Fig. 8(b)) during the

![Fig. 10. SEM micrographs of worn cross-sections of (I) HVAF sprayed WC-CoCr and (II) WC-NiMoCrFeCo; arrows indicate delamination pits on the worn surfaces.](image)

![Fig. 11. High magnification images of (I) WC-NiMoCrFeCo (with bigger carbides) and (II) WC-FeNiCrMoCu (with finer carbides) coatings; arrows indicate plastic deformation/fracturing of bigger carbides.](image)
ball-on-disk testing on these two samples. Stacking a carbide grain as a third body particle and, as a result, chipping material in the form of micro-grooves can dramatically increase the tangential force and consequently the CoF value.

Fig. 11 reveals signs of plastic deformation of the coarser carbide particles in the WC-NiMoCrFeCo coating. This is a typical occurrence with coarse-grained WC-based coatings under sliding wear conditions and it has been interpreted by the authors through microscale finite element modelling in a previous work [37]. Because the bigger carbides sustain most of the contact load with the alumina counterpart and, therefore, bear large normal and shear stresses, they can undergo microscale plastic deformation, whilst, with fine carbides, it is the whole matrix-carbide composite system that is subjected to plastic flow, and individual WC grains themselves appear less affected.

Wear debris from the test performed on the same radius \( (r = 7 \text{ mm}) \) for all coatings were collected and analyzed using SEM and EDS. In Fig. 12 a noticeable difference can be seen in the size and shape of debris particles produced by the WC-CoCr and WC-FeNiCrMoCu coatings and those produced by WC-NiMoCrFeCo and WC-FeCrAl. The debris collected from WC-CoCr contains large, platelet-like particles bigger than 2 \( \mu \text{m} \) and rounded, almost nano-sized particles smaller than 300 nm. The same is true for the WC-FeNiCrMoCu debris with the only

![Fig. 12. SEM images of wear debris from the ball-on-disk testing on the four coatings.](image-url)
difference that micron size platelets are, on average, smaller. All this debris is largely oxidized, as shown by semi-quantitative EDS analyses, an example of which is shown in Fig. 13, spectrum 2. The main constituents of the debris are W, O and Al, suggesting the presence of a mixture of debris from the coating and the alumina ball. Other minor peaks correspond to the elements of the matrix of each composition, whereas the carbon peak is at least partly due to the carbon tape used to collect the wear debris.

Specifically, larger, platelet-like oxidized particles are likely a secondary debris, which results from the compacting of primary, tribo-oxidized debris into the delamination pits found on these coatings and from the subsequent delamination of the compacted debris film itself. Nano-sized particles, instead, result from the comminution and tribo-oxidation of fine debris, resulting either from delamination of the hardmetal, from ductile abrasion of the matrix with subsequent WC pull-out, and (secondarily) from wear of the alumina ball.

Debris from WC-NiMoCrFeCo and WC-FeCrAl, on the other hand, was unimodal in terms of size, being made of quite fine (1 μm or less), agglomerated particles with either rounded or rod-like shape, which are likely the result of tribo-oxidation of debris fragments produced by WC pull-out and cutting of the softer matrix (with some debris from the ball as well). The absence of larger, platelet-like debris in this case is associated to the absence of pits (see Fig. 9), hence absence of secondary delamination of debris films compacted within the pits as discussed previously.

Raman spectra acquired on the wear debris sticking onto the surface of each wear track (Fig. 14) exhibit a main peak around 961 cm⁻¹ belonging to amorphous WO₃·x(H₂O) oxide [49]. Secondary peaks at 126, 270, 717, 806 cm⁻¹ suggest the presence of anhydrous WO₃. Furthermore, the peaks at 270, 540, 687, 865, 878 cm⁻¹ can be attributed to the formation of CO₃(1−x)WO₃ as reported in ref. [50].

3.5. Erosive wear performance

Jet erosion tests under conditions A, according to the standard ASTM G76, show that WC-CoCr and WC-NiMoCrFeCo coatings account for the lowest and highest average mass loss, respectively (Fig. 15). However, the overlapping of rather large error bars (indicating standard deviation) for most of the coatings prevent the achievement of a clear ranking. It was also noted that the low velocity of the erosive particles under conditions A (30 m/s) resulted in a wide plume and, therefore, a shallow crater with large diameter (Fig. 16(a)) which could not be easily captured using white light interferometry technique to calculate the volume loss. By increasing particles' velocity and decreasing test duration (Fig. 16(b)), a deeper erosion crater with smaller radius was obtained, where volume loss could be measured more reliably.

The erosion rate of the four coatings measured under condition B confirms much more clearly that WC-CoCr does show the best performance against erosive wear whilst WC-NiMoCrFeCo exhibits the lowest resistance (Fig. 15). WC-FeNiCrMoCu and WC-FeCrAl coatings exhibited similar, intermediate erosion resistance. Mass loss is also plotted in Fig. 15 for test conditions B. Note that volume loss and mass loss were obtained by distinct measurements (optical profilometry and weighing, respectively), because the density of these coatings could not be measured reliably; hence it was not possible to convert mass loss data into volume loss data. Despite the different measurement procedure, by comparing the mass loss data the same ranking among the four coatings is obtained as with the volumetric measurement. It should indeed be noted that the densities of the various coatings are not much different from one another, since WC is the main phase in all cases whilst the densities of the Co-, Ni- or Fe-based matrices can be expected not to differ too much. It is also worth noting that the width of the error range associated with the volumetric erosion rate under test condition B in Fig. 15 is considerably smaller than it is for the corresponding mass loss data. This indicates that volume loss measurement by (optical) profilometry can be more reliable compared to mass loss measurement i.e., weighing introduces additional uncertainty into the results.

The substrate was not reached in any case under test condition A. Under test condition B, the substrate was not reached with the WC-CoCr and WC-FeCrAl coatings, but it was exposed at the bottom of the erosion craters on the WC-NiMoCrFeCo coating and, occasionally, on the WC-FeNiCrMoCu coating as well. In Fig. 17, in the areas corresponding to spectrum 1 on the WC-NiMoCrFeCo coating and spectra 1, 2 and 3 on the WC-FeNiCrMoCu coating, Fe becomes the main element, together with some Al and O, which is the indication that the substrate had been uncovered. Al in this region was due to residual erosion media embedded on the surface of the ductile substrate. Whilst exposing the substrate toward the end of the test might have contributed to the much higher erosion rate of the WC-NiMoCrFeCo samples in Fig. 15, it also corroborates the lower erosion resistance of this coating, because its thickness was approximately the same as the other coatings (Section 3.1 and Fig. 2).

SEM images with three different magnifications of 800× (column a), 10,000× (column b) and 20,000× (column c) in Fig. 18 show the surface morphology of the erosion scars under condition A (where the substrate was not uncovered in any of the samples). Looking at the SEM images in column a, a smoother surface with fewer valleys and bulges is identifiable for WC-NiMoCrFeCo compared to the rest. Protuberances in all the other three coatings look roughly similar. Column b reveals the removal mechanisms of the coating exposed to erosion wear conditions. Four main removal mechanisms were detectable on all surfaces (Fig. 18, column b and c), including indentation (label I), ploughing (II), shovelling (III) and chipping (IV), shown schematically in Fig. 19. These can all be regarded as manifestations of the general mechanism of abrasive wear [51] of materials deforming primarily in ductile (I-III) or brittle (IV) mode. The simultaneous presence of both ductile and brittle responses is typical of a hardmetal, which indeed possesses intermediate ductility between a pure metal (or metal alloy) and a ceramic.
In particular, the WC-CoCr, WC-FeNiCrMoCu and WC-FeCrAl coatings exhibit mostly similar behavior with indentation being the dominant removal mechanism, although the other mechanisms are detectable, too, as indicated in column b. The dominant mechanisms for the WC-NiMoCrFeCo coating, instead, are both ploughing and indentation, with some signs of shoveling and chipping. Comparatively, the same surface morphologies were observed with the test condition B (70 m/s velocity) where the substrate was not uncovered.

