

Ceramic Coatings by Thermal Spraying – a Comparison between High Velocity Oxy-Fuel and Atmospheric Plasma Spraying

Metals, plastics and ceramics each have particular properties, which make them suitable for different applications. Density, thermal and electrical conductivity, thermal expansion, hardness, Young's modulus, optical properties, melting point, chemical stability, manufacturing cost and environment-friendliness are only some of the aspects which must be considered in the selection of a material class for a given application. Despite the development of a great number of new materials, a single material may not fulfil all the requirements of the intended application. In many cases, simply the modification of the surface of the structural material by means of a coating is sufficient to improve an existing application or to enable new ones.

A common combination is the application of a ceramic coating onto a metallic substrate. Due to their high brittleness and hardness, even at high temperatures, ceramics are in many cases unsuitable as structural materials. Moreover, shaping of complex 3D-parts from ceramics is challenging and the manufacturing costs are generally higher than for metals. However, ceramics provide the benefits of higher corrosion and wear resistance, higher hardness and a lower thermal and electrical conductivity. By the application of a ceramic coating onto a metallic substrate, 3D-parts can be manufactured with the structural properties of a metal and the surface properties

Keywords

ceramic coatings, thermal spraying, high velocity oxy-fuel, atmospheric plasma spraying, feedstock, metallic substrate, wear protection

of a ceramic. Fig. 1 presents examples of ceramic-coated metal parts for engineering applications.

Thermal spraying is a group of coating techniques based on the melting of a solid feedstock, which is then accelerated towards a substrate onto which it re-solidifies, hence forming thick coatings with a lamellar structure, composed of individual splats – flattened, re-solidified droplets. In techniques such as Flame Spraying (FS), High Velocity Oxy-Fuel (HVOF), High Velocity Air-Fuel (HVOF) and Detonation Spraying (DS), the thermal energy required to melt the feedstock originates from the combustion of a mixture of oxygen – or air in the case of HVOF – with a combustible gas or a liquid fuel. Other techniques, such as wire arc spraying (only suitable for metallic coatings) and plasma spraying, make use of an electric arc as an energy source.

While thermal energy is necessary for the melting of the feedstock, kinetic energy is required to accelerate the molten particles towards the substrate with sufficient velocity to obtain an adherent coating with a suitable density for the intended application. The higher the particle temperature becomes, the lower the viscosity upon impact, facilitating spreading of the molten material. In contrast, a high impact velocity with an insufficient temperature could lead to erosion of the substrate, due to the impact of unmelted particles. However, these

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Fig. 1
Examples of ceramic-coated metal parts coated at Rauschert

two parameters are also competing to some extent. A higher particle velocity leads to a shorter residence time in the hot zone of the flame or plasma plume, reducing the particle temperature, and vice versa.

Among all the thermal spraying techniques, the most commonly used method for the deposition of ceramic coatings today is the Atmospheric Plasma Spraying (APS) technique. Due to very high particle velocities, Detonation Spraying (DS) was, for many years, the method of choice to obtain dense ceramic coatings. However, because of market strategy and proprietary rights, DS equipment is not easily available; and only a small number of companies are able to manufacture such coatings. Alternatively, HVOF has been gaining importance as a method to obtain dense ceramic coatings.

Atmospheric Plasma Spraying (APS)

In a typical plasma spraying torch, a cathode is positioned axially to the nozzle, which acts as the anode. Upon the application of an electric potential, an arc forms, leading to the dissociation and ionization of the gas streaming between cathode and anode, generating a plasma. As the ionized gases leave the nozzle, the ions recombine to reform the original gas molecules, liberating an abundance of heat, reaching temperatures above 10 000 K. Plasma spraying processes can be classified according to the atmosphere in which the spray process takes place. VPS (Vacuum Plasma Spraying) and LPPS (Low Pressure Plasma Spraying) are carried out in a chamber under reduced pressure, whereas APS is carried out under atmospheric pressure in natural air [1].

The most common plasma gases are argon, hydrogen, nitrogen and helium. To

obtain ideal conditions, the plasma gas is usually a binary or even ternary mixture of these gases. Despite the use of oxygen-free gases, oxygen from the surrounding air can oxidize the particles before they cool down. Consequently, oxide-free coatings can only be obtained under a controlled atmosphere, such as an inert gas or a vacuum.

