technologies

Review

Advanced Coatings by Thermal Spray Processes

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Abstract: Coatings are pivotal in combating problems of premature component degradation in aggressive industrial environments and constitute a strategic area for continued development. Thermal spray (TS) coatings offer distinct advantages by combining versatility, cost-effectiveness, and the ability to coat complex geometries without constraints of other in-chamber processes. Consequently, TS techniques like high-velocity oxy-fuel (HVOF) and atmospheric plasma spray (APS) are industrially well-accepted. However, they have reached limits of their capabilities while expectations from coatings progressively increase in pursuit of enhanced efficiency and productivity. Two emerging TS variants, namely high-velocity air-fuel (HVAF) and liquid feedstock thermal spraying, offer attractive pathways to realize high-performance surfaces superior to those hitherto achievable. Supersonic HVAF spraying provides highly adherent coatings with negligible porosity and its low processing temperature also ensures insignificant thermal 'damage' (oxidation, decarburization, etc.) to the starting material. On the other hand, liquid feedstock derived TS coatings, deposited using suspensions of fine particles (100 nm–5 μm) or solution precursors, permits the production of coatings with novel microstructures and diverse application-specific architectures. The possibility of hybrid processing, combining liquid and powder feedstock, provides further opportunities to fine tune the properties of functional surfaces. These new approaches are discussed along with some illustrative examples.

Keywords: suspension; solution precursor; plasma spray; high-velocity air-fuel; coatings

1. Introduction

Coatings have always played a pivotal role in enabling industries to combat problems of premature degradation of components that operate in harsh environments. For a long time coatings have been utilized to enhance tribological performance, extend component durability, and even to enable the use of relatively cheaper substrate materials. Cost-effective coatings that impart specific functionalities thus represent a permanent need of the industry and constitute a strategic area for continued development. Thermally sprayed coatings have some distinct advantages over other methods as they can be deposited over a wide thickness range (from tens to hundreds of microns), onto components with complex geometries without the constraints typical of in-chamber processes, and at comparatively lower costs. Consequently, thermal spray variants such as high-velocity oxy-fuel (HVOF) and atmospheric plasma spraying (APS) processes are already industrially well-accepted for developing coatings to combat diverse forms of surface degradation [1]. However, these techniques have begun to gradually reach the limits of their capability while operating conditions that engineering components typically encounter are getting increasingly aggressive for one of many reasons (e.g., increased efficiency, higher productivity, etc.), thereby making the expectations from coatings progressively more demanding.

In all thermal sprayed coatings, including those deposited by HVOF, the porosity inherently present in the above coatings as well as in situ thermal degradation of feedstock are recognized limitations for demanding applications, as these can prevent the aspirations of the user industries from not being fully met. The emergent supersonic high-velocity air-fuel (HVAF) spray technique, which provides highly adherent coatings with negligible porosity because of the higher particle velocities at impact, now provides new opportunities to significantly impact the current state-of-the-art from both a technical and economic standpoint [2]. The HVAF process is also characterized by a lower process temperature compared to HVOF and, consequently, leads to virtually no thermal degradation of the feedstock in the form of in-flight oxidation of metallic constituents, decarburization of carbides, etc.

The long-desired ability to spray nano- and sub-micron sized feedstock can now be realized through use of suspensions rather than conventional spray-grade powders as feedstock. By virtue of the growing realization that this approach can yield more refined coating microstructures and improve performance [3], leading to unique coating microstructures and properties, research in suspension plasma spraying (SPS) has been on the upswing. The recent advancements in axial suspension feeding for SPS technology, in particular, are a game-changer for depositing coatings using suspensions. The enhanced deposition efficiency and high throughput, which are a direct consequence of the high energy capability of axial feed systems that provide for improved thermal exchange between the plasma plume and the injected feedstock, make axial suspension plasma spraying attractive for shop-floor implementation. Recognizing the above advantages, as well as the inherent ability of the process to enable microstructure control (porous, dense, or columnar), the SPS coatings have found application in the fabrication of thermal barrier coatings [4] and also are acknowledged to benefit a vast array of other applications [5].

Thermal spraying has been a focus area of production technologies' research at University West since its inception. Apart from being the most active academic thermal spray research group within Sweden, its growing reputation within the global thermal spray community has been greatly aided by the availability of state-of-the-art facilities, comprising a high power Mettech Axial III plasma spray system, which is widely acknowledged to open new vistas in thermal spraying by enabling axial suspension plasma spraying (ASPS), and a UniqueCoat M3 HVAF facility, which permits the deposition of very dense and well-bonded coatings with minimal thermal damage to coating feedstock (Figure 1). These lend a rare uniqueness and versatility to the group's processing capabilities that are available at few thermal spray groups worldwide. A scientifically strong research environment in thermal spraying, centered around the HVAF and SPS capabilities, has taken shape over the years at the University with the aid of a myriad of projects supported by various funding agencies. An additional key to its success has been the close cooperation between industry and higher education, resulting in a rich history of co-production. The Thermal Spray Group currently has in place a vibrant research program that spans process development, on-line diagnostics, characterization of microstructure, determination of thermo-mechanical properties, assessment of coating performance for targeted applications, and investigation of failure mechanisms, suitably supported by modeling and simulation efforts. For many years, the group's research focus was oriented towards the development of thermal barrier coatings (TBCs) primarily for aero-engine and land-based gas turbine applications [6–9]. The addition of ASPS and HVAF facilities in the past few years, along with the growing expertise of the team, has enabled expansion of the research base further into new areas of wear [10], corrosion [11], and repair [12]. Initial efforts to develop biocompatible [13], hydrophobic [14], and luminescent coatings [15] have also yielded extremely encouraging results.