Cross sectional analysis was performed below the eroded surface to have a better understanding of the wear process. In Fig. 20(a) an erodent particle can be seen in the process of chipping away a fragment of material from the surface of the WC-NiMoCrFeCo coating. Negligible subsurface cracks were observed in the cross-section view of this coating. On the other hand, in all the other three coatings (WC-CoCr, WC-FeNiCrMoCu and WC-FeCrAl), networks of subsurface cracks shown by arrows in Fig. 20(b) were formed because of erodent particles indenting the surface (see the previous discussion and Fig. 18). Pores were artificially generated in the cross-sectional views (circled in Fig. 20(b)) because coating fragments that were surrounded by cracks were pulled out during cutting/polishing. Fig. 20(c) shows a region weakened by the propagation of the crack network that could easily spall off completely. The profile of the surface that would be exposed next, drawn with a curved line, is analogous to the surface morphology of the WC-CoCr, WC-FeNiCrMoCu and WC-FeCrAl coatings in terms of protruberances and valleys as was shown in Fig. 18, column a. On the other hand, the lack of subsurface cracks in the WC-NiMoCrFeCo coating explains the relatively smooth surface after the test, with fewer valleys and bulges. This can be ascribed to the greater mean free path of the matrix in this coarse-grained coating, as previously discussed with respect to sliding wear in Section 3.4. Just as it happened in the sliding wear tests, this microstructural difference results in a more ductile response, which, under erosion conditions, implies a greater incidence of a ploughing

![Fig. 14. Raman spectra acquired on wear products adhered to the surface inside the wear tracks of the various samples.](image)

![Fig. 15. Erosion rate and mass loss of the four coatings under test conditions A and B.](image)
mechanism. Whilst, under sliding wear conditions, this had a favorable effect on wear resistance, under erosive wear conditions it is apparent that the greater incidence of ploughing grooves causes more severe wear (Fig. 15).

3.6. Abrasive wear performance

The performance of the four HVAF-sprayed coatings under abrasive wear conditions, expressed as mass loss as a function of time, is summarized in Fig. 21. The very shallow and rough wear scar that resulted from this test, coupled with the irregularity of its shape (created from the contact of an elastic wheel on an unpolished, rigid surface), makes it complicated to measure volume loss after this test. On the other hand, from the previous section (Section 3.5) it was concluded that the mass loss of the four coatings can be a reliable criterion to evaluate their resistance against wear despite differences in the binder chemistry, due to the similar densities. Hence, mass loss was employed as a measure of abrasive wear loss.

According to Fig. 21, the WC-CoCr coating exhibited the best performance under rubber-wheel testing among all the coatings, followed by WC-NiMoCrFeCo, WC-FeNiCrMoCu and finally WC-FeCrAl. For all the coatings the slope of the plot of mass loss versus time is greater in the
first 10 min of the test. This could be due to the relatively high roughness of the as-sprayed coatings during the early stages of the test: as a result, material is lost at a high rate as contact is initially concentrated on asperities. Continuing the tests for two more 10-minute runs, the slope of the mass loss diagram (i.e., the mass loss rate) decreased to an approximately constant value. This shows that a steady state condition was achieved after having removed the initial roughness of the as-deposited surface. The stable steady-state slope is an indication of the repeatability of the test results.

All wear tracks have similar morphology (Fig. 22), with protruding WC particles (which indicates abrasive removal of the matrix) and signs of large-scale plastic flow. Areas with dark contrast in backscattered electron imaging mode probably correspond to residual abrasive particles attached to the coating. This is confirmed by EDX spectra acquired both on top surfaces (Fig. 23-I, spectra 2 and 3; -II, spectrum 3; -III, spectrum 4; -IV, spectra 1 and 3) and cross sections (Fig. 24-I, spectra 1, 2; -II, spectra 4, 5), where residuals of the abrasive particles are clearly signaled by the detection of Si, Al, and O.

Fig. 18. Morphology of erosion scars on the four coatings tested under condition A. Labels I–IV refer to different erosion mechanisms shown schematically in Fig. 19.

Fig. 19. Common material removal mechanisms in erosion wear, adapted from Ref. [52].
In any case, the abrasion depth was far lower than the coating thickness, so the substrate was never exposed. The top surface of the WC-NiMoCrFeCo coating (Fig. 22, II) exhibits cracks within the coarse carbide grains. Cracking of individual WC particles seems to be somewhat less frequent in all other coatings (Fig. 22, red arrows) and it is generally limited to the fewer, larger carbides. In spite of that, the WC-NiMoCrFeCo coating exhibited the closest abrasive wear resistance to WC-CoCr among all the three coatings with alternative matrices.

In fact, most of the abrasion loss was not due to the removal of individual carbides, but to the long-range propagation of surface and subsurface cracks due to repeated plastic deformation by abrasive particles (Fig. 24, column a). Fig. 24, column a, for instance, shows that in the WC-FeNiCrMoCu coating long-range cracking phenomena are somewhat more severe and lead to the detachment of entire portions of hardmetal lamellae. This occurs to a more moderate extent in the WC-CoCr coating; hence, the different extent of subsurface long-range cracking explains the observed differences in abrasive wear losses.

### 3.7. Corrosion performance

Electrochemical polarization results, after corrosion testing in 3.5% (wt./vol.) NaCl, are summarized in Table 3. The WC-NiMoCrFeCo coating provides better corrosion resistance than the rest: it exhibits the lowest corrosion current density and the highest corrosion potential (Fig. 25). On the other hand, the WC-FeNiCrMoCu and WC-FeCrAl coatings, as well as the WC-CoCr reference, seem to possess slightly lower corrosion resistance, as marked by their higher \( I_{\text{corr}} \) values. Both corrosion potential and corrosion current density values measured on all samples are close to the values reported in [25], concerning the same compositions deposited by HVOF spray process and tested under identical electrochemical conditions.

Polarization curves (Fig. 25) show similar trends for all samples; however, the WC-NiMoCrFeCo sample exhibited lower initial activation of corrosion (lower slope of the anodic curve at low overpotentials), which explains why Tafel fitting results in lower extrapolated \( I_{\text{corr}} \). On the other hand, the less resistant WC-FeNiCrMoCu samples exhibited higher current densities from the very beginning of the anodic polarization curve. Indeed, the increase in current density observed in all other samples at potentials of around +0.6 V vs. Ag/AgCl/KCl, caused by the corrosion rate of WC taking over that of the matrix [53,54], is not apparent with the WC-FeNiCrMoCu coating because the corrosion rate is already higher even at low potentials.