Because of the oxidation and decomposition, at extremely high temperatures, of some feedstocks containing metals and carbides, APS is mostly used to deposit oxide ceramic coatings. The high plasma temperatures ensure a complete melting of the feedstock, even with high feed rates, yielding a high productivity. Coatings with porosity values down to 2 % can be achieved. However, metal and carbide-based coatings for less demanding applications are also frequently deposited by APS using suitable parameters and gas combinations.

High Velocity Oxy-Fuel (HVOF)

In High Velocity Oxy-Fuel (HVOF), a combustible substance is mixed with oxygen and ignited – hence the name oxy-fuel. Typical fuels for HVOF are either gases, such as propane, ethylene or hydrogen, or a liquid, such as kerosene.

One of the main applications of thermal spraying has always been coatings for wear protection, for which high density, hardness and excellent adhesion, in addition to a smooth surface, are crucial properties. These characteristics can be achieved by increasing the particle velocity during spraying. The higher the velocity upon impact, the greater the compaction of coatings. While the thermal contribution is dominant in APS; HVOF is oriented towards high kinetic energy levels. Owing to a con-

vergent-divergent nozzle design, the thermal energy and pressure in the combustion chamber are converted to kinetic energy, yielding supersonic particle velocities.

The maximum gas temperature in HVOF is limited by the flame temperature of the fuel/oxygen mixture, which ranges between 2500–3000 °C, depending on the fuel type and the fuel-to-oxygen ratio. To provide sufficient thermal energy to the feedstock, particles are injected axially inside the burner (i.e. before the nozzle), or in some cases radially into the nozzle. Since the axial injection takes place much closer to the combustion chamber, where the combustion gases are the hottest, this design is especially suited to feedstocks with high melting temperatures, such as ceramics.

The development of HVOF burners has been mainly oriented towards metal and carbide-based coatings. Hence, during recent years, the design of HVOF burners has been optimized to achieve the highest particle velocity possible with reduced temperatures, to avoid phase transformations and oxidation of the feedstock. Recently, interest in HVOF as a method for the manufacturing of ceramic coatings has increased, especially for more challenging applications, such as wear protection and electrical insulation.

Comparative studies

One important difference between APS and HVOF is the type and amount of feedstock used. Due to the higher gas temperatures, feedstocks with larger particle size and/or feed rate can be used in APS without quality loss. HVOF requires finer powders and lower feed rates to ensure complete melting of the particles. Therefore, during the same processing time, APS can yield

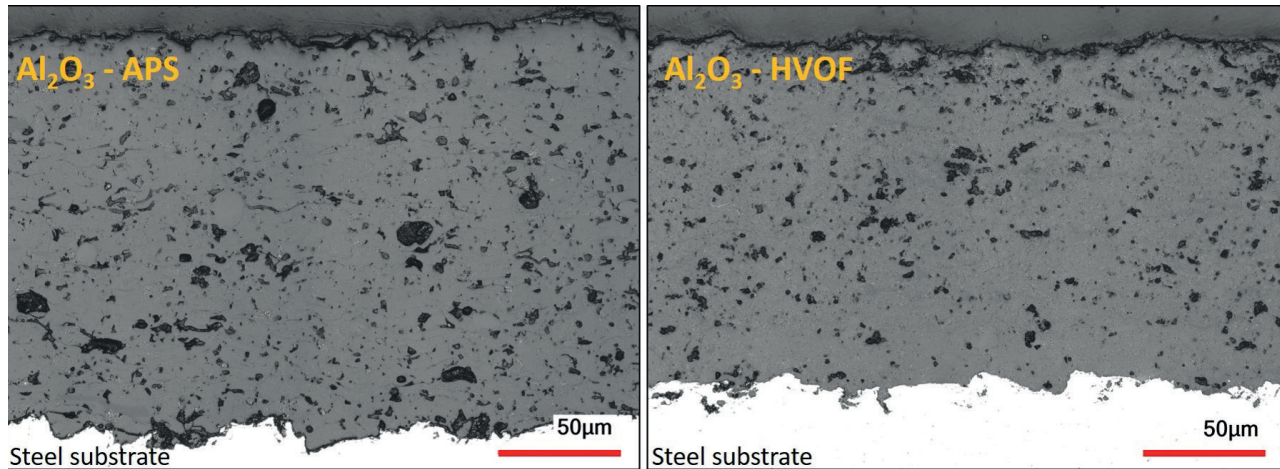


Fig. 2 Comparison of the microstructure of APS- and HVOF-sprayed Al_2O_3 coatings from Rauschert

thicker coatings than HVOF. Moreover, the part cooling requirements during spraying are usually higher for HVOF.