The intent of this paper is to showcase how the benefits that accrue from the above HVAF and ASPS techniques can be harnessed to develop advanced coatings that have the potential to outperform the current state-of-the-art coatings. For example, as stated earlier, HVAF spraying provides highly adherent coatings with negligible porosity and its low processing temperature also ensures insignificant thermal 'damage' (oxidation, decarburization, etc.) to the starting material compared to the other thermal spray variants [16]. This makes the HVAF technique particularly well-suited for the development of a new generation of wear and corrosion resistant coatings. On the other hand, use of suspensions allows the creation of novel coating microstructures, such as columnar microstructures that are much desired for depositing strain-tolerant TBCs [17]. However, SPS can also be an exciting pathway to deposit other diverse function-specific architectures. The possibility of using a hybrid liquid–powder feedstock also opens new vistas for coatings' development as discussed below [18–22].

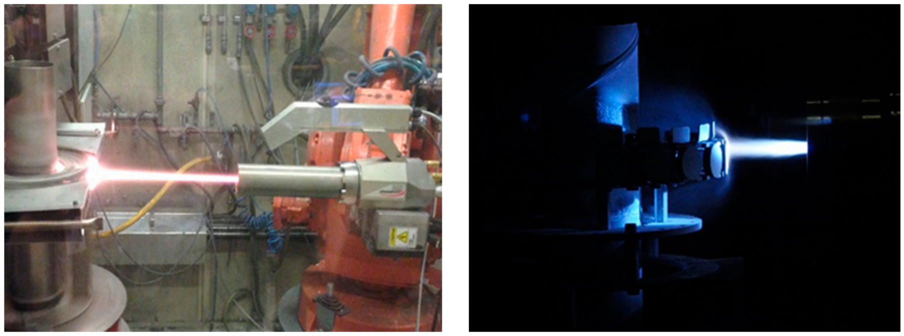

Figure 1. Emergent thermal spray techniques of (**left**) high velocity air-fuel (HVAF) and (**right**) suspension plasma spraying.

2. HVAF Coatings for Wear and Corrosion Applications

In all thermal sprayed coatings, including those deposited by HVOF, the porosity inherently present as well as in situ thermal degradation of feedstock are recognized limitations for demanding wear applications. The supersonic HVAF spray technique provides highly adherent coatings with negligible porosity (<1 vol. %) due to higher particle velocities at impact and provides new prospects to impact the current state-of-the-art approaches, from both a technical and economic standpoint [23,24]. The ability to further refine microstructures significantly employing different nozzle configurations (Figure 2) is an added feature that can be gainfully utilized to deposit high-performance coatings.

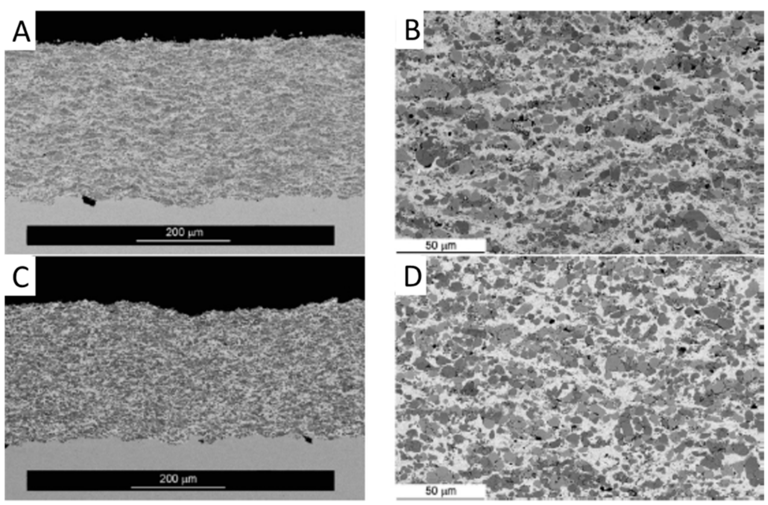

Figure 2. (**A**,**C**) Low and (**B**,**D**) high-magnification micrographs of dense HVAF-sprayed Cr_3C_2–NiCr coatings, illustrating the ability to refine microstructures by varying nozzle configuration. (A,B): M3; (C,D): M2 [23].