SEM cross-section micrographs of corroded samples show that the NaCl solution penetrates non-uniformly through the coating, opening inner porosities during the anodic step of the test (arrows in Fig. 26). The metallic binder appears partially dissolved in some lamellae because of the galvanic couples created between WC particles (more noble) and matrix (less noble). Circles in Fig. 26 indicate the unsupported carbides within such pores. The corrosion resistance of the coatings depends both on the chemical composition of the matrix and the size of WC grains. The former is connected to the different intrinsic corrosion resistances of the alloys, whilst the latter influences the number of galvanic cells formed. These considerations would explain the good corrosion performance of WC-NiMoCrFeCo coatings, the only one studied in this paper with medium-size carbides and a highly corrosion resistant NiMoCrFeCo matrix. In the case of Co-matrix (WC-CoCr) and Fe-based matrices (WC-FeNiCrMoCu and WC-FeCrAl) the formation of a passive or pseudo-passive protective layer is hindered by their lower corrosion resistance.
The worse corrosion resistance of WC-FeNiCrMoCu, in comparison with the corresponding HVOF coatings [25], is probably related to the incomplete melting of the matrix during the HVAF deposition process. This phenomenon implies a lower homogenization of the FeNiCrMoCu alloy, as some Cr is retained by the η-carbides and is not available to promote uniform passivation of the matrix itself. In all but the WC-NiMoCrFeCo coated samples, the substrate was clearly reached by the electrolyte which penetrated through the coating (dark spots indicated by arrows in Fig. 26), triggering the corrosion of the substrate. In fact, EDX analysis (Fig. 27) indicates the presence of iron-containing corrosion products both inside the coatings, moving all the way from the interface to the outer surface (all the point spectra within the coating in Fig. 27), and at the coating-substrate interface, where the corrosion process started. A minor peak of chlorine is occasionally detected in those areas, confirming that they are corrosion products due to the interaction with the NaCl-containing electrolyte. Such percolation could be both due to a residual interconnected porosity after spraying and the formation of new porosity caused by the corrosion of the metallic matrix during the test. Since all the HVAF coatings displayed high density after spraying, the reduced attack to the substrate coated with WC-NiMoCrFeCo can be explained by the higher corrosion resistance of the NiMoCrFeCo metallic binder, which hinders the formation of new porosity and slows down the percolation of the electrolyte during the...
Fig. 23. (a) Low magnification SEM micrographs and (b) EDX analyses of the abraded surface of all coatings after rubber-wheel testing.
It is also noted that the corrosion current densities of the HVAF-sprayed coatings seem somewhat higher than those of the corresponding HVOF-sprayed coatings tested in [25]. There can be two explanations for this outcome. On the one hand, the retention of the multi-phase matrix structure found in the feedstock powder (with metallic phases as well as secondary carbides) causes a less homogeneous distribution of elements and results in a greater number of galvanic couples than do the melt-quenched, homogenized, and largely amorphous matrices of the HVOF coatings. On the other hand, it is important to remark that the samples tested in [25] were deposited onto an AISI 304 stainless steel substrate, so, in the event the substrate was exposed to the electrolyte, its contribution to the overall corrosion rate was likely smaller (although there was no detectable evidence that this had, in fact, occurred).

4. Conclusions

Four HVAF-sprayed WC-based coatings with different binders were evaluated for their mechanical characteristics, wear performance (under sliding, erosion, and abrasion conditions) as well as corrosion behavior in 3.5% (wt./vol.) NaCl aqueous solution. Based on the results, the following conclusions can be drawn:

- The microstructural characteristics of the feedstock powders were mostly preserved during HVAF processing due to the relatively low flame temperature. XRD results also showed very little decarburization in all the coatings, which exhibited high Vickers hardness in the range 1100 HV\(_{0.3}\) – 1300 HV\(_{0.3}\).

- The WC-NiMoCrFeCo coating showed the best sliding wear performance among all compositions, exhibiting both the lowest CoF and the lowest specific wear rate in the ball-on-disk test. Its performance was comparable to that of the reference WC-CoCr coating under two-body rubber-wheel abrasion conditions, whilst it exhibited the poorest jet erosion performance among all coatings. On the other hand, WC-FeNiCrMoCu and WC-FeCrAl coatings, which exhibited lower sliding and abrasive wear resistance than WC-CoCr, exhibited comparable erosive wear performance to WC-CoCr.

- The WC-NiMoCrFeCo coatings are more corrosion resistant than the others in a 3.5% NaCl aqueous solution, because the NiMoCrFeCo matrix possesses better pseudo-passivation ability. Moreover, the rather coarse size of WC particles provides fewer matrix/carbide galvanic couples. On the other hand, Fe-based matrices seem to be slightly disadvantageous in terms of corrosion resistance.

- The ranking of the four coatings based on their performance under various wear test conditions and upon exposure to corrosive media is summarized in Table 4. The different rankings of the coatings under

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Corrosion potentials ((E_{\text{corr}})) and corrosion current densities ((I_{\text{corr}})) of all coatings.</th>
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<tbody>
<tr>
<td>Coating</td>
<td>(E_{\text{corr}}) [mV]</td>
</tr>
<tr>
<td>WC-CoCr</td>
<td>-436 ± 25</td>
</tr>
<tr>
<td>WC-NiMoCrFeCo</td>
<td>-275 ± 29</td>
</tr>
<tr>
<td>WC-FeNiCrMoCu</td>
<td>-468 ± 51</td>
</tr>
<tr>
<td>WC-FeCrAl</td>
<td>-319 ± 29</td>
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Fig. 24. (a) SEM micrographs and (b) EDX analysis acquired on samples’ cross section after abrasion tests; arrows point to cracks and detachment of entire portions of hardmetal lamellae.

Fig. 25. Polarization curves of all coatings.
distinct wear conditions also reflect the different wear mechanisms that prevail. Under sliding wear conditions, the coarse-grained WC-NiMoCrFeCo coating exhibited no brittle removal of material in the form of pitting, unlike all other coatings including the WC-CoCr one, which explained its better wear resistance. On the other hand, two-body abrasive wear by coarse sand particles (rubber-wheel test) was controlled by the propagation of cracks on a much large scale, probably because of the accumulation of plastic deformation damage. In this case, both WC-CoCr and WC-NiMoCrFeCo resisted long-range crack propagation better than did WC-FeNiCrMoCu and WC-FeCrAl. Dry particles' erosion was due to a combination of deep ductile grooving (cutting, ploughing and indentation) and sub-surface brittle fracture and, in this test, the large WC grains and longer matrix mean free path of the WC-NiMoCrFeCo coating might have been disadvantageous as they promoted both ductile grooving of the matrix, and fracturing of individual carbides. In this test, indeed, each abrasive particle delivered a greater amount of energy over a much shorter interaction time than it happened under rubber-wheel abrasion conditions. Despite slight differences among the performances of the three alternative binders, they showed promise as replacements for the reference Co-based binder.

CRediT authorship contribution statement

Kaveh Torkashvand: Conceptualization, Data curation, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. Shrikant Joshi: Conceptualization, Methodology, Project administration, Formal analysis, Writing – review & editing, Funding acquisition, Supervision. Veronica Testa: Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. Filippo Ghisoni: Methodology, Investigation, Formal analysis. Stefania Morelli: Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. Giovanni Bolelli: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – review & editing, Supervision. Luca Lusvarghi: Conceptualization, Writing – review
Francesco Marra: Investigation, Formal analysis. Mohit Gupta: Conceptualization, Methodology, Writing – review & editing, Supervision.

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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Paper E

Tribological performance of thin HVAF-sprayed WC-CoCr coatings fabricated employing fine powder feedstock

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Tribological Performance of Thin HVAF-Sprayed WC-CoCr Coatings Fabricated Employing Fine Powder Feedstock

Kaveh Torkashvand1 · Mohit Gupta1 · Stefan Björklund1 · Shrikant Joshi1

Abstract In this study, sliding and abrasion wear performance of WC-CoCr coatings deposited by high velocity air–fuel (HVAF) spraying with various thicknesses (i.e., 240, 150, 100, 50 and 30 μm), fabricated from fine feedstock powder (5–15 μm), were evaluated. The main aim was to investigate how thinner coatings (30 and 50 μm) perform compared to conventional thick coatings (>100 μm), in an effort to address the supply and cost concerns associated with Co and W. The feedstock powder and deposited coatings were characterized in terms of microstructure. The hardness of the thin and thick coatings was measured using Vickers hardness method from both cross section and top-surface. It was found that, regardless of the thickness, extremely dense coatings with very high hardness (>1500 HV) can be deposited employing HVAF and fine feedstock powder. Thin and thick coatings were found to perform similarly under sliding wear with a normal load of 10 N or lower as well as under abrasion wear conditions which highlights the possibility of employing thinner coatings for a majority of the real applications. The results suggest that peening effect does not have a considerable influence on the microstructure or performance of the deposited coatings. However, for sliding wear tests with a 20 N normal load, it was noticed that wear resistance of the coatings slightly declines with decreasing thickness of the coating beyond 150 μm. The main reason was identified to be the involvement of substrate effect when performing tests under severe Hertzian contact pressure.

