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Advanced coatings by novel high-kinetic thermal spray processes

Abstract

Thermal spraying includes a group of coating processes in which metallic and non-metallic materials are spray deposited as fine particles in a molten or semi-molten condition, or even in fully solid state to form a coating. Thermal spraying allows deposition of relatively thick coatings, from some tens of micrometers up to several millimeters in thickness. Thermally sprayed coatings are used in different applications including protective and functional coatings in mechanical engineering, energy technology, biomedical, steel, automotive and aerospace technologies and in many other industrial sectors. Novel high-kinetic spray processes, e.g., the high velocity air-fuel (HVOF) technology are the latest developments in the area and therefore they are actively studied in the framework of the Hybrid Materials research program in collaboration with Finnish industrial and research partners. Novel multifunctional coatings are under development for specific industrial applications.

Overview of thermal spray coating processing

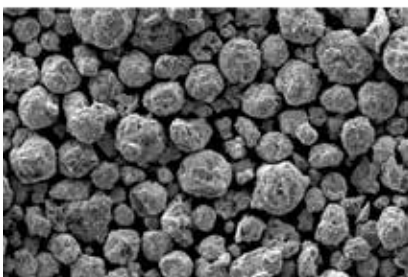
Thermal spraying is a surface engineering technique, which was invented over 100 years ago and has developed from

the early liquid metal spraying into today's large group of modern processes with different application fields. Thermal spray processes are widely used to produce thick (10 – >1000 μm) coatings on component surfaces ranging from millimeter-sized machine parts to large structures such as bridges and oil rigs. The coating is formed in layers by accelerating fine molten, semi-molten or softened particles towards the component surface, where they rapidly flatten and solidify on impact. **Figure 1** presents the principle of a thermal spray process. Feedstock material is usually introduced in powder, wire or rod form. The actual material can be anything between low melting plastics and refractory materials, e.g., oxide ceramics, as long as the material has a melting point, a stable molten state, and does not evaporate or excessively react with the surrounding atmosphere. The material is melted with the heat produced by an electric arc, fuel combustion or an ionized gas, i.e. plasma, and particles are accelerated by the high velocity stream of process gases. Different thermal spray processes are listed in **Table 1** accompanied with some key figures on the process parameters and coating properties. The principal function

Figure 1. Principle and sequence of thermal spray process. ↓

Feedstock material

- Manufacturing process
- Tailored materials



Spray process

- Particle heating
- Particle acceleration



Coating formation

- Particle flattening
- Particle solidification
- Mechanical bonding

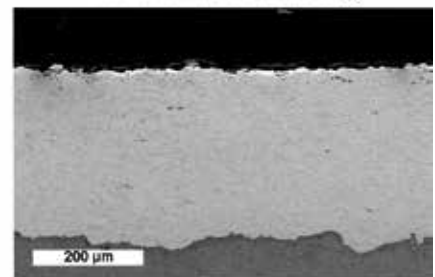


Table 1. Main thermal spray processes, key process parameters and coating properties [1].

| Spray method | Temperature (°C) ^(a) | Particle velocity (m/s) | Adhesion (MPa) ^(b) | Oxide content (%) ^(c) | Porosity (%) | Spray rate (kg/h) | Relative cost ^(d) , low=1 high=5 | Typical coating thickness (mm) |
|--------------|---------------------------------|-------------------------|-------------------------------|----------------------------------|--------------|--|---|--------------------------------|
| Flame | 3000 | 40 | 8 | 10-15 | 10-15 | 2-6 | 1 | 0.1-15 |
| Electric arc | 4000 | 100 | 12 | 10-20 | 10 | 10-25 | 2 | 0.1-15 |
| HVOF | 2000-3000 | 500-800 | >70 | 1-5 | 1-2 | 2-8 | 3 | 0.1-2 |
| HVAF | 1400-2000 | 600-1200 ^(e) | >70 | *** ^(f) | 0-0.2 | Hard metals: 2-30 Metals: 2-23 ^(g) | 2 | 0.1-12 |
| Detonation | 4000 | 800-1200 | >70 | 1-5 | 1-2 | 0.5-2 | 4 | 0.05-0.3 |
| APS | 12000 | 200-400 | 10-70 | 1-3 | 1-5 | 2-10 | 4 | 0.1-1 |
| LPPS/VPS | 12000 | 400-600 | >70 | 0 | <0.5 | 2-6 | 5 | 0.1-1 |
| LPCS | 200-650 | 300-500 | 5-30 | 0 | <0.5 | 0.5-3 | 1 | 0.2-2 |
| HPCS | 500-1000 | 400-1000 | 10- > 70 | 0 | <0.5 | 4-12 | 4 | 0.3-4 |