2.1. Corrosion Protection Coatings

With a specific view to extend capabilities of the Thermal Spray Group beyond its extant expertise on TBCs to address other industrially relevant areas, preliminary investigations were first carried out to demonstrate the promise of HVAF to outperform HVOF coatings in both corrosion and wear prone environments. The results illustrated in Figure 3, summarized from different studies carried out in the authors' group [23–28], provide an ideal foundation to embark on other projects focusing primarily on advantages that can be derived from HVAF deposition of coatings. Motivated by the ability of HVAF to mitigate decarburization of carbide feedstock and also yield nearly fully dense coatings, a majority of the HVAF-related efforts address wear and corrosion applications.

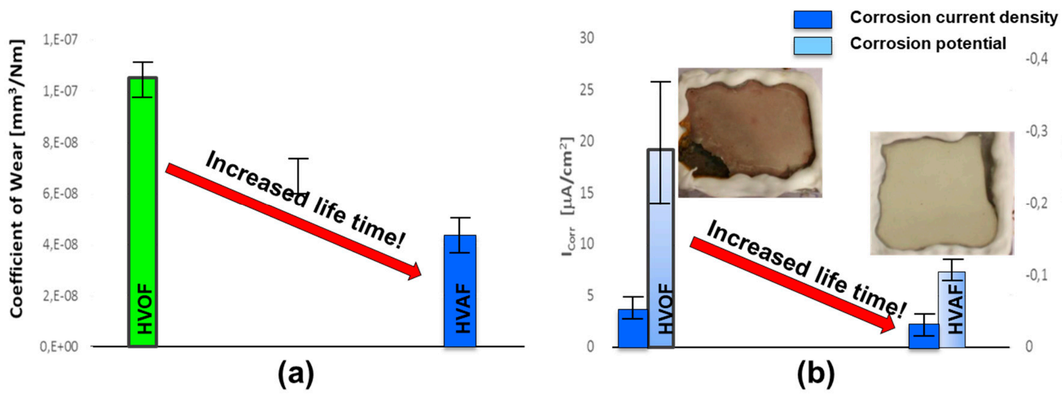

Figure 3. Studies showing superior (**a**) wear and (**b**) corrosion behavior of HVAF WC-CoCr coatings compared to the corresponding high-velocity oxy-fuel (HVOF) coatings. While (a) depicts the coefficient of wear (in mm^3/Nm) under abrasive wear conditions, (b) compares the corrosion current density, I_{corr} (A/cm^2), and the corrosion potential (E_{corr}/V) for HVOF and HVAF coatings deposited using identical feedstock.

For reasons of sustainability and cost, there is growing interest in the use of biomass, waste, and industrial byproducts such as black liquor for power generation. For example, many power generation technologies are capable of using biomass as a fuel, and over 2900 active biomass power plants exist worldwide [29]. Similarly, there are also important financial considerations that make use of black liquor from the kraft process attractive for power generation. Boilers utilizing wastes, prone to significant corrosion and degradation of components in different operating environments, are well-documented [30]. Corrosion from alkali-chlorides is also significant in such boilers and is often further complicated if demolition wood from old buildings or railroad beams, with appreciable content of metals like lead and zinc, is used [31,32]. Similarly, the black liquor recovery boilers (BLRBs) are also beset with problems of corrosion [33]. Power plants also often face the combined attack of corrosion and erosion, with the combustion chamber, surfaces of superheaters and economizers, and ash removal systems being prone to such synergistic damage [34].

Notwithstanding the above, and despite the considerable resources invested to develop means of combating corrosion, it continues to present a major challenge in power production from renewable fuels. Development of new alloys to address the problem has started to yield diminishing returns and, consequently, application of protective coatings is widely acknowledged to be the most promising option. Coatings deposited employing different techniques and utilizing varied material chemistries have been researched and deployed in boilers [35] but a coating that can be maintenance free for an extended period as desired by the industries remains elusive.

In recognition of the above, a chosen focus area at University West deals with the development of advanced HVAF-sprayed coatings to combat corrosion in boilers. Specifically, nearly fully dense Ni-based coatings with the ability to form different protective scales (alumina, chromia, and alumina–chromia) have been studied in considerable detail and also subjected to both laboratory and field testing. The corrosion performance of candidate HVAF-sprayed coatings—$Ni_{21}Cr$, $Ni_{21}Cr_7AlY$, Ni_5Al, $Ni_{21}Cr_9Mo$, $Ni_{21}Cr_9Mo$-SiO_2—has been evaluated through detailed laboratory studies in ambient air, moisture, and HCl-laden environments [36–41]. All coatings were highly protective in all environments in the absence of KCl due to the formation of corresponding protective scales of alumina or chromia on the coating surface. When KCl was introduced, chromia-forming coatings degraded through a two-stage mechanism: (1) formation of K_2CrO_4 and Cl^- followed by diffusion of Cl^- through oxide grain boundaries, leading to the formation of Cl_2, metal chlorides, as well as a non-protective oxide, and (2) inward diffusion of the formed Cl_2 through defects in the non-protective oxide, leading to metal chloride evaporation and breakaway oxidation.