Keywords abrasion · coatings · HVAF · sliding wear · thickness · WC-CoCr

Introduction

When it comes to surface engineering for tribological applications, WC-based coatings, deposited by thermal spray techniques, are recognized as one of the most promising solutions to combat wear (Ref 1, 2). A combination of very high hardness and toughness in these cermet coatings yields excellent performance under severe wear conditions (Ref 3, 4). The high toughness of the coating system is thanks to the addition of around 12–15 wt% (20–30 vol%) of metallic binder, which is conventionally Co (Ref 5) or Co with some addition of Cr for oxidation resistance property at relatively high temperatures (Ref 6). These coatings can be deposited employing various thermal spray techniques, among which high velocity oxy-fuel (HVOF) and high velocity air–fuel (HVAF) spraying methods have been considered more attractive. This is due to a generally suitable in-flight particle velocity and temperature achieved in these techniques, which not only yields a very dense coating microstructure but also minimizes the extent of decarburization (Ref 7, 8).

Comparing HVOF and HVAF spraying methods, HVAF typically provides higher kinetic energy and lower flame temperature because of employing compressed air in this method (rather than oxygen) which has a lower combustion potential compared to oxygen (Ref 9, 10). In other words, this technique enables particles to reach very high in-flight velocity while their temperature does not exceed 1500 °C. Keeping the in-flight temperature low is specifically desirable since it prevents decarburization in WC-based coatings (Ref 11, 12). Decarburization can be more
pronounced when using finer particles (below 20 μm) because of higher specific surface area in a way that the core of the particles can also reach temperatures above the melting point. For instance, employing a modeling technique, it was shown that WC-CoCr powder particles, with sizes smaller than 15 μm, became fully molten when their surface temperature exceeded 1800 °C (Ref 13, 14).

Nonetheless, powder feedstock with finer size distribution is desired in some cases since it can improve microstructural characteristics like density, mechanical properties such as hardness as well as tribological performance (Ref 15). The HVAF technique is best suited for spraying fine WC-based powders without excessive decarburization (Ref 15, 16). This also paves the way to produce coatings with fine microstructures, improved mechanical properties and tribological performance. Moreover, fine feedstock powders sprayed by HVAF technique can potentially result in a better coating uniformity in terms of carbide distribution as well as a lower surface roughness which can lead to reduced effort and cost in finish grinding of coated parts.

A typical thickness of 200–300 μm is generally targeted for WC-based coatings deposited employing thermal spray methods (Ref 2, 17). However, deposition of thinner coatings with improved properties could be feasible thanks to HVAF technique, viable to process fine (5–15 μm) powders. The fabrication of a thinner coating is more favorable from processing time and economical aspects. Fabrication of thinner coating is even more crucial when using WC-CoCr as feedstock powder, considering supply risk concerns around both W and Co elements (Ref 18, 19) as well as environmental concerns around Co (Ref 20, 21).

Reducing coating thickness from a typical 200–50 μm, therefore, can reduce the usage of these elements by a factor of four. Several research studies have been carried out to investigate properties and wear performance of these thick coatings (Ref 15, 22, 23). However, the influence of coating thickness, as an important aspect, has not been explicitly explored in previous studies. Investigating influence of thickness is crucial from various aspects. Coating thickness can potentially influence wear performance, especially when dealing with soft substrates. High Hertzian contact stresses can be induced to coating/substrate system as a result of contact with a rigid ball as the counterpart. Depending on the coating’s thickness as well as contact conditions, the maximum Hertzian stress could locate within the coating or substrate (Ref 24). When coating’s thickness is less than a critical value, a great portion of the applied stress has to be carried by the substrate thereby, thin hard coatings applied on soft substrates are susceptible to fracture due to substrate deformation (Ref 25). It has been investigated that by an increase in thickness and as a result shifting the stresses away from the interface and toward the coating system, thermal spray coatings exhibit better rolling contact fatigue (Ref 26, 27).

Also, in a study by Bolelli et al. (Ref 28), it was shown that sliding wear performance could be improved by increasing the number of torch passes in a HVOF WC-CoCr coating (increase in thickness). This can be exceptionally critical when dealing with thinner coatings (< 50 μm) since a large portion of the concentrated stress from the counterpart can be directed to the substrate. Another important factor to consider is peening effect and its influence on wear performance of the coating. When spraying a thinner coating, the sub-layers are exposed to fewer spray strokes (i.e., fewer hard particles impacting the surface) and consequently a less pronounced effect of peening.

Influence of substrate is another key factor. The role of substrate can start to come into the picture when dealing with thinner coatings, especially when the substrate is considerably softer than the protective coating. There is no extensive study investigating this in the literature about the potential influence of substrate and its extent on the coating performance. In this paper, a comprehensive investigation is conducted on coatings fabricated from fine powder (5–15 μm) with different thicknesses, ranging from 30 μm (thin) to 240 μm (thick), to evaluate their characteristics and wear performance under sliding and abrasive wear conditions. Also, the results were compared with coatings fabricated from coarse powder (15–45 μm) where relevant.

**Experiment Procedure**

**Spraying Process**

Commercially available WC-10Co4Cr powder produced by Höganäs GmbH, with a particle size range of 5–15 μm, manufactured employing agglomeration and sintering processing technique (trade name: Amperit® 558.090) was used as feedstock material. Domex® 355MC HSLA Steel (hot-rolled sheet steel produced by SSAB) coupons (φ = 25.4 mm and thickness of 6 mm) and plates (70 × 25 × 6 mm) were employed as the substrate for sliding wear and abrasion wear, respectively.

An M2 HVAF torch (Uniquacoat Technologies LLC) equipped with a short De Laval nozzle (Fig. 1) was employed to spray the feedstock. This gun configuration offers just enough heat for the particles to soften but not overheat. At the same time, it provides sufficient kinetic energy to the particle to stick to the surface. The torch was fueled with propane and nitrogen was used as the carrier gas.

Samples were mounted on a rotating fixture and grit-blasted using alumina powder. Next, the feedstock powder was sprayed with the process parameters mentioned in Table 2, targeting coating thicknesses of 250 μm (thick)
and 50 μm (thin). Later, the thick sprayed samples (250 μm coating) were ground to 240, 150, 100, 50 and 30 μm thickness and the thin sprayed samples (50 μm coating) were ground to 30 μm thickness (see Table 1). In this paper, the coatings with thicknesses of 30 and 50 μm are referred to as ‘thin’ coatings.

Characterization of Powders/Coatings

Scanning electron microscopy (SEM) was used to analyze the morphology and cross section of powder particles. For this purpose, powder particles were collected on a carbon tape and observed under SEM (HITACHI TM3000 microscope and ZEISS GeminiSEM 450). Also, for cross-sectional SEM observation, powder particles were mixed with epoxy, cold mounted, ground and polished.