Another important aspect to be considered is the processing cost. Fauchais et al. [1] presented an economic analysis of different thermal spraying processes. APS has an economic advantage, since the prices for gases required for HVOF, such as ethylene, hydrogen and nitrogen used in APS. Moreover, the specific energy requirement (i.e. the amount of power necessary to deposit a given mass of coating), is considerably higher for HVOF than for APS. Thus, from an economic point of view, the APS process is

a more viable technique. However, for applications requiring high hardness, density, adhesion and smooth surfaces, HVOF coatings stand out due to their technical advantages.

Fig. 2 presents examples of APS and HVOF Al_2O_3 coatings sprayed at Rauschert with the same feedstock. The micrographs exemplify the typical microstructural differences of coatings deposited with both processes. A higher number of larger sized pores and interlamellar (between splats) porosity and cracking characterize the microstructure of APS coatings. On the other hand, the porosity of HVOF coatings is composed of smaller pores, due to the higher

particle velocity upon impact, which also reduces the surface roughness of the as-sprayed coatings (Fig. 3).

Typically, roughness values of as-sprayed Al_2O_3 APS coatings are in the range of $R_a = 3-4 \mu m$ and $R_z = 22-23 \mu m$, and as-sprayed Al_2O_3 HVOF coatings have $R_a = 2-3 \mu m$ and $R_z = 14-17 \mu m$. However, the higher speed upon impact increases the residual stresses in the HVOF coatings. A careful tuning of the process parameters is required to obtain well adherent, crack-free coatings.

The differences in the microstructures of APS and HVOF coatings also reflect on the surface properties after finish-

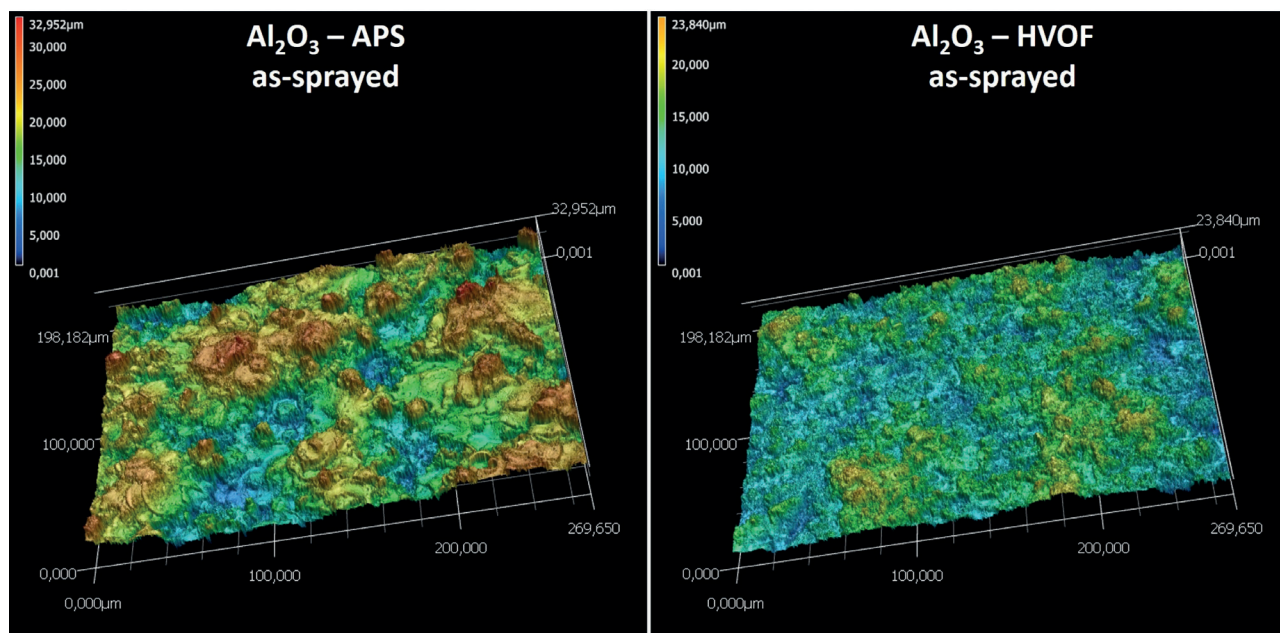


Fig. 3 Topography profile of as-sprayed APS and HVOF Al_2O_3 coatings from Rauschert