Corrosion behavior of the chromia-forming $Ni_{21}Cr$ coating was improved by the addition of alloying elements such as Al and Mo. It was also shown that adding dispersed SiO_2 further increased the corrosion resistance of the coatings. The oxide scale formed in the presence of SiO_2 effectively suppressed Cl- ingress and lowered the corrosion rate, since the formed oxide was continuous, adherent, and rich in Cr. The performance of the coatings in the complex Cl-containing environment was ranked as (from highest to lowest corrosion resistance): $Ni_{21}Cr_9Mo$-SiO_2 > $Ni_{21}Cr_7AlY$ > Ni_5Al > $Ni_{21}Cr_9Mo$ > $Ni_{21}Cr$, confirming the enhanced corrosion protection of chromia-forming coatings in the presence of alloying elements and dispersed SiO_2. While a typical result is summarized in Figure 4, further details regarding this work are available in the various publications mentioned previously [36–41].

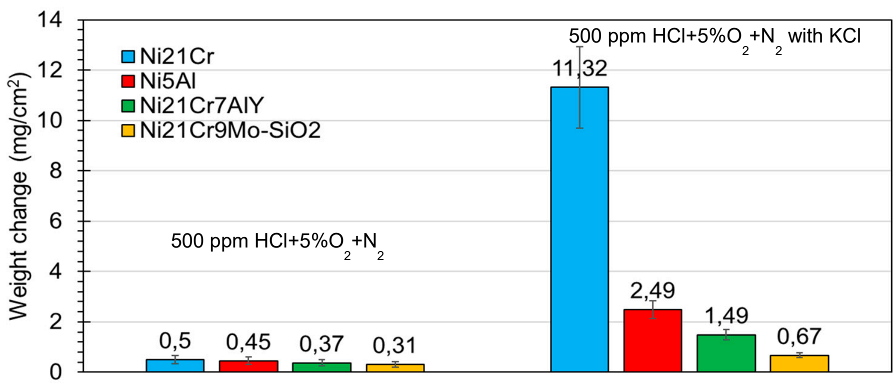

Figure 4. Weight change of the HVAF-sprayed $Ni_{21}Cr$, Ni_5Al, $Ni_{21}Cr_7AlY$, and $Ni_{21}Cr_9Mo$-SiO_2 coatings in HCl-laden environment at 600 °C after 168 h exposed with and without KCl.

2.2. Wear Resistant Coatings

Wear failures have been known to have a great economic impact on the engineering industry globally [42]. Decrease in the cost of operation by reducing overhaul and/or component replacement frequency is often intimately linked to wear of components. Continuous efforts to seek improved solutions to extend durability and enhance performance of wear-prone components have been responsible for the sustained interest in exploring various coatings for this purpose [43]. Although recent developments have enhanced prospects of providing superior protection to wear-prone components, the life of present-day state-of-the-art coatings remains short of industry ambitions. The physical vapor deposited (PVD) or chemical vapor deposited (CVD) coatings are nearly fully dense, provide excellent properties, and are metallurgically bonded to the substrate unlike the mechanically anchored thermally sprayed coatings; however, they are typically thin (<5 μm) and often limited in their ability to address large components by virtue of being in-chamber processes.

Consequently, thermal spray processes have been the focus of a large number of research efforts, and have also been well-established for numerous industrial applications that demand thick coatings. Among the thermal spray methods, HVOF and plasma spray techniques have been particularly extensively investigated for wear applications. The HVOF sprayed coatings offer the possibility of depositing dense and homogenous coatings constitute the current state-of-the-art for many industrial wear applications. A wide range of coatings deposited by the HVOF route have been tested, including WC-Co based coatings and Cr_3C_2-NiCr [44–46]. However, although a few reports investigating wear behavior of HVAF-sprayed coatings have emerged during the past few years [47,48], the evaluation of these coatings in industrial environments remains an uncharted territory. Nonetheless, the continuous demand for increasingly superior performance can potentially be accomplished through one or more of the following: higher density, improved adhesion and cohesion, refined microstructure, and minimal in situ damage to coating feedstock. The HVAF technique presents an ideal opportunity to accomplish the above.

Given the above benefits of the HVAF route, and the correspondingly vast potential for its adoption by the industry, wear resistant coatings based on traditional carbides as well as other promising alternative materials have been a subject of increasing interest at University West. The efforts have already led to some exciting results in terms of obtaining extremely dense coatings with minimal porosity, high adhesion strength, and impressive tribological properties [23–28] and enhanced the knowledge base to serve as the foundation for further industry-relevant developments.