Using a surface roughness tester (Surftest 301, Mitutoyo), average roughness values (Ra) of as-deposited thick and thin coatings were measured following the standard ASME B46.1. Average roughness values and respective standard deviations were calculated from three measurements on each coating.

The sprayed samples were cut and hot-mounted, then ground and polished. The grinding was performed using a 45 μm diamond disk, then polished using 9 μm and 3 μm Kemet liquid diamond solution. Then, a mirror-polished surface was obtained by employing MasterMet 2 dispense. SEM analysis was performed on the mirror-polished samples to investigate the microstructure of the sprayed coatings.

Indentation Testing

Vickers hardness of the samples was measured both on the cross section and top-surface employing Struers Duramin-40 microhardness tester. A normal load of 0.3 kgf was used for the cross-sectional hardness measurement. It should be mentioned that the cross-sectional indentations with 0.3 kgf were performed only on the coatings C30 and C240 to measure coating hardness. Also, to investigate cracking tendency of the coating, cross-sectional indentations with loads 1, 2, 3 and 4 kgf were performed on the C150 sample. To measure the hardness of coatings on the top-surface, various loads, including 0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3 and 4 kgf, were used. For each hardness measurement, five indentations (repetitions) were performed following the standard ASTM E384 (Ref 29) and the standard deviations of the repetitions were presented using error bars. Top-surface indentation, on the other hand, was performed on all the samples (with different thicknesses) to investigate the influence of the substrate.

Ball-on-Disk Sliding Wear Testing

The same grinding and polishing procedure mentioned in Sect. Characterization of Powders/Coatings was performed on the top-surface of as-sprayed coatings to reach a mirror-polished surface for sliding wear testing. Then, sliding wear tests were carried out on the mirror-polished samples according to the ball-on-disk (BoD) testing procedure in the ASTM G99 standard (Ref 30). A tribometer rig (Tribo-meter TRB3, Anton-Paar, Switzerland) was employed to perform BoD tests. Coefficient of friction (CoF) was monitored throughout all the tests. The ball-on-disk tests were performed under various normal loads, including 5 N, 10 N and 20 N. For all the tests, the linear speed was set at 0.2 m/s and the total sliding distance was selected to be 5000 m. Alumina balls with a diameter of 6 mm were employed as the mating counterpart. At least two repetitions were performed for each test on radius 6 and 7 mm of wear tracks. In some cases where results from the two repetitions did not present good repeatability, a third repetition was conducted. Standard deviations of the repetitions were presented using error bars. It has been shown earlier that, for radii between 5 and 9 mm, the specific wear rate was not influenced by the testing radius (Ref 31). All the tests were conducted at room temperature.

Volume losses in the tested samples during the BoD test were measured using white light interferometry (WLI) technique by employing Profilm 3D device (Profilm 3D, Filmetrics, Germany). Since it was not feasible to capture the whole wear track, volume losses were measured at four different locations across the wear track. Based on the measured volume losses, an average cross-sectional area was obtained for the wear track and therefrom the overall volume loss of the wear track was calculated. Then, the specific wear rates for the corresponding coatings were obtained by dividing volume loss over the normal load and sliding distance. A more detailed explanation of the procedure can be found elsewhere (Ref 15, 31).

Dry Sand-Rubber Wheel Abrasion Testing

Coated rectangular plate samples were subjected to dry sand-rubber wheel abrasion tests employing an abrasion rig (abrasion tester, DUCOM, India) following the standard ASTM G-65 (Ref 32). The tests were conducted on as-sprayed samples, using SiO2 quartz-based sand (DUCOM,
India) with a particle size distribution of 100–500 μm as abrasive medium. The sand feed rate was set at 315 g/min and a normal force of 130 N was applied on the coatings to press the sample against a rubber wheel (227 mm diameter, and 13 mm width rotating at a speed of 200 rev/min). Each test was run for a total time of 30 min, with the samples being weighed at 10 min time intervals. The mass loss was measured by weighing the ultrasonically cleaned samples before and after each test using a laboratory weighing scale (PCE Deutschland GmbH) with a precision of ±0.1 mg.

Results

Powder Characteristics

Figure 2(a) and (b) shows the morphology of the used powder. A significant portion of the powder particles exhibited an irregular shape and only the relatively larger particles were found to bear a spherical shape. A uniform distribution of fine carbide grains (sized below 2 μm) along with the binder phase (colored in dark gray) can be identified in Fig. 2(b). Figure 2(c) shows a cross-sectional SEM image of a powder particle. Cross-sectional observation of the particles confirms the uniform distribution of the two phases of binder and carbide grains. However, there were locations where the binder phase appeared to be accumulated. Cross section of irregular and spherical shape particles did not show any significant microstructure difference. It is worth mentioning that cross section of this fine powder (5–15 μm) exhibited a denser microstructure compared to the coarser powder (15–45 μm) of the same chemistry (Ref 4).

Coating Microstructure

Figure 3 shows cross-sectional SEM images of (a) thick coating, with a thickness of 250 μm, and (b) thin coating, with a thickness of 50 μm. In both cases, the coating seemed to be well-adhered to the substrate with no sign of separation or cracks at the interface. Dark gray spots noted at the coating-substrate interface represent alumina residue left from the grit-basting process. An extremely dense microstructure was achieved in both the thin and thick coatings (Fig. 3c and d) with no distinguishable difference in their microstructure throughout the thickness. Very limited signs of pores can be detected as opposed to the coatings deposited from coarser powders which showed pores of bigger sizes and higher percentages (Ref 15). Localized regions of binder accumulation as well as the presence of fine carbide grains, both of which were noted in the starting feedstock powder (see Fig. 2c), are also clearly noted in the coating microstructure (see Fig. 3d and e). Retention of the microstructure is due to the lower flame temperature as one of the main characteristics of the HVAF process (Ref 33).

The average Ra value for the thin coating was around 1.9 ± 0.1 μm, while the value for the thick coating was slightly higher (2.2 ± 0.2 μm).

Cross-sectional and Top-Surface Hardness

Indentation tests on the cross section of the coatings (performed with a normal load of 300 gf) showed Vickers numbers of 1420 ± 29 and 1475 ± 46 for C30 and C240 coatings, respectively. The slightly lower average value of the hardness of the thin coating (C30) could be because of the influence of the softer substrate and the mounting material. For C30 coating, indent diagonals of ~20 μm were marked in the middle of the cross sections, which were only ~15 μm away from the interfaces. This was not the case for C240 samples since the coating was thick enough to locate the indents sufficiently far from the interfaces. However, these hardness values were well above the hardness of the coating fabricated from coarse powder with Vickers number of 1250 ± 45 (Ref 4). As explained in another work (Ref 15) the reason could be due to denser coating being fabricated by decrease in particle size as well as a stronger peening effect when employing finer powder.

<table>
<thead>
<tr>
<th>Code</th>
<th>Coating thickness, μm</th>
<th>Samples’ information</th>
</tr>
</thead>
<tbody>
<tr>
<td>C240</td>
<td>240</td>
<td>Reached thickness by grinding and polishing identically sprayed thick coatings (250 μm)</td>
</tr>
<tr>
<td>C150</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>C100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>C50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>C30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>C30-sprayed thin</td>
<td>30</td>
<td>Reached the thickness by grinding thin coating (50 μm)</td>
</tr>
</tbody>
</table>
Indentation tests were also performed on the top-surface of all the samples with different thicknesses at various loads with the aim of exploring whether there is any influence of the substrate on the apparent hardness of the coatings. Figure 4 shows the scatter of apparent top-surface hardness values performed at different loads up to 4 kgf on coatings with various thicknesses ranging from 150 to 30 μm.

