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Optimization and Characterization of High Velocity Oxy-fuel Sprayed Coatings: Techniques, Materials, and Applications

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Abstract: In this work High Velocity Oxy-fuel (HVOF) thermal spray techniques, spraying process optimization, and characterization of coatings are reviewed. Different variants of the technology are described and the main differences in spray conditions in terms of particle kinetics and thermal energy are rationalized. Methods and tools for controlling the spray process are presented as well as their use in optimizing the coating process. It will be shown how the differences from the starting powder to the final coating formation affect the coating microstructure and performance. Typical properties of HVOF sprayed coatings and coating performance is described. Also development of testing methods used for the evaluation of coating properties and current status of standardization is presented. Short discussion of typical applications is done.

Keywords: thermal spray; coating; HVOF; optimization; characterization; standardization

1. Introduction to Thermal Spray Processes

Thermal spraying is a general term to describe all methods in which the coating is formed from melted or semi-melted droplets. In thermal spraying the material is in the form of powder, wire or rod
and is fed into the flame produced by a spray gun, where it melts and the formed droplets are accelerated towards the substrate to be coated. The thermal and kinetic energy of the flame can be produced either with burning mixtures of fuel gas and oxygen, or by using an electrical power source. Based on the energy source, thermal spray methods can be divided into a few main groups: plasma spray methods (atmospheric plasma APS, vacuum plasma VPS, and low pressure plasma LPPS), combustion flame spray methods (flame spray), high velocity oxy/air-fuel methods (HVOF/HVAF), electrical arc methods (wire arc), detonation method (D-Gun), and, as the latest technology, cold gas methods (CGS).

Since coating is built up from flattened, fast solidified droplets the velocity plays an important role for the obtained density of the lamella structured coating. Temperature of the flame has a strong effect on the suitable materials to be sprayed. Ceramic coatings are mainly manufactured by using atmospheric plasma spray method, while temperature sensitive materials, such as cermets, are more preferably sprayed by methods with a lower flame temperature. In Figure 1 the typical operation ranges for various spray systems are presented.

**Figure 1.** Typical flame temperature and particle velocity operation ranges for various thermal spray systems.

Thermal spray coatings are often applied for better corrosion and wear resistance. Therefore, low porosity and good adhesion are desired properties for the coating. High velocity processes—especially HVOF (High velocity oxy-fuel) spraying—are the preferred methods for producing coating with low porosity and high adhesion. In HVOF spraying, heat is produced by burning mixture of oxygen and
fuel such as hydrogen, kerosene, propane, propylene, natural gas, ethylene, or acetylene. Due to the special nozzle design, a jet with supersonic speed is produced.

The ability to produce dense coatings with low amount of degradation, oxidation of metallic materials, and phase transformations is the main feature of the HVOF process. This is due to the short dwell time of the particles in a relatively cold flame. It is widely used to produce cermet and metal coatings, but the HVOF process has also been demonstrated to be able to deposit dense ceramic coatings.

In the HVOF process, fuel and oxygen are introduced to the combustion chamber together with the spray powder. The combustion of the gases produces a high temperature and high pressure in the chamber, which causes the supersonic flow of the gases through the nozzle. The powder particles melt or partially melt in the combustion chamber and during the flight through the nozzle. The flame temperature varies in the range of 2500 °C–3200 °C, depending on the fuel, the fuel gas/oxygen ratio and the gas pressure. In the HVOF process the particles melt completely or only partially, depending on the flame temperature, particle dwell time, material melting point and thermal conductivity.

A few different HVOF spray systems exist with partly different gun designs and capacities. Each one has differences in design, but all are based on the same fundamental principles. The combination of high pressure (over 3 bar) and gas flow rates of several hundred liters per minute generate supersonic gas velocities. These systems can be roughly divided into the first, second and third generation. In all first and second generation guns, the pressurized burning of gaseous fuel with oxygen is used to produce an exhaust jet traveling at a speed of about 2000 m/s. The main fundamental difference between first and second generation is the design of the nozzle. In the first generation HVOF systems there is typically relatively large combustion chamber and a straight nozzle. With this design maximum of 1 Mach (gas velocity related to the sonic speed) velocities can be produced. The second generation is based on the de Laval nozzle, which enables over 1 Mach velocities at the diverging part of the nozzle. Under standard spray conditions the systems are operated at a power level of about 100 kW and are capable of spraying about 2–3 kg/h of WC-Co. The third generation systems are for power levels ranging from 100 to 300 kW and for higher chamber pressures ranging from 8 bar up to as far as 25 bars, being capable of spray rates up to about 10 kg/h. Table 1 summarizes the key differences between generations.

| Nozzle type | Power level (kW)* | Chamber pressure (bar) | Kg/h (WC-Co) |
|-------------|-------------------|------------------------|--------------|
| 1st generation | straight            | 80                     | 3 to 5       | 2 to 6       |
| 2nd generation | De laval            | 80 to 120              | 5 to 10      | 2 to 10      |
| 3rd generation | De laval            | 100 to 300             | 8 to 12 (up to 25) | 10 to 12      |

*Total Heat Output

From a scientific point of view, particle velocity (v) and particle temperature (T) together with substrate characteristics are the main parameters affecting the deposit formation. They determine the deposit build-up process and deposit properties. Particle velocity and temperature affect the deposit efficiency as well as the microstructure. Trend in HVOF process development has been towards higher...
gas pressures, faster particle velocities and lower particle temperatures as shown schematically in Figure 2. This has a clear influence on the coating microstructure, where amount of oxidation in the lamella boundary is decreased and flattening rate is increased, and due to this the coating density is improved generation by generation, as presented in the Figure 3.

**Figure 2.** The trend in HVOF process development has been towards higher gas pressures, faster particle velocities and lower particle temperatures.

![Figure 2](image)

**Figure 3.** Faster particle velocities and lower particle temperatures in HVOF process have a clear influence on the coating microstructure, where amount of oxidation in the lamella boundary is lowered, the flattening rate increased, and due to this the coating density is improved.

![Figure 3](image)
2. HVOF Process Optimization

HVOF spraying is a very complex process, which has a large variety of variables affecting the deposit formation and hence coating properties. These variables include hardware characteristics (e.g., nozzle geometry and spraying distance) and process parameters, e.g., fuel gas, gas flow density, and powder feedstock. In the spray process, the powder particles experience very high speed combined with fast heating up to its melting point or above. This high temperature may cause evaporation of the powder or some components of it, dissolution, and phase transformations. Due to this complex nature of HVOF technique, the control and optimization of the process in order to achieve coating with desired properties is a highly challenging task. There are different ways of optimizing and analyzing the thermal spray processes and deposit formation. These include statistical methods such as Taguchi and design of experiments (DoE), numerical modeling and simulation, and FE methodology [1-5]. In the Taguchi method, for example, the test matrix can be significantly reduced and the relative importance between variables can be determined sufficiently. The result in Taguchi is dependent on the design and selection of variables and their levels and the result may therefore be misleading. Determining the importance and weight of a large number of variables is very difficult with the HVOF process. This applies to different modeling procedures as well.

Good coating quality with suitable properties and required performance for specific applications is the goal in producing thermal spray coatings. In order to reach this goal, a deeper understanding of the spray process as a whole is needed. Starting material, spray process and particle-substrate interactions all affect the formation of coating with different microstructure and hence the coating properties and eventually the coating performance. Use of submicron and nanostructured powders sets demands for the coating process in order to maintain the fine-scaled structures and enhance the coating properties. For better control of thermal spraying, different sensing devices have been developed during the last decade. These diagnostic tools have enabled better investigation and measuring of the spray process, and helped to understand the impact of different process variables on in-flight particle state (flux, temperature and velocity). In tandem with the diagnostic tool development, a novel comprehensive optimization tool has been developed for thermal spray processes. The process mapping concept was first introduced by Professor Sanjay Sampath [6], and its use has increased since introduction [7-10]. In this chapter the diagnostic equipments are introduced, as well as the process mapping tool and factors related to it. Examples of applying the process maps for process control and coating design are presented.

2.1. Diagnostic Tools for Process Optimization

For the last fifteen years active development of spray process sensing systems has taken place. These diagnostic tools are nowadays robust, user-friendly and cost-effective, and therefore their use has increased strongly. Principle objectives of diagnostic tools are to measure the variables of particles within the spray stream, i.e., velocity, temperature, flux, trajectory, and size distribution, which all have influence on the microstructure and properties of sprayed coatings [9]. The sensors are mainly based on two-wavelength pyrometry and time triggered measurement of velocity. Examples of sensors for thermal spraying are Tecnar DPV2000, Oseir SprayWatch, Tecnar Accuraspray, Inflight Particle
Pyrometer, and Spray Position Trajectory sensor. These are based on either individual particle (DPV2000) or ensemble (group of particles) measurement (SprayWatch, Accuraspray). In its simplest form, the sensors are used for measuring the temperature and velocity of the powder particles in the spray stream. The placing of the sensors can either be fixed on the spray torch or on the side of it. With the former sensors, it is possible to monitor the process continuously, and any variation can be instantly detected. Ensemble measurement is the faster of the two, a few seconds against a few minutes [11]. The diagnostic tools have differences in measuring the spray stream, including volume, number of particles and the ability to scan the spray stream. These differences with single particle and ensemble sensors may lead to different results when measuring temperature and velocity. Comparison with single and ensemble sensors has shown good relation for ceramic and metallic coatings when velocity was measured [12]. However, average particle temperature measured by single and ensemble sensors did not correlate for metallic materials. The reason for this might be that high-temperature ceramic materials have higher total radiated intensity due to higher temperature and higher emissivity, but metals are influenced by oxidation and change of emissivity [12]. Therefore the results of diagnostic tools need careful consideration.

2.2. Process Optimization Procedures

The spraying process is monitored with diagnostic sensors, which measure the particle surface temperature and velocity in the spray stream. It is very important to place the equipment correctly in-line with the spray stream. By controlling the gas flow, the fuel/oxygen ratio, or back-pressure of the chamber, different particle states are formed. In order to examine coating formation in detail, individual splats can be sprayed in parallel with using diagnostic tools. By splat studies on the polished substrate, the particle melting state can be analyzed, and hence it is possible to get more information of the diverse coating build-up process. With splat analysis, it has been shown e.g., that small NiCr particles suffer more oxidation when particle temperatures are high [10]. It is common that high speed particles form air pockets when deposited on the substrate, especially when particles are not fully melted. Fully molten NiCr particles have formed smaller grain sized splats compared to feedstock material [10]. Examples of splats of Al₂O₃ are presented in Figure 4, showing different melting states of sprayed particles resulting from different spray parameters. Characterization of the formed coating by microscopic means and testing the coating after spraying, thickness, porosity, lamellar structure with fully or partially molten particles, flattening ratio, oxidation level, bonding, hardness, elastic modulus etc. are revealed, and can be linked to process variables. When the linkages between process variables, coating microstructure and properties are done, the reverse deduction is also possible. When a certain property is the goal, it is possible to go backwards by process maps and identify the correct process parameters in order to achieve the desired property.
Figure 4. In the SEM figures of splats different melting, flattening and splashing behavior of HV2000 (Praxair) sprayed $\text{Al}_2\text{O}_3$ particles can be detected. The used spray parameters have been (a) 776 L/min $\text{H}_2$ / 272 L/min $\text{O}_2$ / 20 L/min $\text{N}_2$ (fuel ratio 2.85), 150 mm stand-off distance, (b) 776/272/20 (2.85) 200 mm, (c) 699/349/20 (2.00) 150 mm, and (d) 747/301/20 (2.48) 150 mm.