Flame – Flame spraying, wire and powder method

HVOF – High velocity oxy-fuel spraying

Detonation – Detonation gun spraying

LPPS/VPS – Low pressure / vacuum plasma spraying

HPCS – High pressure cold spraying / kinetic spraying

Electric arc – Electric arc wire spraying

HVAF – High velocity air-fuel spraying

APS – Atmospheric plasma spraying

LPCS – Low pressure cold spraying

(a): Temperature of the heat source

(b): Depends on deposit material

(c): Oxide content in metallic deposits

(d): Investment cost of process

(e): Depends on equipment type; e.g. M2 AC–HVAF:

600-700 m/s; M3 SAF 800–1200 m/s

(f): Oxide content is appr. 1.5v2 times oxide content of feedstock

(g): Depends on gun type: M2 AC–HVAF spray gun;

M3 Supersonic spray gun

of the applied coating is to improve the properties of the underlying component and give extra value to it. This usually means increasing the component lifetime by providing wear and/or corrosion resistance, or by providing specific functional properties, e.g. biocompatibility, electrical or surface properties. The largest users of thermally sprayed components are aerospace, pulp and paper, oil and gas, power generation and printing industries.

Protective and functional coatings against wear and corrosion

Metal matrix composite (MMC) powders used in thermal spraying typically consist of hard tungsten or chromium carbide particles embedded in Ni or Co matrix with optional Cr addition to improve the performance in corrosive environment and/or at elevated temperatures. The size of the carbides ranges from 0,1 to 10 µm and of the powder agglomerates from 5 to 50 µm, depending on the high-kinetic spray process. **Figure 2A** shows an example of Cr₃C₂-25NiCr powder particles studied with scanning electron microscope (SEM). **Figure 2B** shows the cross section of the same powder revealing inner porosity of the particle. The carbides (Cr₃C₂) are shown in the figures as grey areas binded by white areas of NiCr alloy. In an ideal MMC coating the hard carbide particles are preserved in the ductile metallic matrix without decarburization, i.e. carbon transfer from carbide into the matrix, which is caused by overheating of the powder particles during spray process-