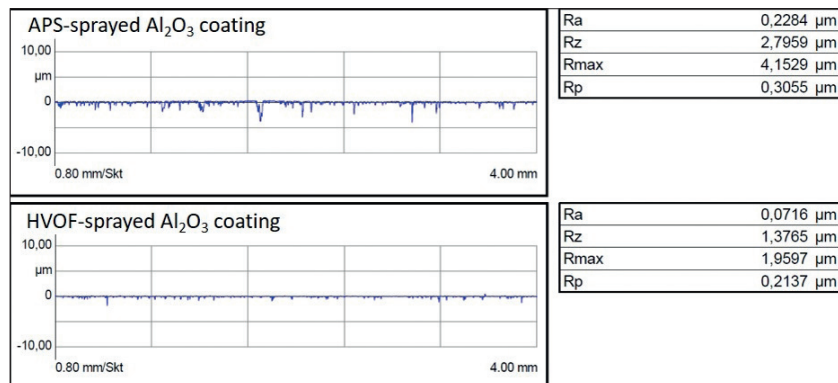


Fig. 4 Comparison of the surface roughness of APS- and HVOF-sprayed Al₂O₃ coatings from Rauschert after finishing

ing. Fig. 4 shows the surface profile and the roughness values of APS and HVOF-sprayed Al₂O₃ coatings after the same finishing process. As evidenced by the surface topography, the surface roughness is a consequence of coating porosity, which results in cavities in the surface after the finishing process. Thus, the denser microstructure of the HVOF coatings leads to a lower surface roughness after finishing.

It should be borne in mind, however, that a comparison between different thermal spraying processes is difficult, due to the large number of factors influencing the coating's characteristics. A thorough optimization of the APS process with a suitable torch could lead to a similar microstructure to the one obtained by HVOF. This, however, would probably lead to increased processing costs, to the point where HVOF becomes a more interesting option. The images presented herein refer to the microstructures of typical industrial coatings, which were developed considering both technical and economic aspects. Although different industrial applications of HVOF ceramic coatings are known, the number of academic studies comparing APS and HVOF coatings is limited.

Lima and Marple [2] compared the properties of APS and HVOF coatings from TiO₂ feedstocks. Despite cooling with air jets, the substrate temperatures increased to approx. 150 °C during APS and 270 °C during HVOF. As expected, the average particle temperature, measured in flight, was higher in APS (2718 °C) than that in HVOF (1811 °C), whereas the average particle speed was over twice as high in HVOF than in APS – 751 m·s⁻¹ against 302 m·s⁻¹. The higher particle speed in HVOF resulted in a

higher level of compressive stresses in the coatings.

The higher particle temperatures and the reducing characteristic of the plasma gas used in APS caused a loss of oxygen from TiO₂, resulting in the formation of suboxides. The porosity of the APS coatings was around 2,5 % and below 1 % for those of the HVOF counterparts. This reduced porosity of the HVOF coatings contributed to a significant improvement in performance during abrasion tests – the material loss was about 40 % lower for the HVOF coating than that of the APS.

Interestingly, no significant difference in coating hardness was measured – all coatings had a hardness of about 850 HV 0,3. However, the crack propagation resistance was about 13 % higher in HVOF coatings than in those of APS.

Killakoski et al. [3] investigated the properties of Al₂O₃-ZrO₂ coatings with approximately 40 % ZrO₂ sprayed by APS and HVOF. APS Coatings had a porosity of around 2 % against values down to 0,88 % for those of HVOF. The highest hardness values were measured for the HVOF coating, 917 HV 0,3 against approx. 800 VH 0,3 for the APS coating. However, APS coatings produced slightly higher values of critical flexural strength and strain tolerance, attributed to the coarser particle size and the less dense microstructure.