Three operational gas/liquid flow variables can be used for the control of HVOF process: (i) choice of used gases/liquids; (ii) total volume flow of gases/liquids; and (iii) the ratio between them (oxygen/fuel). All these have influence on particle velocity (backpressure of the chamber) and particle temperature. Independent operational parameters with HVOF can be oxygen, fuel, nitrogen and air flow. Other variables, which play an important role, include spray distance and deposition rates (combination of e.g., feed rate and robot speed). Gas flow control can be used as a tool for particle state measurements ($T$, $v$), as well as a tool for using different fuels, chamber and nozzle designs, which change the particle state significantly.

The spraying process must be calibrated, so that errors in the measurement can be prevented or estimated. Use of feedback control in the process enables this. Repeating a certain condition whilst performing the process map procedure indicates the data scatter and error, both to temperature and velocity measurement. Errors rise from input parameters (emissivity), instruments, control of gas flows and feed rate, and degradation effects of nozzle and injection wear [8]. These may have influence on the achieved temperature-velocity values during a long process time, and therefore calculation, re-calculation and re-adjusting of spraying parameters are needed throughout the spraying process.
An example of the HVOF spraying of NiCr powder has shown the influence of oxygen-rich flame, resulting in higher temperature and lower velocity [10]. When fuel-rich flame was used, the temperature decreased (as the flame energy decreased), and particle velocity increased. Kinetic and thermal energy transferred to the particles is dependent on the flame energy (enthalpy of the used fuel, fuel density, and ratio of fuel to oxygen). Higher energy levels of the flame yield higher kinetic and thermal energies to the particles. Increment of airflow to the flame decreases the temperature and increases the particle velocity slightly by increasing the drag force to the particles and shortening of their dwell time. Changes in fuel-oxygen mixture cause stronger effect. Feed rate plays also a role on the kinetic and thermal energy. A flame quenching effect has been observed when increasing the feed rate of NiCr powder [10].

The oxide content of the coatings is predominantly determined by the in-flight reactions. Longer flame protects the particles from oxidation by shortening the interaction with the surroundings, and by burning the oxygen within the flame, a so-called shielding effect. Therefore the fuel-rich conditions produce metallic coatings with less oxidation [10]. Higher particle speeds reduce particle overheating, thus preventing the oxidation and decarburization of carbides [13]. On the other hand, higher particle temperature leads to slightly higher oxide content [10].

2.3. Process Mapping

Particle state is influenced by fuel gas chemistry (fuel/oxygen ratio), total gas flow, and energy input, which affect the particle temperature, velocity and hence coating formation dynamics and properties. The process-structure-property relations can be presented by process maps, which can be used as design tool for coating processing. Process maps are interrelationships among the process variables and output responses [12]. The process mapping optimization tool has been widely applied for plasma spray process [12,14], but it can be successfully used for HVOF process as well [10,15].

2.3.1. Concept of Process Mapping

The process map methodology is developed for process control and coating properties optimization. In the process mapping concept, the diagnostic tools are used for understanding the fundamentals of relationships in the thermal spray process, starting from powder to thermal spraying process, to deposit formation, to coating characteristics, and finally to coating performance. In Figure 5, the process map concept for HVOF spraying is presented. A first order process map expresses the relationship between torch parameters and particles in the spray stream, which are measured by diagnostics. A second order process map represents relationship between the spray stream measured responses and coating properties. Systematic evaluation of the processes, eventually leading to optimization of coating properties for specified performance and an assessment of process reliability, can be performed by creating first and second order maps for certain material and thermal spray process. A third order process map, which links coating microstructure and properties to coating performance can also be constructed.
Figure 5. The process map concept for the HVOF process. The relationship between process parameters, measured particle state, coating microstructure and coating properties are described as process maps of different order. The goal of process mapping is to understand the process-structure-properties in order to be able to use the tool for coating design.

2.3.2. First-Order Process Map

A first order process map relates the process variables to particle state (temperature and velocity). The results acquired with diagnostic tools are plotted in a T-v diagram, which is called a first order process map. An example of first-order (T-v) process map is shown in Figure 6, which presents different temperature and velocity ranges for two different fuel mixtures for HVOF sprayed Al₂O₃ [15]. A generalized first-order process map in Figure 1 for different thermal spray processes, presenting the typical temperature and velocity ranges. In the figure it can be seen that HVOF process has moderate temperature and high velocity compared to other common thermal spray processes. First-order process map helps to understand how the particle state influences on the formation of the coating microstructure.
Figure 6. A first-order process map for HVOF alumina, showing particle temperature and velocity ranges for propylene-oxygen and hydrogen-oxygen fuel mixtures [15].

2.3.3. Second-Order Process Map

A second-order process map links the process and deposit interactions. It describes the influence of coating microstructure on the coating properties. In order to produce a second-order map, a certain T-v process window from the first-order map is selected. After the spraying, the coating properties, such as weight, elastic modulus and thermal conductivity, are measured, and thus linked to the process parameters (temperature, velocity). The purpose of the second order map is to provide a tool for designer to choose coatings of selected combination of properties and specify the values of T-v of the particle state. Actual operational parameters are specified from the first-order map. A second-order process map for HVOF sprayed NiCr is presented in Figure 7, showing values of elastic modulus and hardness reflected with different particle temperature and velocity values [10]. A schematic illustration of an idea of the second-order process map is presented in Figure 3, where different HVOF processes are compared in T-v diagram, linking the formed microstructure to the process parameters.

Figure 7. Second-order process maps for HVOF NiCr of elastic modulus and hardness with different particle temperatures and velocities [10].
2.4. Reliability through Process Optimization

More stringent requirements for coatings in different applications enhance the use of process optimization, repeatability, reproducibility and reliability (3 R’s) of the coating process as a goal [16]. However, reliance and manufacturing reproducibility is a complex task due to the multitude of interrelated parameters that influence spraying process and the deposit formation dynamics. The complexity of the process and material variables has made it difficult to understand the process-structure-property relationships as well as industry/application related attributes, such as coating design, property characterization and reliability [8]. Process optimization is used for process development by parameter improvement, tracking instabilities and examining reproducibility, and that way for improved coating manufacturing. A strategy for coating design can be obtained by careful use of process maps, because process parameters can be linked to coating characteristics and hence understanding of the process-microstructure-property relationships is possible [12]. Through process optimization it is possible to produce reliable and reproducible coatings with designed performance together with predictable life of operation [15]. Therefore the process map concept is an excellent tool for analyzing and controlling the effects of spraying parameters in production of coatings. The method can be applied for any thermal spray technology [10]. Also deposition efficiency (DE) can be improved, as well as process efficiency. Materials usage and the amount of defective coated components can be minimized, and that way it is possible to lower the coating production costs.

2.5. Case Studies of Process Optimization with Process Map Concept

Challenges arise when spraying nanoscale carbides, because with fine carbide sizes the dissolution of carbides and carbon loss becomes easier. The powder quality is important, as the size distribution, density, carbon and oxygen content have influence on the deposit formation. Choosing right spray process and optimizing control parameters are essential in generating good coating quality. Agglomerated and sintered WOKA 3652, −45+45 μm WC-10Co4Cr powder was sprayed with DJ Hybrid HVOF spray, with hydrogen as fuel gas. The goal was to increase both wear resistance and fracture toughness. As can be seen in the generalized second order process map for WC-CoCr in Figure 8, a small process window to achieve such characteristics combination was found. The goal of using WC-CoCr with nanoscale carbides was to achieve high hardness combined with good fracture toughness. Thermico CJS (carbide jet spray), a colder HVOF thermal spray process with broader process window, was applied for maintaining the nanoscale carbides within the matrix. With careful process optimization, both the characteristics were enhanced [17].
Figure 8. A generalized second order process map for WC-CoCr HVOF coating. Different coating properties are placed into the temperature-velocity diagram. This process map can be used as a design tool to optimize coating process conditions in order to achieve desired coating property or coating property combinations.

Process map methodology has been used for HVOF spraying of Ni-20%Cr coatings [10]. Design of experiments was used to prepare a first order process map. According to the map, different conditions were chosen to produce the coatings with a low feed rate, and to analyze them with an in-situ coating property sensor (ReliaCoat Technology ICP). It was noted that increase in the feed rate decreased both the particle temperature and velocity. In the same process optimization trials, an increment on airflow feeding was detected to result in lower particle temperature but higher velocity. When spraying distance was increased, the particle temperature was risen and the velocity was reduced. In order to enhance the thermal conductivity, high kinetic energy with high thermal energy of particles was required so as to deposit dense coatings with improved intersplat bonding (metallurgical, intimate mechanical contact), but oxide content must be kept relatively low. Electrical resistivity was enhanced with high thermal-kinetic energy as well. Stiffer coatings were formed with high particle velocity and sufficient melting state.

An example of plasma spray process optimization for yttrium stabilized zirconium (YSZ) plasma sprayed coating showed possibility of controlling the particle state within a small process window (±10 °C average temperature and ±2 m/s average velocity) by using a first order process map while varying process parameters (e.g., gas flow, current). However, different melting states were observed in the temperature distribution diagrams for various sprayings, as well as differences for deposition efficiencies, and modulus between the coatings. These results indicate that temperature and velocity measurement solely do not describe the melting state of the particles [15].

2.6. Thermal Energy and Kinetics of Particles in Spray Stream

In order to better understand the melting behavior of particles in the spray stream, another factor has been developed besides the use of temperature. Especially with ceramic materials, with low thermal conductivity, the particle surface temperature does not directly indicate the particle melting status due
to large temperature gradient within the particle [9,18]. The particle surface may even evaporate before the core melts. In the case of metallic materials, the oxidation of particles occurs in the spray stream. This phenomenon can have an effect on the measured temperature values and emissivity value. Melting index (MI) also takes into account the time particles stay under the influence of flame and particle size. It can be expressed as [12]:

$$ MI = \frac{T \Delta t_{fly}}{D} $$

(1)

where $T$ = measured particle surface temperature [K], $D$ = particle size [m], and $\Delta t_{fly}$ particle in-flight time assuming constant acceleration of particles [s]. In the MI formula the $\Delta t_{fly} = 2L/v$, where $L =$ spray distance [m], and $v =$ particle velocity [m/s]. MI can be defined as the ratio of particle residence time in the flame to the total time needed for particle to melt: $MI = \Delta t_{fly}/\Delta t_{melt}$ [9]. There is also more thorough description of melting index, which attaches thermal resistance and energy balance analysis to the formula [9]:

$$ MI = \frac{\Delta t_{fly}}{\Delta t_{melt}} = \frac{24k}{\rho h_{fg}} \cdot \frac{1}{1 + 4/Bi} \cdot \frac{\left( T_f - T_m \right) \cdot \Delta t_{fly}}{D^2} $$

(2)

where $k$ is the thermal conductivity [W/mK], $\rho$ is the density of the material in liquid state [kg/m$^3$], $h_{fg}$ is the enthalpy of fusion [J/kg], and $T_f$ is the flame temperature near the in-flight particle [K], $T_m$ is the melting point of the material [K], $D$ is the particle size [m], and Bi is the Biot number [9].