3. SPS Coatings for TBC Applications

Plasma spraying with liquid feedstock offers an exciting opportunity to obtain coatings with characteristics that are vastly different from those produced using conventional spray-grade powders. The two extensively investigated variants of this technique are suspension plasma spraying (SPS), which utilizes a suspension of fine powders in an appropriate medium (typically alcohol or water), and solution precursor plasma spraying (SPPS), which involves use of a suitable solution precursor that can form the desired particles in situ. The advent of axial injection high power plasma spray systems in recent times has eliminated concerns regarding low deposition rates/efficiencies that were wisely associated with use of liquid feedstock until recently. The 10–100 µm size particles that constitute conventional spray powders lead to individual splats that are more than an order of magnitude larger compared to those resulting from the fine (approximately 100 nm–2 µm in size) particles present in suspensions in SPS or formed in situ in SPPS. The distinct characteristics of the resulting coatings are directly attributable to the above very dissimilar 'building blocks' responsible for their formation. Coatings built by the SPS process involve extremely fine droplets arising from fragmentation of a suspension stream resulting in small particles being exposed to the plasma plume in flight after solvent evaporation and depositing them on the bond coat asperities, as schematically illustrated in Figure 5.

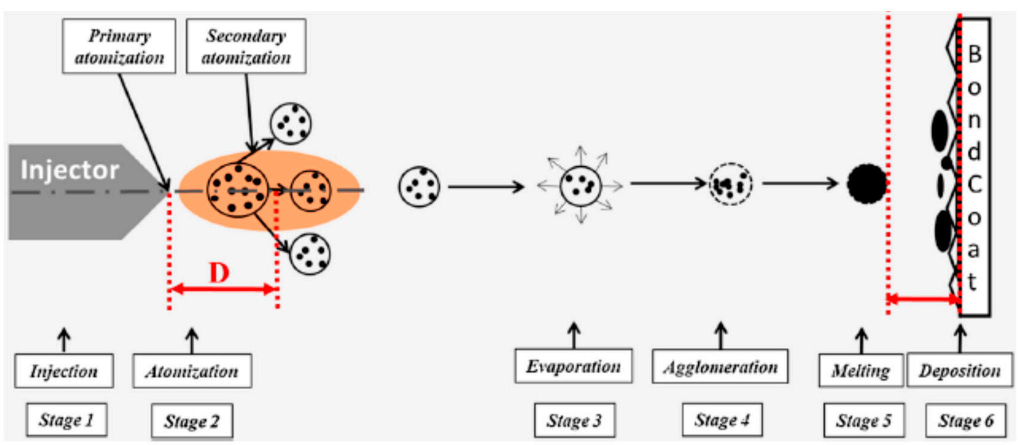

Figure 5. Schematic of various stages leading to coating formation by suspension plasma spraying (SPS) [49].

An overwhelming proportion of SPS studies reported so far have been exclusively driven by interest in TBCs. This is attributable to the use of nano or sub-micron sized feedstock enabling realization of a unique columnar microstructure similar to the electron beam physical vapor deposition (EB-PVD) processed TBCs [50]. It may also be mentioned that the deposition rates achievable by SPS are significantly faster than in the case of EB-PVD and the former is, therefore, also deemed more economical [51]. Typical columnar SPS coating microstructures produced with yttria-stabilized-zirconia suspensions are shown in Figure 6 [52]. As can be noted from the figure, a columnar microstructure with fine scale porosity within columns and column gaps can be obtained. Such a fine scale porosity within columns is desirable, since it lowers the thermal conductivity of the TBC.

After the initial excitement and corresponding research interest primarily centered around the columnar structures much sought for TBC applications, SPS research has also grown to explore new top-coat compositions, such as the rare earth zirconate-based pyrochlores, zirconate-based perovskites, hexaaluminates, and garnets (yttrium aluminum garnet), as well as other architectures involving multiple ceramic layers [53,54]. These aspects have also been the focus of SPS TBC research at University West, with particular interest in multi-layer gadolinium zirconate (GZ)-ytrria stabilized zirconia (YSZ) coatings [55–59]. These efforts have also provided invaluable insights into mechanisms responsible for TBC failure in diverse environments (thermal cycling, burner rig, and calcium-magnesium-aluminosilicate CMAS exposure [57], see Figure 7).

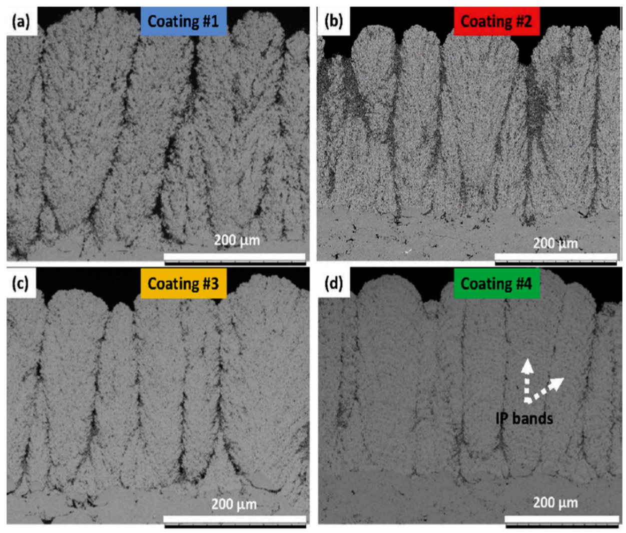

Figure 6. Cross-sectional SEM micrographs showing distinct columnar ytrria stabilized zirconia (YSZ) thermal barrier coating (TBC) microstructures deposited by SPS process [25].