Liu and colleagues [4], compared APS- and HVOF-sprayed coatings made from different feedstocks composed of Al₂O₃ with 13 % TiO₂. Moreover, coatings from the same feedstock were sprayed with two different APS torches. As expected, HVOF coatings were highly dense (1,2 % porosity), whereas APS coatings had small and large pores,

resulting in values in the range of 6–26 %, depending on the feedstock and torch used. The average hardness of APS coatings was in the range of 700–800 HV 1,0, whilst an average of 920 HV 1,0 was measured for HVOF coatings. The toughness of the HVOF coatings was considerably higher than the values measured for the APS counterparts. Moreover, the values measured on APS coatings varied greatly, showing dependence on the torch used. The mass loss of the best performing APS coating during the abrasion test was twice that of the HVOF coating, providing evidence of the HVOF coating's higher wear resistance under the investigated conditions.

Toma et al. [5] compared the electrical properties of Al₂O₃ and MgAl₂O₄ (spinel) coatings deposited by HVOF and APS. It is well known that the typical α-Al₂O₃ phase mainly transforms into γ-Al₂O₃ during thermal spraying, which usually has a negative influence on the mechanical properties and electrical insulation. The authors demonstrated that alumina coatings deposited by HVOF had a 5-fold higher volume fraction of α-Al₂O₃ compared to the APS counterparts. Coatings prepared by HVOF were considerably denser for both materials.

The HVOF-sprayed spinel coatings had the highest dielectric breakdown strength, reaching values over 30 kV·mm⁻¹. Interestingly, the APS-sprayed spinel coatings reached the lowest values of dielectric breakdown strength – below 20 kV·mm⁻¹. The DC electrical resistance, at room temperature and 30 % relative humidity (RH), was in the order of 10¹¹ Ω for all coatings. However, at 95 % RH, values for the APS-sprayed alumina coatings were in the order of 10⁴ Ω, one order of magnitude lower than the other three variants.

At 200 °C, HVOF coatings outperformed the APS counterparts of the same material, but the resistance of all coatings was in the order of 10¹⁰ Ω of magnitude, with the exception of spinel HVOF coatings, which reached slightly higher values (approx. 1,3 x 10¹¹ Ω).

Berger and co-workers [6] compared APS and HVOF coatings from TiO₂/Cr₂O₃ feedstocks with different TiO₂ to Cr₂O₃ ratios. After spraying by APS, a significant amount of amorphous phases was detected in the coatings. Dense and homogeneous coatings were sprayed with both techniques for all compositions, although HVOF coat-

ings seemed slightly denser, with a finer microstructure than APS coatings. For almost all the compositions, HVOF coatings were harder. The highest values were obtained with pure Cr_2O_3 coating, reaching 1350 HV 0,3, compared to approx. 1200 HV 0,3 for the APS counterpart. The electrical resistivity of the coatings was higher for HVOF with all feedstock compositions. The results for dry sliding and abrasive wear resistance measurements correlated well with the measured hardness values.

Conclusions

The deposition of ceramic coatings onto metals is an intelligent approach to obtain parts with the surface characteristics of a ceramic, but with the structural properties of metals. This method provides lower manufacturing costs compared to ceramic

parts, especially for small series production and/or large parts. The most common thermal spraying techniques for the deposition of ceramic coatings are APS and HVOF, both available at Rauschert. While the particle temperatures are usually higher in APS, HVOF yields higher particle velocities.

Even though APS is usually preferred from an economic point of view, many studies show that HVOF has technical advantages. HVOF-sprayed coatings have higher density, hardness and better wear resistance. However, it is important to keep in mind that thermal spraying has an exceptionally large number of parameters, thus the APS process can be optimized to yield technically improved coatings, which usually leads to increased processing costs.

Conversely, HVOF can be optimized to reduce processing costs, which is likely to reduce the technical performance of the

coatings. Moreover, the choice of a suitable feedstock for each process is crucial, increasing the difficulty in making a direct comparison between coatings from both methods.

As a competent partner with more than 30 years of experience in the development and production of ceramic coatings, Rauschert offers its clients APS and HVOF solutions with customized properties for a wide range of applications, including wear protection, electrical and thermal insulation and anti-adherent coatings.

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