With this approach MI is non-dimensional, which allows cross-comparison of melting state among a range of materials. From Equation 2, it can be detected that if the flame temperature is higher than the melting point of the material, a positive MI value will be obtained, which corresponds to fully molten particles. Otherwise, the material will be unmolten (MI < 0) or partially molten (0 ≤ MI < 1). Since it is difficult to monitor the real time flame temperature in the vicinity of the flying particles, for simplifications particle surface temperature, $T$, has been often used instead of $T_f$. Metallic particles oxidize during the spraying process, which has effect on the measured temperature by diagnostic sensors. Oxidation reactions are exothermic, which raises the particle temperature in-flight. Extent of oxidation taking place with the metallic particles is described by Oxidation index (OI) [9].

Like temperature, the velocity values alone do not give sufficient information of the particles impinging on the substrate material and hence the deposit build-up process. Therefore either kinetic energy (KE) or Reynolds number (Re) can be used for describing the kinetic behavior of the particles. Kinetic energy is related to particle mass (m) and velocity (v) [9]:

$$ KE = \frac{1}{2}mv^2 $$

(3)

Reynolds number can be described with factors such as particle size, material density and viscosity [17]:

$$ Re = \frac{Dv\rho}{\mu} $$

(4)
where $D = \text{particle diameter [m]}$, $\rho = \text{density of the material in liquid state [kg/m}^3\text{]}$ and $\mu = \text{dynamic viscosity [kg/ms]}$. Both the kinetic energy and Re are important factors describing the impact, extent of spreading and flattening, and hence the nature of splat-substrate and splat-splat contact [9]. Melting state, kinetic energy and local deposition temperature are likely the most important factors controlling the microstructure and properties of the coatings [10].

Other factors besides particle state correlations that strongly effect deposit formation dynamics (wetting, spreading-splashing, flattening, solidification, and interlocking/bonding dynamics) and hence deposit characteristics, are substrate temperature and roughness, deposit conditions (rate, spray angle), and deposit rate [12]. Another factor affecting particle behavior and temperature is exothermic reaction of oxide formation (e.g., $\text{Cr}_2\text{O}_3$), which generates additional heat during flight [10].

### 2.7. Monitoring Deposit Formation In-Situ

Analysis of coating characteristics is mainly performed after the actual coating process. However, the actual deposit formation process is difficult to monitor. An in-situ coating property sensor (ICP) has been developed to monitor coating curvature evolution and substrate temperature during the spraying process [12]. Measuring curvature is possible by monitoring the substrate displacement with non-contact lasers. Temperature measurement is performed with multiple thermocouples attached to the back of the substrate material during both deposition and cooling. With this information, it is possible to calculate residual stresses, CTE, and elastic modulus of the coatings. The technique and the measurement method are described in detail by Matejicek et al. [19].

The particle state influences stress build-up during spraying process and coating residual stresses have an effect on the coating properties. The residual stresses depend strongly on the particle velocity and on the particle temperature [12]. Compressive stresses are formed due to peening at high particle velocities. As an example, in curvature measurements of NiCr it has been noticed that in the first pass, the quenching stresses prevail due to limited plastic deformation of the substrate [10]. Following passes induce compressive stresses due to the peening effect. The higher the velocity, the higher is the buildup of the compressive stresses. Peening intensity of the impacting particles can be monitored during spraying through an in-situ curvature technique. Correlation of it can be made to the microstructure, splats, residual stress and hardness of deposits [10]. Difference in CTE’s (coefficient of thermal expansion) between the coating and substrate material also causes stress in the coating. Evolving stress and substrate temperature are main factors when considering strain hardening of the coating, compaction, and residual stress development [10].

### 2.8. Effect of Feedstock Properties on Coating Formation

Powder properties and characteristics (e.g., particle shape, structure and size, powder density and flow ability, purity, phase content, agglomeration) depend on the detailed powder manufacturing method, i.e., crushing and milling, water and gas atomization, spray drying, agglomeration and sintering [13]. Studies have shown implication of different feedstock for the formed coating, as the particle characteristics are very different in the spray process (e.g., temperature and velocity). When powders from the same material, but with different morphologies or different size distribution, have been sprayed with similar temperature and velocity range, the formed coatings have shown substantial
differences in several properties e.g., elastic modulus [12]. Examples of different spray powder morphologies are presented in Figure 9. The feedstock characteristics (particle form, size distribution, density and chemistry) have an effect on deposit evolution and process efficiency by change in thickness per pass, and to other properties, such as thermal conductivity.

**Figure 9.** SEM images of thermal spray powders representing different morphologies. 
- **a)** Ball mill mixed, agglomerated and sintered Al$_2$O$_3$/SiC;  
- **b)** spray dried Cr$_2$O$_3$;  
- **c)** gas atomized Ni20Cr; and  
- **d)** fused and crushed Al$_2$O$_3$ powder by Praxair.

### 3. Characterization of HVOF Coatings and their Properties

The optimization of the coating microstructures and properties is a challenging task, not to mention the performance of the coating in a particular environment or application as presented in Figure 10. There are a number of influencing factors and interdependencies that influence the intrinsic coating properties as discussed above. These interdependencies are complicated and sometimes even impossible to handle although the systematic process optimization approach described in the previous chapter shows promise as an effective tool for such a task.
Figure 10. A typical optimization route of coating performance by controlling the intrinsic coating properties via optimization of coating microstructure and coating/substrate system interactions.

As described in previous chapters, the typical route for the optimization of coatings performance is via its intrinsic properties that in turn are controlled by the microstructure and coating/substrate—system interactions. For example, in wear applications such coating properties as hardness, elastic modulus and fracture toughness, along with porosity of the coating, are under focus. If the application requires environmental resistance, whether against corrosive media or oxidation, it is important to control the phase structure of the coating as well as its porosity. In both cases, also the system properties, i.e., adhesion of the coating to the substrate and internal stresses must be under control to obtain a coating that has an optimal performance at the particular applications.

Before discussing the typical properties and the range of their variance in HVOF coatings we will introduce the most usual methods for characterizing the properties of HVOF coatings. It is important to acknowledge that although most of them are quite generally applied in materials characterization, thermal spray coatings bear many special features that must be taken into account when their properties are evaluated.

3.1. Characterization of Intrinsic Coating Properties: Special Features and Limitations

Characterization of coating microstructures and properties are usually carried out by methods developed for microstructural characterization in general. While most of these are directly applicable for HVOF coatings as well, there are certain precautions, which should be considered and taken into account. This concerns especially the preparation of samples for characterization of microstructural features of coatings.

3.1.1. Coating Hardness

Hardness of the coating is usually measured either from the cross section or the surface of the coating. Two types of methods are commonly used, i.e., traditional hardness measurement preferably
carried out by Vickers’ method or instrumented indentation techniques, where the hardness is evaluated from the load-displacement data.

When Vickers hardness is measured from the cross-section of thermal sprayed coating the applied loads should not lead to the formation of cracks. According to standard EN ISO 14923 the thickness of the coating should be at least three times the indentation diagonal \(d\). This is observed to be the absolute minimum thickness required to make reliable measurements and, to be on the safe side, the upper corner of the indentation should be located at least at a distance of one diagonal from the surface of the coating, and the lower corner a similar distance away from the substrate. When Vickers hardness is measured from the top surface of the coating, the thickness is recommended to be ten times the plastic depth of the indentation to avoid any effect from the substrate on the measurement. Therefore, nanoindentation is currently used for a more detailed mechanical property characterization, such as for measuring hardness and elastic modulus of individual phases like carbides or matrix material of the coating or even from single splats [20-22].

3.1.2. Elastic Modulus

There are several methods to deduce the elastic modulus or Young’s modulus of the coating (E). Among them impulse excitation technique (IET), ICP sensor, and instrumented indentation test are most common. IET-standard procedures are described in ASTM E 1876-99 [23] and ENV 843-2 [24]. Elastic modulus can conveniently be determined by instrumented indentation. Values of E are calculated from the load-displacement data usually following the procedure proposed by Oliver and Pharr [25]. Because of the elastic field of the indentation is always larger than the plastic field, the boundary conditions of hardness measurement described above should be considered to be minimum requirements for elastic modulus measurements. Since elastic modulus is very sensitive to coating microstructure and especially to coating porosity and other faults, its value can also be used when estimating the uniformity and quality of the coating in comparison to other thermally sprayed coatings.

3.1.3. Coating Toughness

The toughness of a material describes its ability to absorb energy before and during fracture [26]. Because of the brittle nature of many thermal sprayed coatings, fracture mechanics play an important role in evaluation of the usability and performance of the coatings. Fracture mechanical theories, equations and measuring techniques of bulk ceramics, also possessing brittle nature, have been the starting point for studying the fracture behavior in the thermal sprayed coatings. Because of the required sample size in the methods developed for bulk materials, the indentation fracture toughness (IF) technique seems to be the only reasonable and suitable test for thermal sprayed coatings. The basic idea is to apply a large enough load with Vickers diamond pyramid tip to initiate cracks from the diagonal corners of the indentation mark. From the measured average crack length and applied indentation load, the fracture toughness \(K_{IC}\) can be calculated. It describes the critical stress intensity factor of mode I crack. Indentation fracture toughness \(K_{IC}\) can be measured from the cross-section or the surface of thermal sprayed coating. From the surface, one usually gets four corner cracks with the same length, and the boundary conditions described e.g., in JIS R 1668-2005 [27] can be used.
Because the applied loads needed for the initiation of cracks in the fracture toughness measurement are higher than those used in the hardness measurements, one must check that the maximum plastic depth of the indentation is less than one tenth of the coating thickness. When measuring fracture toughness from the cross-section of the coating, the obtained result describes the lamellar cohesion. Cracks in the coatings grow more easily in the direction parallel to the substrate—vertical cracks are usually produced only in the brittle ceramic coatings. The cracks parallel to the substrate will usually initiate and propagate in the lamella boundary. Because of this preferred crack growth direction, the equations and boundary conditions developed for homogenous bulk ceramics do not apply and some modifications are needed. If the cracks grow only in the parallel direction, the average crack length ($l$) should be calculated by dividing the total crack length ($\sum$ of the cracks) by two, not by four as when measured from the surface. One requirement is that the cracks should initiate near the diagonal corners. If other major cracks than the corner cracks are developed, the measurement is not anymore valid. This prerequisite may lead to difficulties of finding valid measurements, especially if the coating possesses large residual stresses [22].

3.1.4. Coating Porosity

There are a number of different methods that can be used for determination of the coating porosity. Nondestructive methods such as water adsorption, mercury intrusion porosimetry, helium pycnometry, Archimedean method, and other more sophisticated and tedious methods such as small angle neutron scattering (SANS) or x-ray computed microtomography (CMT) [28] have all been employed for quantitative measurement of porosity. Accurate counts of porosity and its distribution can be obtained by the latter two methods, but they both require special instrumentation, which is not generally available for industrial use.

The most common practice to analyze the porosity of a coating is to prepare a metallographic cross-section sample of the coating and to determine its porosity from the micrographs taken with light microscope or a scanning electron microscope (SEM) e.g., by image analysis. Porosity within a microstructure can in principle be easily detected by image analysis because of the contrast difference between the dark pores (voids) and the more highly reflective coating material with sufficient resolution. Some reports claim that image analysis can reproducibly detect and measure microstructural features (pores, cracks, etc.) to a 95% confidence level within thermal spray coatings [29].