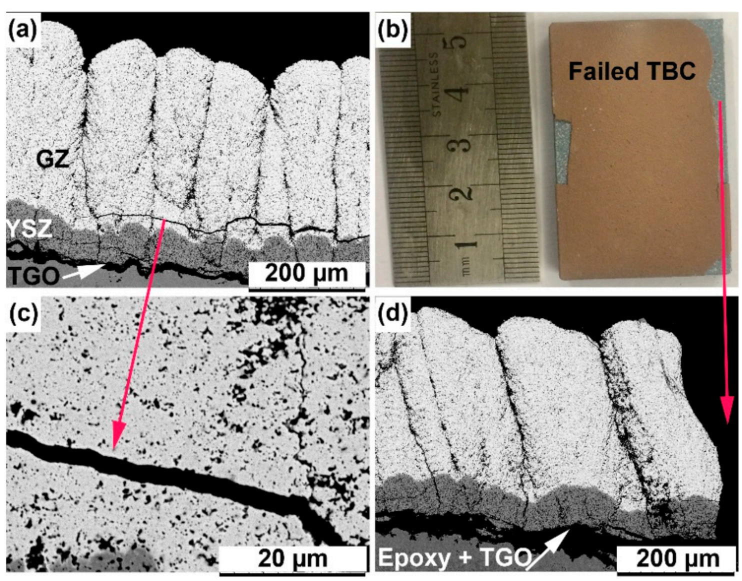

Figure 7. A triple layered GZ-based TBC (GZ dense/GZ/YSZ) failed during thermal cyclic fatigue test. (**a**) SEM micrograph showing failure in TGO; (**b**) photograph of failed specimen; (**c**) SEM micrograph showing horizontal crack in GZ; (**d**) SEM micrograph from different region showing failure in TGO [57]. (GZ = gadolinium zirconate; YSZ = yttria stabilized zirconia; TGO = thermally grown oxide).

While it is true that interest in SPS TBCs is motivated by the ability of the process to conveniently yield strain-tolerant columnar microstructures, it is to be emphasized that column formation in SPS is intimately related to suspension properties (surface tension, viscosity, density, etc.). These properties are known to influence droplet/particle trajectory in flight and its momentum just prior to impact with the surface, and the subsequent shadowing effect that contributes to column formation. Plasma spray parameters (power, enthalpy, gas flow, spray distance, etc.), as-sprayed bond coat roughness, etc. also have a crucial influence on the columnar microstructure, including column density and overall porosity [60,61]. Thus, a complete understanding of column formation is important and has been a subject of specific interest at University West [17,62–66]. This has, for example, led to a very clear experimental visualization of column formation as depicted in Figure 8.