Apparent Vickers hardness numbers exhibited a similar trend for all C150, C100, C50 and C30 coatings, when conducted at loads up to 0.5 kgf. Average hardness values experienced a slight decreasing trend from 1500 HV0.1 to 1400 HV0.5 by increasing the normal load from 0.1 to 0.5 kgf. This slight decrease could be due to indentation size effect (Ref 34). Due to this effect, hardness values tend to increase as the indentation depth decreases. By further increasing the load from 0.5 to 1 kgf, no considerable decrease was observed for the three coatings C150 and 100 and C50. However, a clear decline from 1400 HV0.5 to 1000 HV1 was observed in C30 coating. C150 and C100
coatings experienced a further slight decrease from 1400 HV0.5 to 1330 HV4 when further increasing the load from 0.5 to 4 kgf. C50, on the other hand, showed a notable declining trend by the increase in normal load in a way that the apparent hardness value of 1270 HV2 (when performing under 2 kgf) was decreased to 1000 HV3 and 800 HV4 when increasing normal load to 3 kgf and 4 kgf, respectively. For C30 coating, this declining trend was also observed to become even more marked for higher loads with the apparent hardness value decreasing to around 490 HV2 and 350 HV3 for 2 kgf and 3 kgf, respectively (Table 2).

It is well-known that the mechanical properties (such as hardness) of a hard coating can be influenced by a softer substrate (Ref 35, 36). This effect is governed by the penetration depth of the indent and thickness of the coating in a way that by the increase in penetration depth, the influence of the substrate becomes more dominant. However, according to the empirical rule (Bückle), the influence of the substrate is avoidable if the penetration depth is less than 1/10th of the coating thickness (Ref 37). Penetration depth can be calculated based on the Vickers hardness equation explained in standard ASTM E384 (Ref 29). Table 3 presents the penetration depth of the indents performed at various loads on coatings of different thicknesses. By comparing Table 3 and Fig. 1, it can be seen that whenever the penetration depth exceeds 1/10th of the coating thickness (values in bold font), a significant drop in the apparent surface hardness value is evident, thereby reflecting the influence of the substrate. For the rest of the indents, regardless of coating thickness, the penetration depth is almost the same for a given normal load. Figures in italic font indicate values just exceeding the 1/10th threshold.

Figure 5(a), (b) and (c) shows SEM micrographs of indents on top-surface of C30 coatings corresponding to 0.5 kgf, 1 kgf and 4 kgf of normal load. In the case of 0.5 kgf normal load, no cracks or breakage of the coating was observed around the indent. By increasing the normal load from 0.5 to 1 kgf, formation of cracks, mostly within the penetration area (inside the indent, designated as I), were observed. Also, signs of limited crack propagation can be traced outside of the indent (designated as II). For the indent performed at the highest load (4 kgf), rigorous cracking occurred inside and outside the indent. In this case, the coating was greatly fractured in the form of cone-cracking, surrounding the indent. This can be due to the particular stress field in a Vickers indentation. This stress field results in great plastic deformation of the substrate under the indent, and as a result, deformation and breakage of the hard coating (Ref 38-40).

Different cracking behavior of the indents was observed when performing on the cross section. Radial in-plane cracking was indicated for loads higher than 2 kgf (Fig. 5d, e and f). No cracking was observable for the loads 1 kgf or less, while signs of crack initiation were detected at 2 kgf (Fig. 5d). The cracks were in the form of in-plane due to the presence of soft substrate and the mounting material.

**Sliding Wear**

Sliding wear performance of all the coatings with various thicknesses was evaluated by performing BoD testing and comparing the specific wear rate values. Also, CoF was monitored for all the tests throughout the tests and post-wear analysis was performed on the resulting wear tracks.

Figure 6(a) shows CoF evolution for the three coatings C30, C100 and C240 during BoD testing performed under 20 N as normal load. All the tests were reached a steady-state CoF after about 10,000 s of running-in period. CoF value for each test was relatively steady with limited spikes, which is usual for this type of coatings (Ref 31, 41). CoF average values for all the tests were recorded to be between 0.25 and 0.35. Under 20 N normal load, C240...
coating showed slightly lower CoF value among all, however, no clear reasoning can be suggested for this behavior since it greatly depends on the stochastic nature of the contact between the two surfaces.

Figure 6(b) presents the specific wear rates for all the coatings tested under 20 N normal load. All the coatings with various thicknesses performed outstandingly, revealing a very low specific wear rate of the order of $10^{-8}$ (mm$^3$ N$^{-1}$.m$^{-1}$). The two coatings C240 and C150 exhibited similar performance with the average specific wear rate of around $1.5 \times 10^{-8}$ (mm$^3$ N$^{-1}$.m$^{-1}$). In none of the coatings, the substrate was exposed and this was

Table 2 HVAF spraying parameters employed for coating deposition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air, psi/bar</td>
<td>99/6.82</td>
</tr>
<tr>
<td>Fuel, psi/bar</td>
<td>95/6.55</td>
</tr>
<tr>
<td>Carrier gas flow rate, l/min</td>
<td>40</td>
</tr>
<tr>
<td>Powder feed rate, g/min</td>
<td>160</td>
</tr>
<tr>
<td>Standoff distance, mm</td>
<td>200</td>
</tr>
<tr>
<td>The traverse speed of the spray torch, m/min</td>
<td>100</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Nitrogen</td>
</tr>
</tbody>
</table>

Table 3 Penetration depth of top-surface indentation (in μm) on different coatings under various loads and a comparison with 1/10 of coating thicknesses (t)

<table>
<thead>
<tr>
<th>Load (kgf)</th>
<th>C30 (t/10 = 3 μm)</th>
<th>C50 (t/10 = 5 μm)</th>
<th>C100 (t/10 = 10 μm)</th>
<th>C150 (t/10 = 15 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 kgf</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>0.1 kgf</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>0.2 kgf</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>0.3 kgf</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>0.5 kgf</td>
<td>3.8</td>
<td>3.7</td>
<td>3.7</td>
<td>3.6</td>
</tr>
<tr>
<td>1 kgf</td>
<td>6.1</td>
<td><strong>5.3</strong></td>
<td>5.3</td>
<td>5.2</td>
</tr>
<tr>
<td>2 kgf</td>
<td><strong>12.4</strong></td>
<td>7.7</td>
<td>7.5</td>
<td>7.4</td>
</tr>
<tr>
<td>3 kgf</td>
<td><strong>18.6</strong></td>
<td><strong>10.5</strong></td>
<td>9.2</td>
<td>9.2</td>
</tr>
<tr>
<td>4 kgf</td>
<td>21.4</td>
<td><strong>13.7</strong></td>
<td><strong>10.7</strong></td>
<td>10.6</td>
</tr>
</tbody>
</table>

![Fig. 5](image) SEM micrographs of the indents performed on top-surface of C30 coatings (a, b and c) and cross section of C150 coating (d, e, and f) at various loads indicated in the pictures. Cracking tendency of the indents performed on top-surface inside and outside of the indents indicated by I and II, respectively. Cracking tendency of the indents performed on the cross section in the form of radial in-plane cracks, shown by III.
expected considering the extremely low specific wear rate (see penetration depth in Fig. 10(e)). By decreasing coating thickness to 100, 50 and 30 μm, a slight increasing trend in specific wear rate was observed so that the specific wear rate of C30 coating was measured to be $4 \times 10^{-8}$ (mm$^3$ N$^{-1}$ m$^{-1}$). To explore the possible explanation of this slight increase in specific wear rate, post-wear analysis was conducted on the as-tested C30 and C240 coatings. This is subsequently discussed in Sect. Abrasion Wear. Specific wear rates for alumina balls were measured in the case of C30 and C240. The values for the two coatings were similar with a rate of $\sim 1.6 \pm 0.1 \times 10^{-9}$ (mm$^3$ N$^{-1}$ m$^{-1}$). This was expected considering the same wear track width in the case of C30 and C240 coatings Fig. 10(e).