There is a lot of criticism presented on this procedure since the preparation of the samples has a large influence on the values obtained, i.e., the preparation may result in formation of pores (in brittle coatings such as ceramics) or closure of pores (in ductile metallic coatings) resulting in erroneous values of porosity. In ISO/TC107/WG1, porosity measurement of thermal sprayed ceramic coatings by SEM cross-sectional photography and image analysis has been evaluated by a number of participating members. In a round robin test organized by the working group, five samples having a different ceramic coating were tested by each participant to obtain the respective porosity values. Further examinations have also been conducted by NIMS in Japan about the role of image analysis software, SEM and surface polishing procedures to rationalize the reasons for the observed differences. A preliminary and partial analysis of these results is given in ref. [30], and the final report is published as
an ISO Technical Report TR 26946. The findings can be summarized as follows. The differences in grinding/polishing conditions of the cross-sectional sample have a major influence on the porosity value obtained. Especially the pressure during polishing has an important role. It could be hypothesized that if the grinding pressure in the beginning of the polishing procedure is too low, the defects formed during the specimen cutting and preparation are not removed completely and too high value of porosity is obtained. If the pressure applied in the polishing is too high the sample preparation itself results in pull offs and too high porosity value. Furthermore, it is important to recognize that the imaging mode in SEM has an influence such that secondary electron image (SEI) typically yields lower values of porosity than the backscattered electron image (BEI) because the distinction of the coating matrix and the pores is more difficult in the SEI image, and the fraction of image judged to be a pore as a result has decreased. Based on this hypothesis an optimum pressure can be found, which results in a minimum value of porosity. Whether this is the actual porosity of the coating or higher than the real value depends on the mechanical properties of the particular coating.

An additional challenge is that the total percentage of porosity does not always give enough information on the quality of the coating even if determined correctly. A more detailed account of pores and cracks is actually needed if the coating properties and performance are to be judged or predicted in more detail. Therefore it would be advantageous to divide the net porosity into classes, such as coarse and fine globular pores and crack networks according to their process of formation [31]. Coarse pores refer to the size range of 3–10 µm pores, which are formed due to incomplete filling of interstices between impacting particles and previously deposited particles and typically formed, when the impacting particles are not completely molten. Fine pores are approximately 0.1–3 µm in size resulting from incomplete contact between lamellae during coating formation, and are therefore more or less oriented parallel to the substrate surface. The fine cracks approximately 0.01–0.5 µm in thickness result from relaxation of stresses generated within the splats during cooling and are thus oriented typically perpendicular to the lamellar plane.

3.2. Characterization of Coating Substrate System Properties: Challenges and Special Features

3.2.1. Coating Adhesion

Adhesion is one of the most important parameters, which influences the performance of thermal spray coatings—substrate system in practical applications of coatings. For many applications the adhesion of the coating is crucial to the performance of the coated part (e.g., [32]). Since no metallurgical bonds are formed between the rapidly cooling deposit and the substrate, the surface finish and the deposition conditions during the first spray pass are of uttermost importance in obtaining good adhesion.

A standard method for the measurement of adhesion of thermal spray coatings is by tensile adhesive test [33]. This test is widely used although according to [34] more than 80 other methods are reported for the measurement of coating adhesion. However, in case of porous ceramic coatings tensile adhesion testing has an inherent problem of being prone to penetration of the adhesive used for gluing the tensile test holder through the coating. This may result in too high a value of adhesion in the test. Therefore, other types of tests have been proposed for the measurement of adhesion of thermal spray
ceramic coatings. Two of these are currently used or studied as an alternative for the tensile test, \textit{i.e.}, shear test and scratch test.

Shear test developed in the frame of the EU-CRAFT-project “Shear Test for Thermally Sprayed Coatings” presents the main advantage of being possibly used in real time, \textit{i.e.}, during the production process [34]. The small size of the substrate specimens allows them to be prepared in advance in large quantities, and no limitation of porosity or adhesive strength of the adhesive occurs. Therefore the shear test is more relevant to represent the real stress state acting on the mechanical parts during service. The main disadvantages are the samples characteristics (coating should be thicker than 150 µm) and the need of special equipment to perform the test.

Scratch test, which is widely used for testing adhesion of thin films to substrate, is with modifications currently considered also for determining the thermal spray coating adhesion. ISO TC 107 WG 1 is carrying out an international round robin test to study the feasibility of this test for the determination of the coating adhesion of ceramic thermal spray coatings. Preliminary results of this round robin test will be available by the end of 2011.

3.2.2. Evaluation of Internal Stresses

An important coating-substrate system property is the residual stress state of the coating after spraying. There are only few methods that can be used to measure the residual stresses of thermally sprayed coatings. The generally applied method for measuring the residual stresses in metallic materials is by XRD using standard \(d \text{ vs. } \sin^2 \Psi \) XRD techniques (see e.g., [35]). In order to apply this method for the determination of residual stresses of thermally sprayed coating one needs to know the so-called X-ray elastic constants (XEC). XEC can be calculated using techniques based on the mechanical loading of the samples. However, the experimental behavior of the thermally sprayed coatings shows that the calculation of XEC is unreliable. Considering the characteristics of dense material to which the X-ray diffraction is sensitive, the use of XEC values calculated for the same phase of the bulk material can, according to [36], be used for the determination of stresses in the coatings with an engineering accuracy.

When internal stresses are measured during spraying using the so called \textit{In-situ} Coating Property (ICP) sensor, it is possible to adjust the residual stresses to a large extent during spray by controlling the deposition parameters. In this way, the various stages of stress build-up can be monitored and the various stress contributions can be evaluated separately. The ICP sensor can also be used to extract in-plane elastic modulus of the coatings deposited. It is based on laser sensing of deflections in a strip during thermal spraying which is converted to sample curvature. A simultaneous measurement of temperature is achieved via multiple thermocouples. Elastic modulus and CTE of the coating can be calculated from the coating-substrate composite curvature change due to thermal mismatch [37].

3.2.3. Evaluation of Wear Resistance

Wear resistance of thermally sprayed coatings is of high interest for many applications. In general, wear resistance of a coating in a particular environment is a system property influenced by the coating and substrate material and in particular the type of wear environment. Therefore, it is impossible to quantify the wear resistance of the coating accurately without knowing these factors. However, for
particular types of wear environments there are tests, which give relative performance of different coatings quite accurately. One of the most used wear tests for thermally sprayed coating is the rubber wheel abrasion test (e.g., ASTM G-65), which is meant for testing material’s resistance against abrasive type of wear. These tests are also extensively used for a wider screening of coatings, since the possible problems in coating microstructure (not so easily observed e.g., by metallographic means) are often manifested in the results of the abrasion test. Other tests exist for other types of wear situations, such as tests for adhesive wear (e.g., pin-on-disc types of test) and tests for erosive conditions (various modifications exists, e.g., slurry test depicted in standard ASTM G75-95 [38]).

3.2.4. Evaluation of Wet Corrosion Resistance

Corrosion resistance of thermally sprayed coating is always a system property. This is influenced first of all by the corrosive environment in question, but also by the coating properties (composition, phase structure and microstructure including the cracks and the pores) and the coating-substrate-environment interactions. It is very rarely possible to produce fully liquid or gas impenetrable coatings even by sealing the coatings afterwards. Therefore, it is not only the corrosion resistance of the coating, but of the substrate-coating system, which should be considered in each particular application where corrosion is a factor.

Measurement of the corrosion resistance of a coating-substrate system is typically carried out by immersion tests in actual conditions or by accelerated immersion tests in the laboratory. These tests in combination with metallographic and analytical studies help to identify the corroding parts of the system, whether this is corrosion of coating in general, selective corrosion of some specific phase of the coating, or corrosion of substrate via cracks or open porosity of the coating finally leading to coating detachment.

Electrochemical measurements may also be used to evaluate the response of coating—substrate system to corrosive environments. Typical measurement may include the determination of the free corrosion potential and the polarization behavior of the system. If the environment is selected such that the electrolyte causes corrosion only in the substrate, the corrosion current may yield information on the through porosity of the coating as well as on the possible passivation system while the pores of the coating are filled with corrosion products from the substrate.

4. Typical Properties of HVOF Coatings

Coatings prepared by various HVOF techniques have properties typically different from those produced by other thermal spray methods. As discussed in the previous chapter this results mainly from the characteristics of the HVOF process and in particular the combination of particle velocities and temperatures. Therefore, it is important to recognize that nominally similar coating compositions may have a wide variance in properties depending on the details of the processing. On the other hand, this also implies that properties of the coatings can be adjusted according to demands of the application at least to some extent.
4.1. Wear Resistant HVOF Coatings

Wear control is of uttermost importance for many applications of thermally sprayed coatings. These applications include various moving parts such as rotating rolls and axels e.g., for printing equipment, paper and pulp machinery, etc. Among different thermal spray methods high velocity oxy fuel (HVOF) spraying has proven to be especially suitable for deposition of carbide and metallic coatings because of relatively low flame temperature and supersonic particle velocities [16]. Under certain restrictions it can also be used to produce high quality ceramic coatings for wear protection.

4.1.1. Wear Resistant Cermets

Typical wear resistant coatings are based on cermet, i.e., metal-ceramic composites, predominantly combining various mixtures of metal matrix including cobalt (Co), chromium (Cr) and nickel (Ni), and tungsten carbide (WC) or chromium carbide (Cr$_3$C$_2$). The most common combinations—WC-12 wt.% Co or WC-17 wt.% Co—are widely used in applications where high wear resistance is required. Theoretically the compositions correspond to 20% and 27% of cobalt in volume, but may slightly vary depending on spraying conditions and decomposition of WC during spraying.

For WC-Co-based material it is well known that during flight sprayed particles melt to different extents depending on their size, density and dwell times. Molten Co dissolves the WC grains whereas carbon loss occurs by diffusion through the liquid followed by reaction with the oxygen from the surroundings. There can be large amounts of carbon and tungsten dissolved in the matrix metal, especially in the outer regions of sprayed particles. During cooling, Co-rich liquid becomes supersaturated resulting from the formation of W$_2$C and other mixed carbides. High cooling rates can even be responsible for the formation of amorphous/nanocrystalline matrix phase. During cooling, precipitation of mixed carbides like eta-carbide [(Co$_6$W$_6$)C] phase may occur in the Co-rich material. All of these effects are most visible on the outer core of the particles. In the small size particles, the whole particle can be influenced by decarburization [39]. If cooling is fast enough, the matrix will stay amorphous and supersaturated of W and C. When the coating is heat-treated afterwards, precipitation of eta-carbide starts at temperatures above 600 °C resulting in marked increase of hardness and reduction of residual stresses in the coating [22,40].