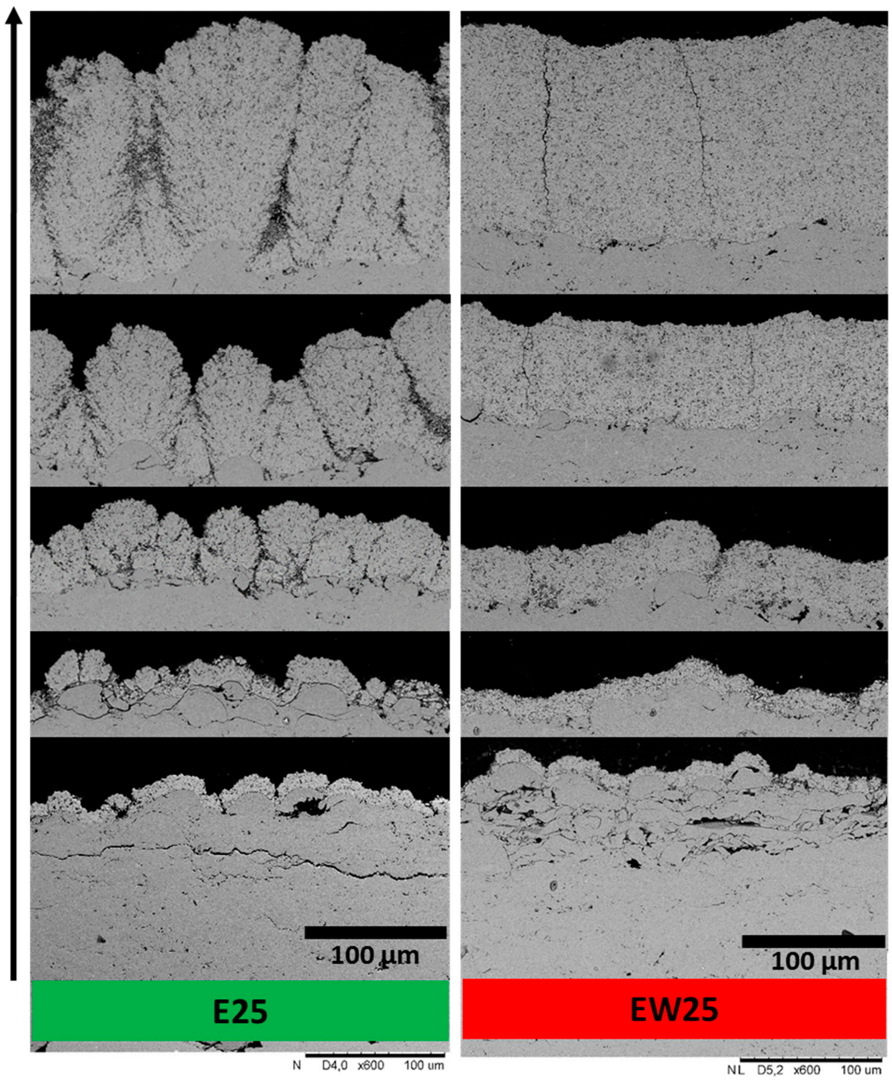

Figure 8. Evolution of SPS YSZ microstructure using an ethanol (E25) and ethanol–water (EW25) based suspensions with identical solid loading of 25 wt. %. The former leads to a columnar coating and the latter to a dense vertically cracked coating [49].

4. SPS Coatings for Non-TBC Applications

Apart from aiding in the development of TBCs with superior properties [67], the above efforts have also served to lay an extremely sound formation that can enable microstructure control during plasma spraying of fine-particle laden suspensions. With growing familiarity with the process, reports on use of SPS to deposit other materials such as alumina, titania, hydroxyapatite, etc. have begun to emerge [68–70]. Even so, there have been no efforts seriously targeting use of this technique for deposition of wear-resistant coatings and evaluation of SPS coatings in an industrial wear environment has never been attempted so far.

A desire to further build on the SPS expertise has now led to dedicated efforts aimed at utilizing the SPS route to deposit various other oxides and carbides that can be potentially promising candidates for tribological applications. In this context, some early work has already been carried out with Al_2O_3, Cr_2O_3, Cr_3C_2, and TiC suspensions, as well as graphene [71–73]. These have yielded microstructures and properties that inspire confidence (Figure 9) to be further investigated in detail.

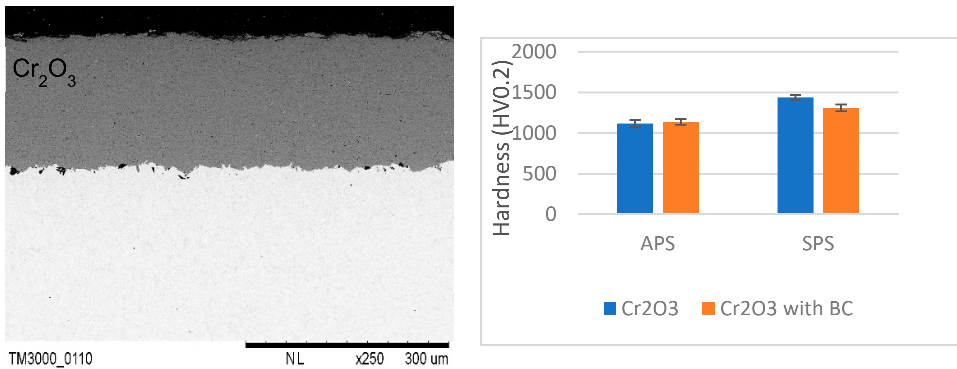

Figure 9. Preliminary results with SPS chrome oxide coatings revealing (**left**) dense coatings with good microstructural integrity and (**right**) hardness levels that are comparable or exceed those typically achieved by conventional powder-derived plasma spray coatings. (APS = atmospheric plasma spray).

5. Prospects for Powder-Suspension 'Hybrid' Coatings

Recent advancements in axial suspension plasma spray (ASPS) technology, and the high energy capability of axial feed systems with improved thermal exchange between the plasma plume and the injected feedstock [74], have served to dispel the initial apprehensions relating to poor deposition efficiency and throughputs that were associated with use of liquid feedstock. The demonstrated ability in recent times to achieve deposition rates that can compete with traditional spray-grade powder-based plasma spraying has motivated the Thermal Spray Group at University West to also explore hybrid plasma spraying, employing both powders and suspensions. There have indeed been prior studies involving hybrid processing using powders and solution precursors, employing traditional radial feeding plasma systems [18–20]. However, compared to solution precursors, the relatively reduced energy demand with use of suspensions makes the process more forgiving and prima facie provides an attractive alternative. The tremendous scope of hybrid plasma–suspension processing has just begun to be explored at University West in realization of the fact that the immense versatility of such an approach, especially when implemented with a high-power axial-feed plasma torch, remains industrially unappreciated.

Hybrid powder–suspension plasma spraying provides an opportunity to very conveniently combine two or more constituents at very different relative lengths. This is accomplished by using conventional 'coarse' spray grade powders (usually 10–100 μm in size) and fine powders (approximately 100 nm–2 μm) in the form of a suspension form. This opens up vistas for conveniently achieving on-demand function-dependent architectures if the powder and suspension feeding can be independently controlled. For example, sequential feeding of a suspension followed by a powder can yield a layered coating with the two layers comprised of features (splats, pores, etc.) involving entirely distinct length scale. Similarly, simultaneous feeding of both can yield a composite coating with a distributed fine second phase in a coarser matrix or vice-versa. In a specific variant of the simultaneous feeding arrangement, the relative feed rates of the two feedstocks can also be continuously varied to obtain functionally graded coatings (see Figure 10) [21].