As shown in Fig. 6(b), the specific wear rate of C240 coating was higher than that of the C30 coating when testing under 20 N normal load. Figure 7(a) shows average CoF values for all the coatings after the initial running-in period (after 10,000 s), comprising standard deviation calculated from the average CoF values of test repetitions. Average CoF values fluctuate between 0.2 and 0.4 for C240 and C30 tested under 5, 10 and 20 N load. The average CoF for the C240 under 20 N was around half of the value for C30 (22 vs. 41) tested under the same load. No correlation could be found between the CoF and load for the other two coatings.

In order to investigate the possible reason for this behavior, BoD tests were performed under lower loads, including 10 N and 5 N. Figure 7(b) shows specific wear rate values for thin and thick coatings in terms of various normal loads. Under 5 N of normal load, C30 performed even slightly superior to the thick coating. Also, for the case of 10 N normal load, the wear performance of the two thick and thin coatings was comparable. Hence, it can be concluded that wear performance of thick and thin coatings is similar under BoD testing when the normal load is 10 N or less. In other words, when surface pressure is less than a certain value, the tribological behavior of the coatings was similar and not significantly influenced by their thickness. To confirm this, another suitable tribological test was selected, with less surface pressure, to evaluate the performance of the thin and thick coatings. In abrasion testing, under standard ASTM G65, contact pressure is expected to be lower because of the distribution of normal load over a larger area of the surface.

**Abrasion Wear**

Figure 8 shows weight loss of C240 and C30 coatings along with results from another thick WC-CoCr coating fabricated from coarse powder (15–45 μm) under sand-rubber wheel testing during three time intervals of 10 min. Reasonably constant slopes for both the tests indicate that the tests reached steady-state situation from the very beginning of the first 10 min, and also reflect the repeatability of the tests. In the case of thick coating fabricated from coarse powder, Thick-Coarse, it can be seen that, unlike C30 and C240, the steady-state situation was not achieved and mass loss shows a decreasing trend, with the mass loss during the first 10 min being higher (Ref 4). The reason could be the rougher surface finish in the case of coatings fabricated from the coarse powder (see Sect. Coating Microstructure) and the consequent preferential removal of the significant surface asperities during the early stages of testing. A similar slope and, as a result, an almost identical total mass loss at the end of the tests suggested comparable abrasion wear performance of the thick and thin coatings.

**Influence of Peening Effect**

It was shown that both thick (C240) and thin (C30) coatings performed comparable under reasonably milder surface pressure. However, all the coatings discussed thus far...
were first sprayed thick to an identical thickness (about 250 microns) and then ground to different thicknesses. The motivation for this was to prevent any deviation in coating microstructure or properties originating from a potential difference in the spraying process. However, in HVAF-sprayed WC-based coatings, considerable potential compressive stresses are expected due to the peening effect. Besides, the induced compressive residual stresses increase with coating thickness and this is attributable to the progressively higher number of particle impacts. Moreover, the underlying coating during each spraying scan is subjected to a peening effect (Ref 42–44). Therefore, a thin coating ground from an initial thick coating (C30) can potentially represent different properties than a thin coating which was originally sprayed thin (C30-sprayed thin specimen), if the role of peening is significant. Hence, the tribological behavior of these coatings should be separately evaluated.

Figure 9 shows the specific wear rate of the two C30 and C30 sprayed thin coatings. Comparable performance of the two coatings can be concluded. This result can rule out the possible influence of the peening effect on wear performance of the WC-CoCr coatings fabricated from fine powder feedstock. This result aligns with a negligible difference in the microstructure of the two coatings, as discussed in Sect. Coating Microstructure. This observation is in contrast with the results in the study by Bolelli et al. (Ref 28), in which the peening effect and consequent densification were suggested to be responsible for a better wear performance in thicker HVOF-sprayed (2 torch scans vs. 5 torch scans) WC-CoCr coarse (from powder size of 15–45 μm) coatings. However, this contradiction can be originated from the difference in spraying techniques employed (i.e., HVAF vs. HVOF). For the case of HVOF coatings, it was observed that the coatings become denser and harder by increasing the number of torch scans (Ref
While in the HVAF case (this study), no clear difference was observed in the coating microstructure when changing thickness. In other words, the coating is already pretty dense for peening not to have such a significant role in the densification of sub-layers.

Discussion

It was seen that for 20 N normal load, a clear decline occurred in wear performance of the thin coatings. There could be two possible reasons for this decline: i) influence of peening or compressive residual stresses and ii) influence of the substrate. The peening effect can be considered negligible from various points of view. Firstly, in Fig. 6, it can be seen that the two coatings C240 and C150 (which is C240 polished to 150 \( \mu \)m) performed the same, although most top layers of the coating ground down to 150 \( \mu \)m from about 250 \( \mu \)m in case of C150 have undergone more strokes and as a result more peening effect than the C240 coating. Besides, considering that peening results in a more densified microstructure, the performance should have experienced an improvement. While according to Fig. 6, the wear performance declines by moving toward layers that have undergone more stroke scans (less thickness). Moreover, it is clearly shown in Fig. 9 that C30 (sprayed 250 \( \mu \)m and ground to 30 \( \mu \)m), with a higher peening effect, performed similar to C30_sprayed thin (sprayed 50 \( \mu \)m and ground to 30 \( \mu \)m), with a lower peening effect, which again confirms the negligible influence of peening here. The negligible difference in hardness value (under lower loads than 0.5 kgf) of the thin and thick coatings as well as coating microstructure throughout the thickness are the other reaffirmations of this.

Substrate, on the other hand, was found to have a great influence on apparent surface hardness as well as wear performance under certain testing conditions. According to the Hertzian theory of contact mechanics for sphere on a flat surface (Ref 45), the contact radius \( a_c \), the average Hertzian contact stress \( \sigma_{avg} \), the maximum Hertzian contact stress \( \sigma_{max} \), and the maximum shear stress \( \tau_{max} \) can be calculated using Eqs. 1, 3, 4 and 5.

\[
a_c = \left( \frac{3F_nR}{4E_r} \right)^{1/3} \tag{Eq 1}
\]

\[
\frac{1}{E_r} = \frac{1 - v_b^2}{E_b} + \frac{1 - v_c^2}{E_c} \tag{Eq 2}
\]

\[
\sigma_{avg} = \frac{F_n}{\pi a_c^2} \tag{Eq 3}
\]

\[
\sigma_{max} = \frac{3}{2} \sigma_{avg} \tag{Eq 4}
\]

\[
\tau_{max} = \frac{F_n}{2\pi a_c^2} \tag{Eq 5}
\]

where \( F_n \) is the applied normal load, \( R \) is radius of the ball as the counterpart, \( E_r \) is reduced Young’s modulus, \( E_b \) and \( E_c \) are the Young’s modulus of the ball and the coating, respectively, and \( v_b \) and \( v_c \) are the Poisson’s ratios of the ball and the coating, respectively. Maximum shear stress occurs at a depth of \( z \) below the surface according to Eq. 6 (Ref 46).

\[
z = 0.638a_c \tag{Eq 6}
\]

Calculated values for the average Hertzian contact stress, the maximum Hertzian contact stress, the maximum shear stress and the corresponding depth at the beginning of the test are presented in Table 4. The calculation was done based on the following mechanical properties for the coating and the alumina ball as the counterpart: \( E_c = 257 \) GPa, \( v_c = 0.28 \) (Ref 47), \( E_b = 370 \) GPa and \( v_b = 0.22 \) (Ref 48).