In oxidizing atmospheres or at temperatures above approximately 450°C the resistance of Co-WC is not adequate, and alloying of cobalt binder e.g., with chromium or use of other type of cermet coatings such as Cr$_3$C$_2$-25 wt.% NiCr are frequently employed to protect against wear at such elevated temperatures [41]. However, in comparison to WC-Co coatings Cr$_3$C$_2$-NiCr coatings are less wear resistant in many cases. Likewise to WC powders Cr$_3$C$_2$ containing powders are susceptible to a range of decomposition reactions during thermal spraying and require careful optimization of the spraying process in order to obtain desired coating properties. This has prompted efforts to look for other type of cermet for high temperature applications. TiC and TiB$_2$ are potentially attractive alternatives to Cr$_3$C$_2$ for use in high temperature wear resistant cermet applications since it exhibits a high hardness, low density and good oxidation resistance. Wear properties of TiB$_2$-containing cermet coatings have been addressed e.g., in refs. [42,43]. HVOF spraying of Ni(Cr)-65 wt.% TiB$_2$ and Fe(Cr)-70 wt.% TiB$_2$ powders resulted in TiB$_2$-containing coatings that were found to perform better in abrasive wear with
Coatings having composition of Ni(Cr)-65 wt.% TiB₂, Ni(Cr)-40 wt.% TiB₂, and Ni(Cr)-40 wt.% TiB₂ with 5 at.% excess boron in order to promote matrix amorphization have also been studied [42]. The size of the TiB₂ particles within the cermet was found to depend critically on the initial composition; large particles were favored by low binder fractions and the presence of the excess boron. The presence of the larger boride particles was concluded to impart the wear resistance of these coatings in abrasion by alumina or silica abrasives [43].

Other cermets studied for high temperature erosion include e.g., WC-CoCr, TiC-CoCr, NbC-CoCr [7]. In a study of the erosion-corrosion resistance of these coatings, Wang [44] noticed that peak wastage occurred at intermediate carbide contents at both shallow and steep impact angles for all of the HVOF carbide-cermet coatings tested. At shallow impact angles, this peak occurred on the side of lower carbide contents, while at steep impact angles the peak occurred on the side of higher carbide contents. At both shallow and steep impact angles, wastage in erosion-corrosion test decreased with decreasing carbide size of homogeneous distribution in the HVOF carbide-metal cermet coatings. It was concluded that the erosion-corrosion behavior of carbide/metal cermet coatings and the dependence of mass loss on carbide content are related to the morphology of the coatings and characteristics of erodent particles. Also Hawthorne et al. [45] noted that coating composition and microstructural integrity are the main factors determining the relative erosion resistance of the cermet coatings. They also noted that the WC-10Co-4Cr matrix coating was more resistant to erosion–corrosion damage in aqueous slurry testing than was the WC-12Co cermet coating. Similarly WC-10Co-5Cr coating has been found in simulative laboratory test to be a potential candidate for coating of hydro turbine components by Mann and Arya [46]. At low erosive conditions the erosion-corrosion resistance has been found to increase when increasing Cr-content from 5 to 8.5 wt.% [47].

An interesting development in the corrosion resistant HVOF coatings is being made with the amorphous coatings. Amorphous coatings with a composition of Fe₄₈Cr₁₅Mo₁₄C₁₅B₆Y₂ have been prepared by means of high velocity oxygen fuel (HVOF) thermal spraying under different conditions by Zhou et al. [48]. These coatings present dense layered structure and low porosity with some fraction of nanocrystals. The coatings are spontaneously passivated with wide passive region and low passive current density in chloride containing acidic solutions exhibiting excellent ability to resist localized corrosion.

4.1.2. Wear Resistant Ceramic Coatings by HVOF

HVOF spraying is applied mainly to cermet and metallic coatings because of the limited melting power of most of the HVOF spraying guns and systems. However, due to the higher kinetic energy, shorter dwell time of particles in the flame, and lower flame temperature compared to the plasma spray, HVOF offers an interesting combination to produce dense coatings with controlled phase transformations [49]. For high quality coatings particle melting state and possible phase transformations during particle flight in the thermal spray flame as well as coating build up mechanism including splat interface and stress stages must be controlled. Despite some limitations there are several reports on successful depositions of ceramic coatings by HVOF spraying techniques (e.g., [7,15,49-51]).
In order to produce high quality ceramic coatings by HVOF, the spraying system should have a high enough melting power to melt the powder particles during the short flight. It has been shown that the particle temperature and the melting state control the deposit efficiency and the build-up rate while the flattening behavior is dominated by particle kinetic energy [15]. The powders used for spraying must have a narrow size distribution and their average size should be somewhat smaller than for powders generally used for HVOF spraying. Selection of fuel gas is of high importance and the necessity of finding correct temperature-velocity combination is a must for successful deposition of high quality ceramic coatings. The coating density and mechanical properties are strongly affected by particle velocity when complete melting is achieved. The particle state in the case of HVOF is very sensitive to the standoff distance and is found to be an influential parameter controlling microstructure and properties. It has been noted that in HVOF the interpass interfaces play a dominant role in thermal, electrical and tribological properties [16].

4.1.3. Comparison of APS and HVOF Wear Resistant Coatings

It has been quite generally recognized that the wear resistance properties of HVOF coatings are superior to their APS counterparts. Li et al. [41] have compared the impact wear resistance of Cr$_3$C$_2$-25%NiCr coatings prepared by APS- and HVOF- spraying. They found that the wear resistance of Cr$_3$C$_2$-25%NiCr coatings under different impact conditions increases in the order of APS-Ar/H$_2$, APS-Ar/He and HVOF spraying. The HVOF sprayed Cr$_3$C$_2$-25%NiCr coatings showed the best impact wear resistance due to the denser structure and fewer defects since the wear mechanisms of Cr$_3$C$_2$-25%NiCr coatings under impact are influenced by the cohesive defects such as stratification, porosity and microcracks in the lamella, and therefore control of these factors has a large impact on the wear resistance of the coatings.

Similar findings have been made by the present authors on HVOF sprayed ceramic coatings. Although only a few HVOF spraying guns exist on the market that are suitable for depositing ceramic coatings, the coating properties obtained by the HVOF techniques have shown quite amazing improvements in comparison to coatings deposited by APS [52]. HVOF sprayed coatings show clearly improved density and less pores and cracks than the APS sprayed as depicted in Figure 11. The abrasion wear resistance of the coatings as measured in a standardized rubber wheel abrasion test is improved more than tenfold when the coating is made by HVOF spraying. The difference is more than 15 times with the alumina and chromia coatings where the spray parameters have been optimized. The HVOF zirconia coatings perform more than 20 times better than the corresponding APS coatings. It must be noted though that the reference value for comparison is for Thermal Barrier Coating (TBC), where maximum density is not aimed. However, the obtained results show that HVOF spraying of ceramics can be an effective method to produce dense, well-adhered ceramic coatings with good environmental protection capability. This can be attributed mainly to the lower porosity and improved cohesion of the ceramic coating structure when produced by HVOF techniques.
Figure 11. Comparison of abrasive wear resistance of plasma sprayed and HVOF sprayed oxide ceramic coating coatings: yttria-stabilized zirconia (YSZ), alumina (Al$_2$O$_3$), and chromia (Cr$_2$O$_3$). Compiled based on [52].

These findings were later confirmed by Bolelli et al. [53], who compared Al$_2$O$_3$ and Cr$_2$O$_3$ coatings deposited onto steel substrates by high velocity oxygen-fuel (HVOF) flame spraying using H$_2$ as fuel gas, and by conventional atmospheric plasma spraying (APS). In this study it was recognized that HVOF-sprayed coatings exhibited lower porosity and smaller average pore area than the APS ones. The HVOF-sprayed coatings possessed higher Vickers micro hardness, higher indentation fracture toughness and higher elastic modulus than the APS ones. During ball-on-disk tests against SiC, various wear mechanisms were observed. At room temperature and at low normal load, all of the coatings developed stable tribofilms under mild wear regime ($<10^{-6}$ mm$^3$/Nm) while at higher temperature and/or normal load, brittle fracture wear prevailed. Under these latter conditions, HVOF coatings become superior to APS ones, thanks to their higher toughness. Analogously, in dry particle abrasion, where brittle fracture prevails, the tougher HVOF coatings outperform APS ones.

Also in this study the HVOF ceramics were found to display lower overall porosity, and smaller and more rounded pores than the APS ones. Excellent interlamellar cohesion was noticed by FEG-SEM observations of fractured cross-sections. A large degree of melting of HVOF-sprayed nanostructured Al$_2$O$_3$ powder was found. While some glassy or poorly crystallized splats existed in Al$_2$O$_3$ coatings, the Cr$_2$O$_3$ ones were fully crystalline. In all cases, smaller and more equiaxed grains appeared in HVOF coatings, while grains were larger and mostly columnar in APS ones. In general, HVOF sprayed ceramics are harder and tougher than corresponding APS ones, and HVOF Al$_2$O$_3$ and n-Al$_2$O$_3$
are even tougher than APS Cr$_2$O$_3$ indicating the great influence of microstructure on coating mechanical properties [53].

As discussed in Chapter 3.1.4, the pore structure has a major impact on the mechanical properties of the coatings. Coarse pores in the size range of 3–10 µm are formed when the impacting particles are not completely molten because of incomplete filling of interstices between impacting particles and previously deposited particles. Fine pores approximately 0.1–3 µm in size result from incomplete contact between lamellae during coating formation being more or less oriented parallel to the substrate surface. The fine cracks approximately 0.01–0.5 µm in thickness result from relaxation of stresses generated within the splats during cooling and thus oriented typically perpendicular to the lamellar plane. It is the difference in the distribution of the latter two types of pores (fine pores and cracks), which probably can explain the huge difference in the wear properties of the plasma sprayed and HVOF sprayed ceramic coatings.

4.2. Corrosion and Oxidation Resistant HVOF Coatings

HVOF-spraying is a versatile technique that can yield high-density coatings with porosities less than 1% by optimization of the process variables. Because of these microstructural improvements of deposits produced by HVOF as compared with traditional spraying methods (including APS) the HVOF coatings have widely been studied for their corrosion resistance and consequently, there are a plethora of publications on the corrosion properties and performance of HVOF coatings. These can be divided into two categories, i.e., those reporting oxidation resistance of HVOF coatings and the others regarding wet corrosion properties.

Resistance of MCrAlY coatings to oxidation in different oxidizing atmospheres has been studied and compared with that of VPS coatings by Brandl et al. [54]. Under the chosen oxidation conditions, which assured a high oxygen partial pressure, the oxidation kinetics of the HVOF and VPS coatings were very different, i.e., the oxidation rate of the HVOF sprayed coating is considerably lower than that of the VPS coating. This observation was proposed to result from the formation of finely divided $\alpha$-Al$_2$O$_3$ during spraying hindering the grain boundary diffusion of the elements. As a consequence the oxide scale growth was very low.

Corrosion behavior of an HVOF Ni based self-fluxing alloy NiWCrBSi coatings in a chloride solution has been studied by Gil & Staia [55]. Since anticorrosion coatings must be impermeable to protect steel structures in corrosive environments optimization of deposition conditions must be determined. The optimization process indicated that especially the spraying distance, the fuel to oxygen ratio, and the powder feed rate have a significant effect on the porosity and consequently to the corrosion resistance of these coatings. Zhao et al. [56] noted that the corrosion of the NiCrBSi coating first occurs around the particles that have not melted during spraying and defects such as pores, inclusions and microcracks. Corrosion then proceeds along the paths formed by pores, microcracks and lamellar structure resulting in exfoliation or laminar peeling off the coating. Adjustment of the thermal spray parameters to reduce the electrochemical unevenness or sealing the pores can improve the corrosion resistance of the coating.