The above hybrid approach has already been successfully demonstrated for diverse material systems, using a novel feedstock injection system designed for independent control of the powder and suspension feedstock [22]. For example, Figure 11 depicts the surface morphology and the fractured cross-sectional surface of a hybrid coating deposited by axial plasma spraying of a conventional spray-grade alumina powder and a YSZ suspension fed simultaneously. Such alumina–YSZ hybrid coatings have been found to yield very promising mechanical properties [75] and motivated other tribologically exciting material systems, such as Tribaloy 400-chromium carbide and Tribaloy 400-titanium carbide, to be evaluated comprehensively. This comprises work currently in progress at University West.

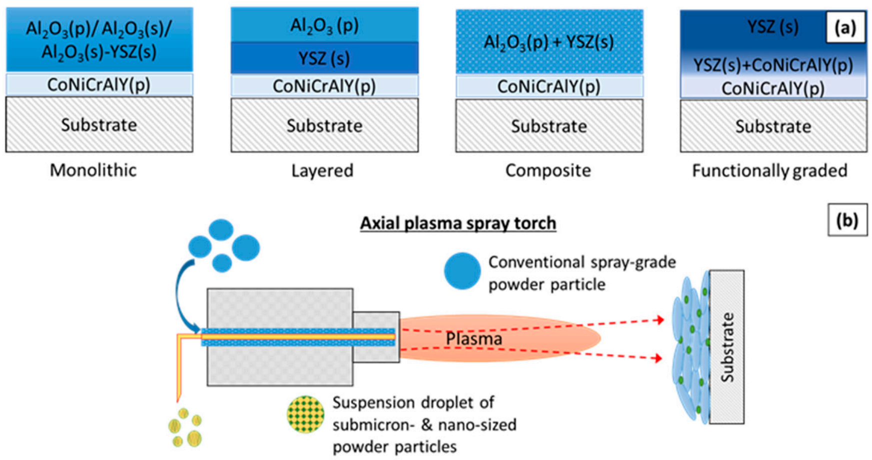

Figure 10. (**a**) Illustration of different coating architectures generated using the hybrid plasma spray setup involving feeding of conventional spray-grade powder (p) and suspension (s) feedstocks as schematically shown in (**b**) [47].

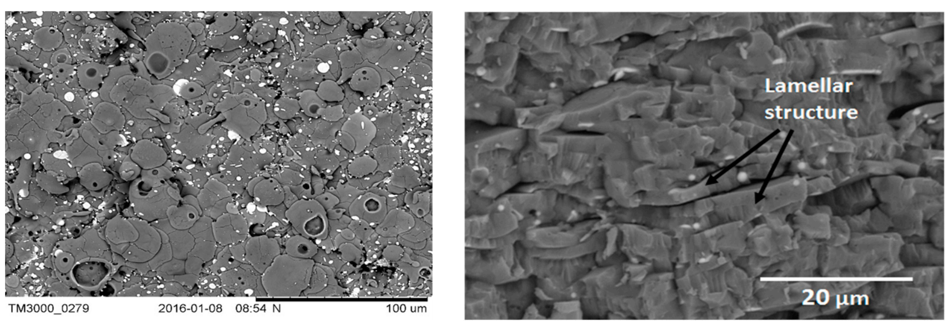

Figure 11. (**left**) Surface morphology of a typical alumina (powder)–YSZ (suspension composite coating showing multiscale structure [22] and (**right**) transverse fractured surface of the composite coating showing vertically aligned solidification feature in alumina splats with distributed YSZ (seen as the brighter phase in both micrographs) [21].

6. Summary

The HVAF and SPS coating techniques are the two most exciting thermal spray variants that have been the subject of growing research attention in recent years. The benefits that these two methods afford compared to the relatively older HVOF and APS techniques are being increasingly recognized and, consequently, these processes are being actively considered for various demanding applications. While adapting the HVAF and SPS methods to applications of industrial interest can potentially be immensely rewarding, it relies on developing a deeper understanding of these methods, such as establishing process parameter–microstructure–property correlations, to deposit function-specific coatings.

The unique HVAF and ASPS facilities are only available in an academic research environment at University West within Sweden. The advanced coatings that can be produced by the above HVAF and SPS processes are summarized herein with some illustrative examples. These methods hold technical as well as economic advantages over conventional thermal spray variants like APS and HVOF owing to their ability to provide denser coatings (in case of both SPS and HVOF), refined microstructures (SPS), and superior cohesion and adhesion (HVAF). Layered and composite coating architectures deposited by the above routes, too, have the potential to further enhance performance and extend longevity of the coatings.

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Conflicts of Interest: The authors declare no conflicts of interest.

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