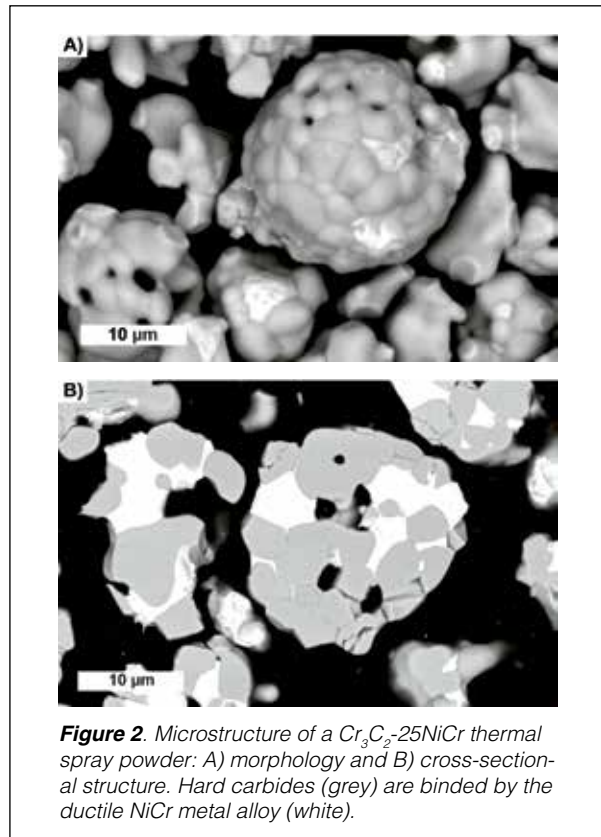


Figure 2. Microstructure of a Cr₃C₂-25NiCr thermal spray powder: A) morphology and B) cross-sectional structure. Hard carbides (grey) are binded by the ductile NiCr metal alloy (white).

ing. This is a common problem with the first and second generation high velocity oxy-fuel (HVOF) torches and has been compensated by using larger primary carbide size and larger powder particle size. For this reason the trend in the thermal spraying of metallic and MMC materials has for years been towards higher particle velocities and lower particle temperatures, which can be seen in the development of the spray equipment, see **Figure 3**. Also the particle size and primary carbide size have been decreasing as the risk of overheating the particles has become smaller. The decreased amount of thermal energy transferred to the particles has been replaced with higher kinetic energy to maintain high deposition efficiency. At the same time, the increased particle velocities have also led to denser coating structures. The most recent step has been the development of modern high velocity air-fuel (HVAF) processes that can produce particle velocities of over 1000 m/s.

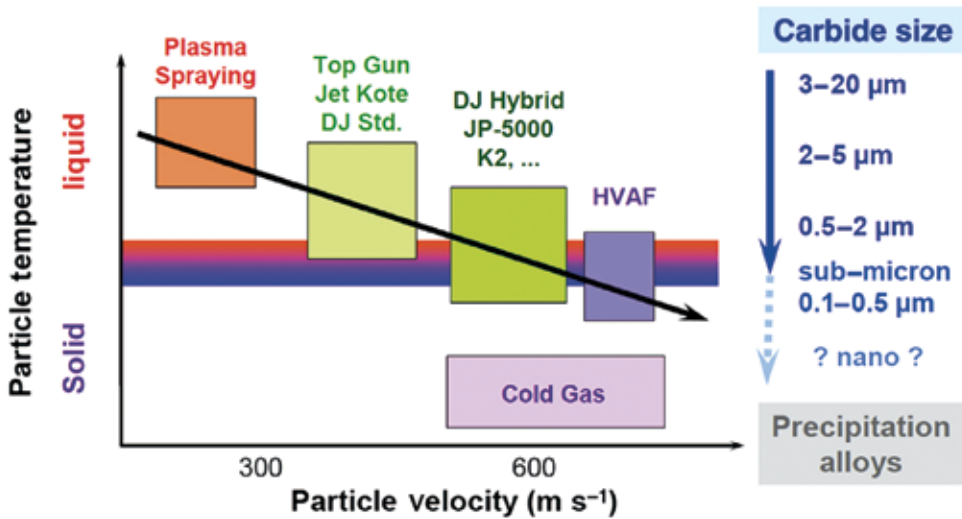


Figure 3. Graph showing the trend in thermal spraying of carbide materials, moving towards higher particle velocities and lower particle temperatures. Top Gun, Jet Kote etc. are different HVOF systems. (Source: H.C. Starck GmbH) [1].

Research activities at TUT/DMS

The Department of Materials Science (DMS) of Tampere University of Technology (TUT) is strongly involved in the FIMECC's 5 years long Hybrid Materials research program, which started in the beginning of 2014. One of the projects in the program concentrates on thick metal and MMC coatings against wear and corrosion in harsh environments, e.g., at elevated temperatures. These coatings are sprayed with high-kinetic thermal spray processes, i.e. HVOF and HVOF spray processes. Comparison of different thermal spray processes has started and research is being carried out at Tampere University of Technology (TUT) in collaboration with the project partners VTT, Aalto University and a large group of Finnish industrial companies, both thermal spray companies and end users of the coatings. The latest addition to the wide range of different spray equipment at TUT was the 3rd generation HVOF equipment (M3 Supersonic Air Fuel) from Uniqucoat Technologies LLC, installed in 2013. Close collaboration has been carried out with Oseir Ltd. within the Hybrid Materials program to develop a new and highly sensitive diagnostic system for thermal spraying (Figure 4). Online diagnostic tools are used to measure the particle in-flight parameters, i.e. temperature and velocity, which play an important role in the comparison of different spray processes. The need for new