Hastelloy C coatings can offer corrosion protection in many aggressive environments. Similar to many other coatings aimed for corrosion resistance, the key question is whether the through porosity of
the coating in spraying can be controlled. Kawakita et al. [57] used quantitative analyses of dissolved substances derived from coated steel during immersion in HCl solution to evaluate the quality of Hastelloy C high-velocity oxyfuel (HVOF) sprayed coatings. This technique enables the detection of even small amounts of through-pores and separately calculates both coating through porosity and corrosion resistance. For Hastelloy C coatings, the number of pores extending through the coating was found to depend on the coating thickness and on the coating’s stacking structure.

Electrochemical behavior of various HVOF-sprayed corrosion resistant coatings in acidic medium has been made by [58]. A total of eight different chromium-containing coatings with varying proportions of alloying elements (Ni, Mo, Si, Fe, Co, W, B and C) aiming for a corrosion behavior comparable to that of stainless steel AISI 316 were studied and compared with that of bulk AISI 316. The results indicate that HVOF-sprayed AISI 316 coating offers a lower corrosion resistance compared to bulk AISI 316 while high nickel- and chromium-containing coatings appear to offer a corrosion resistance comparable to bulk AISI 316. In addition, other alloying elements like molybdenum were proposed to be essential for obtaining higher corrosion protection. In extension of this study Chidambarama et al. [59] confirmed that HVOF sprayed nickel-chromium alloy coatings containing molybdenum were confirmed to exhibit corrosion resistance comparable to bulk AISI 316.

Hard chromium displacement by HVOF coatings has been a long-standing goal for spray industry and, consequently, there are several studies made on the corrosion resistance of HVOF coatings in comparison with hard chromium e.g., [60-65]. According to the studies, several HVOF coatings offer potential for replacing hard chrome at least from the corrosion point of view. For example according to Guilemany et al. [66] polarization curves of Cr$_3$C$_2$-NiCr recorded after immersion tests showed a lower current and higher corrosion potential for Cr$_3$C$_2$-NiCr coating than several other samples studied including hard chromium coatings.

High temperature corrosion resistance of HVOF coatings has also been studied intensively. For example Cr$_3$C$_2$-NiCr, NiCrBSi, Stellite-6 and Ni-20Cr are coatings of particular interest [e.g., 67]. The high temperature corrosion resistance of the coatings may generally be attributed to the formation of oxides and spinels of nickel, chromium or cobalt on the surface of the coating. The high temperature corrosion resistance of all the coatings was found superior to bare nickel-based superalloy. In the presence of Na$_2$SO$_4$-V$_2$O$_5$ salt deposits NiCr coating was found to be most protective followed by Cr$_2$C$_3$-NiCr coating. WC-Co coating was least effective to protect the substrate steel [68]. It was concluded that the formation of Cr$_2$O$_3$, NiO, NiCr$_2$O$_4$, and CoO may contribute to the development of high temperature corrosion resistance in the coatings. In cyclic oxidation [68] NiCrBSi coating was also found to be very effective in decreasing the corrosion rate in the Na$_2$SO$_4$-60% V$_2$O$_5$ molten salt environment at 900°C. The high temperature corrosion resistance imparted by NiCrBSi coatings was attributed to the formation of oxides of silicon, chromium, nickel and spinels of nickel and chromium.

4.3. Nanocrystalline Powders and Coatings

During the last ten years considerable efforts have been made to develop thermally sprayed coatings having structural elements in the submicron or nanometer scale. Although the rapid cooling of melted particles during the coating deposition produces very fine structures—typical grain sizes being in submicron scale or even amorphous—the unmolten particle, e.g., carbides in cermets can controllably
be reduced in size only in powder processing. Because of the large influence of carbide size to the properties of cermets, this has prompted large efforts in producing powders having carbides in submicron and nanometer dimensions. Also, toughening of ceramic coating by nanosized metallic particles has aroused considerable interest and resulted in development of powders with nanosized metal particles. Finally, nanostructural powders produced by spray-drying and sintering offer several advantages via their melting behavior. It goes without saying that in order to take advantage of these powder technologies, optimization of the spraying process is a must.

The dissolution phenomenon of the carbides is more emphasized for WC-Co materials having sub-micron or nanosized carbides. Increasing the surface area of the carbides by reducing their size, the control of the spray conditions becomes more critical in order to avoid the overheating of the particles and fully benefit the positive effects from nanosized carbides for properties. For example, McCartney et al. [69] found that the nanocomposite had a poorer wear resistance than the conventional coating under the conditions examined. Wear was dominated by the loss of ductility in the Co-rich binder phase due to its amorphization. The differences in the wear behavior of the coatings could, thus, be explained in terms of differences in powder characteristics, the extent of reaction and decarburization during spraying, and the subsequent development of the microstructure in the coating during splat solidification at high cooling rates. In order to overcome this problem a shift towards the colder HVOF processes has taken place. For example in CJS HVOF process the process conditions can be adjusted more suitable for the deposition of nano or sub-micron sized carbides. In Figure 2 the relative difference in the particle temperature for the DJ Hybrid and CJS processes is demonstrated with some measurement points and from that the process window is estimated. The particle velocity and temperature measurements have been carried out for the same powder for both processes in order to demonstrate the difference. The process conditions effect on the carbide dissolution so that there is no W2C formation in the coating sprayed with CJS. Powder size used for the CJS process was 5–25 micron and that for the DJ Hybrid process 15–36 micron.

Turunen et al. [7] studied the spraying of nanostructured Al2O3 and Al2O3-Ni HVOF powders and properties of coatings deposited thereof. It was found that by optimizing spray parameters high quality coatings with improved properties are obtained. Introduction of nanopowders to the coating process improved the hardness and wear resistance of the pure Al2O3-coating. Introduction of nickel alloying decreased the hardness and wear resistance of the coatings, but increased the toughness of the coatings via introduction of small nickel particles into alumina matrix and between the alumina splats. Addition of a small amount of nickel into alumina can thus be used to markedly modify the properties of the coating.

5. Applications of HVOF Coatings

Due to the excellent characteristics of HVOF coatings as mentioned in the previous chapter, there is a large variety of suitable materials, different HVOF sub-processes, such as CJS, and hence the possibility to tailor coatings for a large variety of applications; therefore, the use of HVOF is broad among several industries, and is increasing all the time. Examples of application areas include process industry, where the coatings are applied to ball and gate valves; pulp and paper industry with coatings to rolls and blades; aerospace industry, where coatings are used for turbine vanes as bond coats for
thermal barrier coatings, turbine sections, landing gears; and automotive industry, which applications include piston rings and cylinder bores [16]. Even some ceramic coatings, which have been previously sprayed by plasma process, are sometimes applied by HVOF spray method. Also raw materials with small-scale component, e.g., nanosized carbides, have enhanced the HVOF coating properties and potential applications as well. In the following, examples of HVOF coating applications and materials are briefly presented.

Typical HVOF coating materials are metals and cermets. Variety of materials is almost endless, and therefore the application areas are wide among different industries. At a very low porosity, below 1 %, HVOF coatings are suitable for protecting the substrate material against corrosion. Because of high hardness combined with high bond strength to the substrate and good inter-lamellar bonding, the use of HVOF coatings is extensive for wear protection applications, such as paper and pulp processing rolls and other wear-resistant parts in paper machines. Increased use of ceramics, and their dielectrical and thermal properties, has opened the door for HVOF coating use in electrical applications and as environmental barrier coatings (EBCs) in power and aerospace industry.

Applications, where coatings are used for protection from wear and friction, are very broad with HVOF technique. HVOF hardmetal coatings containing carbides and/or nitrides, such as WC-CoCr, WC-(W,Cr)2C-Ni, and (Ti,Mo)(C,N)-Ni/Co, have very good hardness and tribological properties and hence are suitable for wear protection of machine parts [70]. HVOF sprayed WC-Co/NiCrFeSiB coating with high hardness values and low porosity has been studied for use in coal-fired power plant piping against erosion [71]. Due to brittle nature of the hard metal coating, the applications and conditions must be carefully chosen.

In the energy industry, especially power plant boilers experience both high temperature corrosion and erosion, and HVOF coatings can be applied to protect the tubing in the boilers, especially in the superheater area. HVOF sprayed NiCr and Cr3C2-20NiCr coatings have proven very good high temperature corrosion resistance in biomass fired boiler exposures [72]. NiCrBSi and Stellite-6 coatings tested in coal-fired boilers have shown good hot corrosion resistance [73]. HVOF coatings, such as NiCrSiB and Ni-Cr-Fe-Nb-Mo alloys, for high temperature erosion and corrosion protection have been widely used in waste-to-energy plants in order to [74]. Thermal barrier coatings (TBCs) are used for enhancing the service life of gas turbines and diesel engine components. The ceramic coatings are mainly manufactured with atmospheric plasma spraying (APS) due to high melting temperature of the materials, but the applied bond coats under the APS ceramic coatings to improve adhesion are increasingly made by HVOF technique, bond coat materials being e.g., CoNiCrAlY, NiCoCrAlTaY, NiCrAlY, or NiCr [75].

Different material forming techniques require use of coatings, as the components deteriorate easily in the processes. Deep-drawing is a widely used sheet metal forming process in the aircraft and automotive industries. High tribological demands of the forming tools can be fulfilled with HVOF cermet coatings, such as superfine structured WC-Co, which has high hardness enhancing sliding and abrasive wear [2]. HVOF coatings have been studied for the protection and upgrade of aluminum injection mould tooling, particularly for the low-cost and flexible manufacture of automotive components. Smooth, hard and very well bonded coatings with low porosity and homogeneous microstructure have been manufactured from WC-CoCr, and Cr2C3-NiCr through careful optimization of deposition [76]. Steel sheet continuous hot-dip galvanizing bath with molten metal is a very
detrimental process for the galvanizing components. Three different high temperature corrosion resistant HVOF coating types have been applied to galvanizing bath components. These include WC-Co, oxide-based, and quite recently developed MoB/CoCr coatings [77]. Optimization of the coating composition and microstructure is of utmost importance in order to extend the operating lifetime of the galvanizing hardware. Also bond coats may be used because of the mismatch between coating and substrate material. HVOF WC-CoCr cermet coatings on aluminum substrate could be used for plastic injection moulds due to high hardness, low sliding wear, low porosity, and good endurance against impacts [78]. MoCoB-Co/Cr cermet coating could be used for protection of glass sheet forming moulds because it has excellent high temperature properties, such as low friction coefficient to glass, oxidation resistance, and low mechanical abrasion [79].

Hard chromium plating has been an excellent and very widely used technique, but due to carcinogenic effect of hexavalent chrome ion (Cr$^{6+}$) in the manufacturing process, finding substituting solutions for the technique has been extensively studied during the last decade and possibilities of thermal spray coatings have been explored as replacer. HVOF Co-base alloy Tribaloy-800 coating has shown good friction and wear properties also in high temperature (500 °C) [1]. Due to good durability of the coating, it could be used for the protection of machine components vulnerable to frictional heat and wear, e.g., sliding surfaces such as high-speed spindle. To replace hard chromium coatings in applications under erosion-corrosion exposure, both HVOF sprayed WC-Ni and Cr$_3$C$_2$-NiCr have been tested to be promising alternatives for those conditions [80]. Cr$_3$C$_2$-NiCr HVOF coatings manufactured from fine-scale and nano-fractioned powders have proved to have very good mechanical, wear and corrosion properties, and could therefore be used as substitute to hard chromium coating in applications such as cylinders in earth moving machines and piston rings and valve stems applications in automotive industry [81,82]. HVOF coatings can be applied to landing gears in aircrafts to replace the hard chromium coatings. The HVOF process provides high hardness, good wear strength and better resistance to fatigue with WC-CrC-Ni coating compared to hard chromium coating [83].