According to Table 4, location of the maximum shear stress for loads 5 N, 10 N and 20 N occurs at 19 \( \mu \)m, 25 \( \mu \)m and 31 \( \mu \)m from the surface, respectively. It is clear that by increasing normal load not only the Hertzian stress is increased but the location of maximum shear stress is also moved toward the substrate. Meaning that in the case

<table>
<thead>
<tr>
<th>( F_n, N )</th>
<th>( \sigma_{avg}, ) GPa</th>
<th>( \sigma_{max}, ) GPa</th>
<th>( \tau_{max}, ) GPa</th>
<th>( z, ) ( \mu m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.94</td>
<td>1.41</td>
<td>0.44</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>1.18</td>
<td>1.78</td>
<td>0.56</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>1.49</td>
<td>2.24</td>
<td>0.70</td>
<td>31</td>
</tr>
</tbody>
</table>

![Fig. 9 Wear results for C30 and C30_sprayed thin coatings](image)
of thinner coatings under higher loads, most of the load is to be carried by the substrate (soft) and as a result, plastic deformation of the substrate and the coating. This can explain the jump in specific wear rate in case of C30 when testing under 20 N normal load (see Fig. 7b), where the maximum shear stress is close or within the substrate. However, no big difference was observed in wear mechanisms of thin and thick coatings, as shown in Fig. 10. Instead, it seems that in the case of C30 coating, the coating material was more plastically deformed, or in other word, the ball was more sank into the surface. This results in a deeper wear track for coatings C30 while the width of the wear tracks is similar (see Fig. 10e).

In other words, for thinner coatings, when the normal load (surface pressure) exceeds a certain value, the apparent surface hardness declines because of substrate influence. This suggests the surface being apparently softer and easier to penetrate. Figure 11 shows a schematic view of wear tracks under 20 N normal load. In both cases, some material is removed \( (dw) \) which can be considered roughly the same for the two thick and thin coatings. On the other
hand, in both cases, material can be plastically deformed ($d_{p1}$ and $d_{p2}$) which itself is correlated to the apparent hardness of the surface. In the case of C30, apparent hardness is lower and higher penetration depth is expected compared to the coating C240 ($d_{p2} > d_{p1}$). Surface hardness investigation in Sect. Cross-sectional and Top-Surface Hardness confirms lower apparent hardness of the thinner coatings when the surface load exceeds a certain limit.

To further affirm the influence of high surface pressure and as a result, involvement of substrate, a rough calculation was made for the surface pressure in the cases of sliding wear and abrasion wear and they were compared to a real application.

Figure 12 shows contact surfaces in BoD and abrasion after the tests are finished. Normal pressure on the coatings can be calculated by having area of the contact surface and considering the normal load of 20 N for BoD and 130 N for abrasion (at the end of the tests). Normal pressure of at least 220 MPa was applied in the case of BoD testing, while this value for abrasion was only about 0.3 MPa. Also, according to Table 4, average Hertzian contact stresses of 0.94 GPa, 1.18 GPa and 1.49 GPa are applied to the coating/substrate (at the beginning of the sliding wear testing) under 5 N, 10 N and 20 N load, respectively. However, it is very unusual to find an application where Hertzian stress surpasses 1 GPa (Ref 47). For instance, one of the applications of WC-based coatings could be automotive breaking disks (Ref 49). Normal pressure in an automotive braking disk was calculated to give an idea of surface pressure in a typical real application. The surface area of a typical braking pad is around 9,000 mm$^2$ and the normal load can be in a range of 5 to 15 kN (Ref 50). Thus, the normal pressure was calculated to be in a range of 0.5 to 1.6 MPa. Therefore, it can be seen that normal pressure in a BoD testing with 20 N normal load can be far more severe compared to some of the real applications. Hence, thinner WC-based coatings can be considered a promising route to save operation costs as well as the usage of conflict elements such as W and Co in the applications where the surface pressure is not very extreme.

**Summary and Conclusions**

Tribological performance of HVAF-sprayed WC-CoCr coatings was evaluated under sliding and abrasion wear conditions. Also, microstructural and mechanical characteristics of the coatings were studied in order to better explain the wear behavior of the deposited coatings. It can be concluded that;

- Microstructure and hardness of the thick and thin coatings seemed to be comparable without any noticeable difference.
- Sliding wear performance of the coatings with thicknesses lower than 150 μm, under 20 N normal load, showed to be slightly inferior to that of conventional thick coatings. By further investigation, performing hardness measurements at various loads, calculating values and locations of the Hertzian contact stresses as well as BoD tests at lower loads, it was concluded that the severe high pressure (> 1 Gpa Hertzian stress) and as a result influence of substrate is the reason of slight decline in wear performance of thinner coatings under BoD test with 20 N normal load.
- Thin and thick coatings exhibited similar performance when testing under sliding wear with a normal load of 10 N or lower. Also, the apparent top-surface hardness of all the coatings was similar for the load of 0.5 kgf or lower.
- Sprayed thick and sprayed thin coatings showed similar performance under sliding wear conditions, indicating a negligible peening effect influence.

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High-temperature sliding wear performance of HVAF WC-based coatings with alternative binders

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Towards more sustainable approaches for protecting surfaces against wear

WC-Co coatings, with and without chromium additives, are widely used in the industry for severe tribological applications. However, concerns about cobalt supply and its environmental and health impacts have led industries to explore sustainable binder alternatives. As a deposition technique, high velocity air-fuel (HVAF) spraying technology offers a promising solution by producing dense WC-based coatings with minimal material degradation during spraying. Moreover, the combination of high velocity and low flame temperature in HVAF enables the deposition of finer powders, which are more susceptible to thermal damage, with minimal decarburization. This results in denser coatings with improved properties compared to conventional spraying techniques. Therefore, this thesis aims to evaluate more sustainable approaches to depositing WC-based wear-resistant coatings, involving (a) HVAF as a less energy-intensive technique compared to other methods like high velocity oxy-fuel (HVOF), (b) alternative Co-lean/free binders, and (c) fabrication of thin (‘flash’) coatings from finer feedstock powders.

Characteristics and tribological behaviour of HVAF-sprayed WC-CoCr coatings were investigated by spraying feedstock powders with varying particle sizes (ultra fine: 15/5, fine: 20/5, medium: 30/5 and coarse: 45/5 µm) employing different nozzle configurations (various lengths and divergence-convergence configurations). Additionally, different WC-based feedstocks, comprising alternative binders to traditionally used CoCr (namely NiMoCrFeCo, FeNiCrMoCu and FeCrAl) were investigated. Results showed that the HVAF spraying excelled in processing WC-based powders with various size distributions, enabling the deposition of thinner coatings from “ultra fine” powders (‘flash’ coatings) with similar properties/performance as thick coatings. This leads to reduced material usage while offering potential for considerable component life extension, both of which are important elements of sustainability. Additionally, it was concluded that the Co-lean/Co-free binders demonstrated comparable, and in some cases superior performance than the reference Co-based binder under various wear conditions. All of these together can represent a significant step forward towards more sustainable approaches for protecting surfaces against wear.

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Kaveh comes from Malayer, Iran. He earned his BSc and MSc in Mechanical Engineering from University of Zanjan, Iran. For two years, he honed his skills as a Mechanical Engineer in automotive and motorcycle industries. Seeking new horizons, he moved to Sweden in 2019 to commence his doctoral journey at University West. His PhD research delved into investigating tribological behavior of HVAF WC-based coatings for various industrial applications. His work promises to pave the way for greener solutions in surface protection against wear.