diagnostic tools is growing as thermal spray processes are reaching higher particle velocities (Figure 4B) with lower particle temperatures (Figure 4C), making the particle detection and analysis more challenging.

Harder, denser and ductile novel coatings by HVOF spraying technology

High velocity air-fuel (HVOF) spray process was developed in the late 1980s and has since then evolved into one of the most promising thermal spray processes for metallic and MMC materials. HVOF is based on the HVOF process but it uses compressed air instead of expensive oxygen as the oxidizer in the combustion process. This reduces the costs of spray operation as a compressor can be used to produce the needed amount of air. At the same time the maximum flame temperature is reduced by almost 1000°C, bringing the particle temperatures closer to the melting point of common metallic materials, e.g. Ni, Co and Cr, which are used as matrix alloy in the MMC powders and as main elements in many of the metallic alloys sprayed for elevated temperatures and corrosion environments. The coatings sprayed with a modern HVOF system show dense structure and preserve even the finer carbide particles in the coating (Figure 5A). Some porosity is typically observed within the powder particles after manufacturing process (Figure 2B),

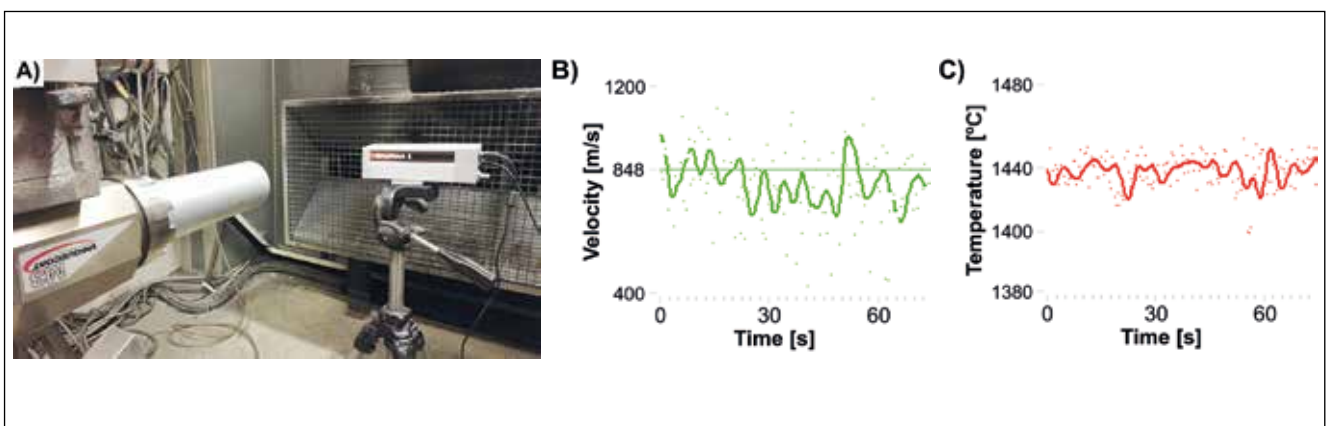


Figure 4. A) New Spraywatch 4 diagnostic system ready to measure, B) measured particle velocities and C) measured particle temperatures.