Other versatile applications for HVOF coating include magnetic and biomedical use. HVOF sprayed ferromagnetic Fe-Si based deposits, which have been produced from nanostructured powder, can be used in several magnetic applications even at high temperatures [84]. HVOF hydroxyapatite (HAp) coatings are applied in various biomedical applications due to excellent biocompatibility of HAp [85]. Use of nanostructured Hap has been studied for biomedical use and the results are promising, as the coating exhibits high density and crystallinity, and good microstructural uniformity [86]. In the biomedical field, HVOF-sprayed nanostructured titania coatings could be used for prosthetic devices and other applications, where superior mechanical behavior is required [87].

6. Summary and Conclusions

In this work, HVOF thermal spray techniques have been reviewed. HVOF techniques have significantly developed over the last two decades and new modifications and improvements of the technology have been introduced on the market. The latest developments in spray technology also take advantage of the developments that have occurred in powder production, especially in nanostructured powders. However, in order to fully exploit the excellent properties of HVOF coatings, it is emphasized that optimization of the spraying process is a must. As compared to APS coatings, HVOF
Coatings offer a number of advantages in terms of coating microstructure and properties resulting in improved performance in many applications. This holds especially true for metal and cermet coatings. For the deposition of ceramic coating, HVOF process offers improvements of coating quality in spraying of ceramics such as alumina. However, deposition efficiency of HVOF spray is typically lower than that of APS, and may hinder the wider use of the HVOF in many applications despite the clear improvement of properties.

HVOF coatings are nowadays applied in a variety of industries. Major application areas are within industries where coatings are used for protection from wear, friction and corrosion. Other applications for HVOF coatings include, e.g., magnetic and biomedical use.

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References

1. Cho, J.Y.; Zhang, S.H.; Cho, T.Y.; Yoon, J.H.; Joo, Y.K.; Hur, S.K. The processing optimization and property evaluations of HVOF Co-base alloy T800 coating. J. Mater. Sci. 2009, 44, 6348-6355.
2. Tillmann, W.; Vogli, E.; Baumann, I.; Kopp, G.; Weihs, C. Desirability-Based Multi-Criteria Optimization of HVOF Spray Experiments to Manufacture Fine Structured Wear-Resistant 75Cr3C2-25(NiCr20) Coatings. J. Therm. Spray Technol. 2010, 19, 392-408.
3. Mostaghimi, J.; Chandra, S.; Ghafouri-Azar, R.; Dolatabadi, A. Modeling thermal spray coating processes: A powerful tool in design and optimization. Surf. Coat. Technol. 2003 163-164, 1-11.
4. Dongmo, E.; Wenzelburger, M.; Gadow, M. Analysis and optimization of the HVOF process by combined experimental and numerical approaches. Surf. Coat. Technol. 2008, 202, 4470-4478.
5. Bansal, P.; Shipway, P.H.; Leen, S.B. Residual stresses in high-velocity oxy-fuel thermally sprayed coatings—Modelling the effect of particle velocity and temperature during the spraying process. Acta Mater. 2007, 55, 5089-5101.
6. Sampath, S.; Jiang, X.; Kulakarni, A.; Matejicek, J.; Gilmore, D.L.; Neiser, R.A. Development of process maps for plasma spray: Case study for molybdenum. Mater. Sci. Eng. A 2003, 348, 54-66.
7. Turunen, E.; Varis, T.; Gustafsson, T.E.; Keskinen, J.; Fält, T.; Hannula, S.-P. Parameters optimization of HVOF sprayed nanostructured alumina and alumina-nickel composite coatings. Surf. Coat. Technol. 2006, 200, 4987-4994.
8. Vaidya, A.; Srinivasan, V.; Streibl, T.; Friis, M.; Chi, W.; Sampath, S. Process maps for plasma spraying of yttria-stabilized zirconia: An integrated approach to design, optimization and reliability. Mater. Sci. Eng. A 2008, 497, 239-253.
9. Zhang, W.; Sampath, S.A. Universal method for representation of in-flight particle characteristics in thermal spray processes. J. Therm. Spray Technol. 2009, 18, 23-34.
10. Valarezo, A.; Choi, W.B.; Chi, W.; Gouldstone, A.; Sampath, S. Process control and characterization of NiCr coatings by HVOF-DJ2700 system: A process map approach. J. Therm. Spray Technol. 2010, 19, 852-865.
11. Fauchais, P.; Vardelle, M. Sensors in spray processes. J. Therm. Spray Technol. 2010, 19, 668-694.
12. Sampath, S.; Srinivasan, V.; Valarezo, A.; Vaidya, A.; Streibl, T. Sensing, control, and in situ measurement of coating properties: An integrated approach toward establishing process-property correlations. J. Therm. Spray Technol. 2009, 18, 243-255.
13. Handbook of Thermal Spray Technology; Davis, J.R., Ed.; ASM International: Materials Park, OH, USA, 2004; pp. 338.
14. Vaidya, A.; Streibl, T.; Li, L.; Sampath, S.; Kovarik, O.; Greenlaw, R. An integrated study of thermal spray process-structure-property correlations: A case study for plasma sprayed molybdenum coatings. Mater. Sci. Eng. A 2005, 403, 191-204.
15. Turunen, E.; Varis, T.; Hannula, S.-P.; Vaidya, A.; Kulkarni, A.; Gutleber, J.; Sampath, S.; Herman, H. On the role of particle state and deposition procedure on mechanical, tribological and dielectric response of high velocity oxy-fuel sprayed alumina coatings. Mater. Sci. Eng. A 2006, 415, 1-11.
16. Dwivedi, G.; Wentz, T.; Sampath, S.; Nakamura, T. Assessing process and coating reliability through monitoring of process and design relevant coating properties. J. Therm. Spray Technol. 2010, 19, 695-712.
17. Hannula, S.-P.; Suhonen, T.; Varis, T.; Turunen, E. Challenges in processing and characterization of thermal sprayed coatings. In Proceedings of "Product Property Prediction—P3" Conference, Dortmund, Germany, 12–13 April 2010; p. 12.
18. Vaidya, A.; Bancke, G.; Sampath, S.; Herman, H. Influence of process variables on the plasma sprayed coatings—An integrated study. In Proceedings of International Thermal Spray Conference, Singapore, Singapore, 28–30 May 2001; pp. 1345-1349.
19. Matejicek, J.; Sampath, S. In-situ measurements of residual stresses and elastic moduli in thermal sprayed coatings: Part 1: Apparatus and analysis. Acta Mater. 2003, 51, 863-872.
20. Fisher-Cripps, A.C. Nanoindentation, 2nd edition, Mechanical Engineering Series; Springer: New York, NY, USA, 2004, p.263.
21. EN ISO 4516:2002. Metallic and other inorganic coatings. In Vickers and Knoop Microhardness Tests?; European Committee for Standardization: City, Country 2002.
22. Suhonen, T.; Varis, T.; Turunen, E.; Liu, X.; Yanling, G.; Söderberg, O.; Hannula, S.-P. Modelling the effect of microstructure on mechanical properties of HVOF sprayed WC-CoCr coatings. In Proceedings of WMRIF Workshop for Young Scientists, Tsukuba, Japan, 22–25 July 2008.
23. ASTM E 1876-09. Standard Test Method for Dynamic Young’s Modulus, Shear Modulus, and Poisson's Ratio by Impulse Excitation of Vibration. American Society for Testing and Materials: West Conshohocken, PA, USA, 2009.
24. ENV 843-2:1997. Advanced Technical Ceramics—Monolithic Ceramics, Mechanical Properties at Room Temperature—Part 2: Determination of Elastic Moduli. European Committee for Standardization: City, Country1997.
25. Oliver, W.C.; Pharr, G.M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J. Mater. Res. 1992, 7, 1564-1583.
26. Griffith, A.A. The phenomena of rupture and flow in solids. Phil. Trans. Roy. Soc. London A 1920, 221, 163-198 (This article has been republished with additional commentary in Trans. ASM 61, 871, 1968).

27. JIS R 1688:2005. Testing Method for Fracture Toughness of Porous Fine Ceramics; Japanese Standards Association: Tokyo, Japan, 2005.

28. Deshpande, S.; Kulkarni, A.; Sampath, S.; Herman, H. Application of image analysis for characterization of porosity in thermal spray coatings and correlation with small angle neutron scattering. Surf. Coat. Technol. 2004, 187, 6-16.

29. Fowler, D.B.; Riggs, W.; Russ, J.C. Inspecting thermal sprayed coatings. Adv. Mater. Proc. 1990, 11, 41-52.

30. Komatsu, M.; Kuroda, S.; Sodeoka, S.; Sakoda, N.; Lee, S.W. Porosity measurement of thermal sprayed ceramic coatings by SEM cross sectional photography and image analysis—Round Robin test for ISO standardization. In Proceedings of Asian Thermal Spray Conference, Xi’an, China, 22–24 October 2009.

31. Mailhot, K.; Gitzhofer, F.; Boulos, M.I. Absolute coating porosity measurement using image analysis. In Proceedings of the 15th ITSC, Nice, France, 1998; Volume 1, pp. 917-922.

32. Final Report. Aircraft Accident Investigation of Copterline Oy, Sikorsky S-76C+ in Tallinn Bay, Estonia on 10th August 2005. Ministry of Economic Affairs and Communications, Estonia. 6 August 2008. Retrieved 11 August 2008.

33. EN 582:1993. Determination of Tensile Adhesive Strength; European Committee for Standardization: City, country 1993.

34. Marot, G.; Lesage, J.; Démaréaux, P.H.; Hadad, M.; Siegmann, St.; Staia, M.H. Interfacial indentation and shear tests to determine the adhesion of thermal spray coatings. Surf. Coat. Technol. 2006, 201, 2080-2085.

35. Noyan, I.C.; Cohen, J.B. Residual Stress—Measurement by Diffraction and Interpretation; Springer-Verlag: New York, NY, USA, 1987; p. 626.

36. Pina, J.; Dias, A.; Lebrun, J.L. Mechanical stiffness of thermally sprayed coatings and elastic constants for stress evaluation by X-ray diffraction. Mater. Sci. Eng. A 1999, 267, 130-144.

37. Matejicek, J.; Sampath, S. In-situ measurements of residual stresses and elastic moduli in thermal sprayed coatings: Part 1: Apparatus and analysis, Acta Mater. 2003, 51, 863-872.

38. ASTM G75-95. Standard Test Method for Determination of Slurry Abrasivity (Miller Number) and Slurry Abrasion Response of Materials (SAR Number); American Society for Testing and Materials: West Conshohocken, PA, USA, 1995.

39. Verdon, C.; Karimi, A.; Martin, J.-L. A study of high velocity oxy-fuel thermally sprayed tungsten carbide based coatings. Part 1: Microstructures. Mater. Sci. Eng. A 1998, 246, 11-24.

40. Stewart, D.A.; Shipway, P.H.; McCartney, D.G. Influence of heat treatment on the abrasive wear behavior of HVOF sprayed WC-Co coatings. Surf. Coat. Technol. 1998, 105, 13-24.

41. Li, X.M.; Yang, Y.Y.; Shao, T.M.; Jin, Y.S.; Barbezat, G. Impact wear performances of Cr3C2—NiCr coatings by plasma and HVOF spraying. Wear 1997, 202, 208-214.

42. Jones, M.; Horlock, A.J.; Shipway, P.H.; McCartney D.G.; Wood, J.V. A comparison of the abrasive wear behaviour of HVOF sprayed titanium carbide and titanium boride-based cermet coatings, Wear 2001, 251, 1009-1016.
43. Horlock, A.J.; McCartney, D.G.; Shipway, P.H.; Wood, J.V. Thermally sprayed Ni(Cr)-TiB2 coatings using powder produced by self-propagation high temperature synthesis: Microstructure and abrasive wear behaviour, Mater. Sci. Eng. A 2002, 336, 88-98.
44. Wang, B.-Q. The dependence of erosion—Corrosion wastage on carbide/metal binder proportion for HVOF carbide-metal cermet coatings, Wear 1996, 196,141-146.
45. Hawthorne, H.M.; Arsenault, B.; Immarigeon, J.P.; Legoux, J.G.; Parameswaran, V.R. Comparison of slurry and dry erosion behaviour of some HVOF thermal sprayed coatings, Wear 1999, 225-229, 825-834.
46. Mann, B.S.; Arya, V. Abrasive and erosive wear characteristics of plasma nitriding and HVOF coatings: Their application in hydro turbines. Wear 2001, 249, 354-360.
47. Berget, J.; Rogne, T.; Bardal, E. Erosion-corrosion properties of different WC-Co-Cr coatings deposited by the HVOF process—Influence of metallic matrix composition and spray powder size distribution. Surf. Coat. Technol. 2007, 201, 7619-7625.
48. Zhou, Z.; Wang, L.; Wang, F.C.; Zhang, H.F.; Liu, Y.B.; Xu, S.H. Formation and corrosion behavior of Fe-based amorphous metallic coatings by HVOF thermal spraying, Surf. Coat. Technol. 2009, 204, 563-570.
49. Lima, R.S.; Marple, B.R. From APS to HVOF spraying of conventional and nanostructured titania feedstock powders: A study on the enhancement of the mechanical properties, Surf. Coat. Technol. 2006, 200, 3428-3437.
50. Turunen, E.; Varis, T.; Gustafsson, T.; Keskinen, J.; Lintunen, P.; Fält, T.; Nowak, R.; Hannula, S.-P. Process optimization for nanostructured HVOF-sprayed Al2O3-based ceramic coatings, Key. Eng. Mater. 2006, 317-318, 545-554.
51. Turunen, E.; Varis, T.; Keskinen, J.; Fält, T.; Hannula, S.-P. Improved mechanical properties by nanoreinforced ceramic composite HVOF coatings, Adv. Sci. Technol. 2006, 45, 1240-1245.
52. Turunen, E.; Hirvonen, A.; Varis, T.; Fält, T.; Hannula, S.-P.; Sekino, T.; Niihara K. Application of HVOF techniques for spraying of ceramic coatings. Adv. Technol. Mater. 2007, 9, 63-68.
53. Bolelli, G.; Lusvarghi, L.; Manfredini, T.; Mantini, P.F.; Polini, R.; Turunen, E.; Varis, T.; Hannula, S.-P. Comparison between plasma- and HVOF-sprayed ceramic coatings. Part I: Microstructure and mechanical properties. Int. J. Surf. Sci. Eng. 2007, 1, 38-61.
54. Brandl, W.; Toma, D.; Krüger, J.; Grabke, H.J.; Matthäus, G. The oxidation behaviour of HVOF thermal-sprayed MCrAlY coatings. Surf. Coat. Technol. 1997, 93-95, 21-26.
55. Gil, L.; Staia, M.H. Influence of HVOF parameters on the corrosion resistance of NiWCrBSi coatings. Thin Solid Films 2002, 420-421, 446-454.
56. Zhao, W.-M.; Wang, Y.; Dong, L.-X.; Wu, K.-Y.; Xue, J. Corrosion mechanism of NiCrBSi coatings deposited by HVOF. Surf. Coat. Technol. 2005, 190, 293-298.
57. Kawakita, J.; Kuroda, S.; Kodama, T. Evaluation of through-porosity of HVOF sprayed coating. Surf. Coat. Technol. 2003, 166, 17-23.
58. Chidambarama, D.; Clayton, C.; Dorfman, M. Evaluation of the electrochemical behavior of HVOF-sprayed alloy coatings. Surf. Coat. Technol. 2004, 176, 307-317.
59. Chidambarama, D.; Claytona, C.R.; Dorfman, M.R. Evaluation of the electrochemical behavior of HVOF-sprayed alloy coatings—II. Surf. Coat. Technol. 2005, 192, 278-283.
60. Rastegar, F.; Richardson, D.E. Alternative to chrome: HVOF cermet coatings for high horse power diesel engines. Surf. Coat. Technol. 1997, 90, 156-163.

61. Nascimento, M.P.; Souza, R.C.; Miguel, I.M.; Pigatin, W.L.; Voorwald, H.J.C. Effects of tungsten carbide thermal spray coating by HP/HVOF and hard chromium electroplating on AISI 4340 high strength steel. Surf. Coat. Technol. 2001, 138, 113-124.

62. Sahraoui, T.; Fenineche, N.-E.; Montavon, G.; Coddet, C. Alternative to chromium: Characteristics and wear behavior of HVOF coatings for gas turbine shafts repair (heavy-duty), J. Mater. Processing Technol. 2004, 152, 43-55.

63. Guilemany, J.M.; Espallargas, N.; Suegama, R.C.; Benedetti, A.V. Comparative study of Cr3C2-NiCr coatings obtained by HVOF and hard chromium coatings. Corros. Sci. 2006, 48, 2998-3001.

64. Bolelli, G.; Cannillo, V.; Lusvarghi, L.; Ricco, S. Mechanical and tribological properties of electrolytic hard chrome and HVOF-sprayed coatings. Surf. Coat. Technol. 2006, 200, 2995-3009.

65. Bolelli, G.; Lusvarghi, L.; Manfredini, T.; Mantini, P.F.; Turunen, E.; Varis, T.; Hannula, S.-P. Comparison between plasma- and HVOF-sprayed ceramic coatings. Part II: Tribological behaviour. Int. J. Surf. Sci. Engin. 2007, 1, 62-79.

66. Guilemany, J.M.; Espallargas, N.; Suegama, P.H.; Benedetti, A.V. Comparative study of Cr3C2-NiCr coatings obtained by HVOF and hard chromium coatings. Corros. Sci. 2006, 48, 2998-3013.

67. Sidhu, T.S.; Prakash, S.; Agrawal, R.D. Evaluation of hot corrosion resistance of HVOF coatings on a Ni-based superalloy in molten salt environment, Mater. Sci. Eng. A 2006, 430, 64-78.

68. Sidhu, H.S.; Sidhu, B.S.; Prakash, S. The role of HVOF coatings in improving hot corrosion resistance of ASTM-SA210 GrA1 steel in the presence of Na2SO4-V2O5 salt deposits. Surf. Coat. Technol. 2006, 200, 5386-5394.

69. Stewart, D.A.; Shipway, P.H.; McCartney, D.G. Abrasive wear behaviour of conventional and nanocomposite HVOF-sprayed WC-Co coatings. Wear 1999, 225-229, 789-798.

70. Berger, L.M.; Woydt, M.; Saaro, S. Comparison of self-mated hardmetal coatings under dry sliding conditions up to 600 °C. Wear 2009, 266, 406-416.

71. Ramesh, M.R.; Prakash, S.; Nath, S.K.; Sapra, P.K.; Venkataraman, B. Solid particle erosion of HVOF sprayed WC-Co/NiCrFeSiB coatings. Wear 2010, 269, 197-205.

72. Oksa, M.; Kärki, J.; Varis, T.; Turunen, E. Corrosion resistance of HVOF coatings in a biofuel boiler plant. In Proceedings of EUCORR 2005 The European Corrosion Congress, Lissabon, Country, 4–8 September 2005; p. 9.

73. Sidhu, T.S.; Prakash, S.; Agrawal, R.D. Studies of the metallurgical and mechanical properties of high velocity oxy-fuel sprayed stellite—6 coatings on Ni- and Fe-based superalloys. Surf. Coat. Technol. 2006, 201, 273-281.

74. Kawahara, Y. Application of high temperature corrosion-resistant materials and coatings under severe corrosive environment in waste-to-energy boilers. J. Therm. Spray Technol. 2007, 16, 202-213.

75. Lima, C.R.C.; Guilemany, J.M. Adhesion improvements of thermal barrier coatings with HVOF thermally sprayed bond coats. Surf. Coat. Technol. 2007, 201, 4694-4701.

76. Gibbons, G.J.; Hansell, R.G. Thermal-sprayed coatings on aluminium for mould tool protection and upgrade. J. Mater. Process. Technol. 2008, 204, 184-191.
77. Matthews, S.; James, B. Review of thermal spray coating applications in the steel industry: Part 2—Zinc pot hardware in the continuous galvanizing line. J. Therm. Spray Technol. 2010, 19, 1277-1286.

78. Bolelli, G.; Lusvarghi, L.; Barletta, M. HVOF-sprayed WC-CoCr coatings on Al alloy: Effect of the coating thickness on the tribological properties. Wear 2009, 267, 944-953.

79. Hamashima, K. Application of new boride cermet coating to forming of glass sheets. J. Therm. Spray Technol. 2007, 16, 32-33.

80. Espallargas, N.; Berget, J.; Guilemany, J.M.; Benedetti, A.V.; Suegama, P.H. Cr3C2-NiCr and WC-Ni thermal spray coatings as alternatives to hard chromium for erosion-corrosion resistance. Surf. Coat. Technol. 2008, 202, 1405-1417.

81. Fedrizzi, L.; Rossi, S.; Cristel, R.; Bonora, P.L. Corrosion and wear behaviour of HVOF cermet coatings used to replace hard chromium. Electrochim. Acta 2004, 49, 2803-2814.

82. Picas, J.A.; Fornard, A.; Matthäus, G. HVOF coatings as an alternative to hard chrome for pistons and valves. Wear 2006, 261, 477-484.

83. Bonora, R.G.; Voorwald, H.J.C.; Cioffi, M.O.H.; Junior, G.S.; Santos, L.F.V. Fatigue in AISI 4340 steel thermal spray coating by HVOF for aeronautic application. Procedia Engin. 2010, 2, 1617-1623.

84. Cherigui, M.; Fenineche, N.E.; Ji, G.; Grosdidier, T.; Coddet C. Microstructure and magnetic properties of Fe-Si-based coatings produced by HVOF thermal spraying process. J. Alloys Compd. 2007, 427, 281-290.

85. Gadow, R.; Killinger, A.; Stiegler, N. Hydroxyapatite coatings for biomedical applications deposited by different thermal spray techniques. Surf. Coat. Technol. 2010, 205, 1157-1164.

86. Lima, R.S.; Khor, K.A.; Li, H.; Cheang, P.; Marple, B.R. HVOF spraying of nanostructured hydroxyapatite for biomedical applications. Mater. Sci. Eng. A 2005, 396, 181-187.

87. Gaona, M.; Lima, R.S.; Marple, B.R. Influence of particle temperature and velocity on the microstructure and mechanical behaviour of high velocity oxy-fuel (HVOF)-sprayed nanostructured titania coatings. J. Mater. Process. Technol. 2008, 198, 426-435.

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