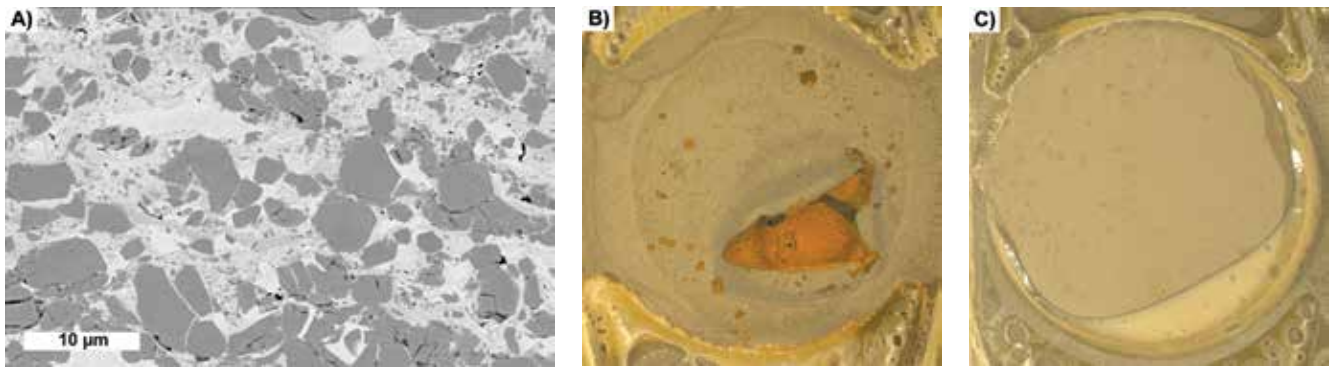


Figure 5. A) Microstructure of HVOF sprayed Cr_3C_2 -25NiCr coating, B) HVOF sprayed Cr_3C_2 -25NiCr coating after exposure to 3.5% NaCl water solution and C) HVAF sprayed Cr_3C_2 -25NiCr coating after same exposure.

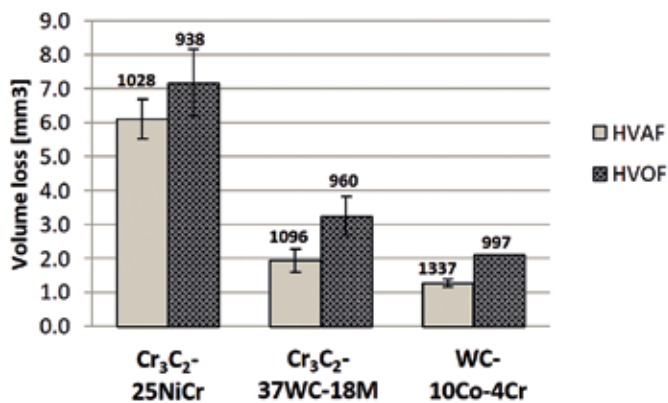


Figure 6. Volume losses of different HVOF and HVAF sprayed coatings after rubber wheel abrasion test. Vickers microhardness (HV0.3) is shown above the data columns.

but this cannot be observed in the HVAF sprayed coating due to high kinetic energy at the moment of impact, which firstly makes the particle flatten and secondly densifies the underlying coating layers. This densification closes the open porosity in the sprayed coating and provides better protection against corrosive environments by preventing the corrosive media from reaching the vulnerable metal substrate (Figure 5C). This, however, is often not the case when coatings are sprayed with conventional HVOF

processes (Figure 5B). Denser coatings sprayed with finer feedstock powder also influence the wear properties of the coatings and typically improve the wear resistance when sprayed with HVAF (Figure 6). This is due to the higher cohesion of the coating as compared to conventional HVOF sprayed coating.

Alternative materials for tomorrow's needs

The material development is constantly evolving as better performing metal alloys and new mixtures of alloys and carbides are sought to serve in more demanding process environments. Some of them are new Cr_3C_2 based powders manufactured for example with highly corrosion resistant Inconel 625 type superalloy matrix (Figure 7A) or with fine WC particles to improve the wear resistance of the coating (Figure 7B). The costs of thermal spraying are strongly tied to the price of feedstock materials, which is one of the reasons to look for well performing alternative materials to replace the more expensive coating materials. Many of the elements currently used in thermal spray coating materials are also classified as critical raw materials due to their availability and significant price fluctuations. Examples of such are, for instance, W, Ni, Co, and even Cr. However, good examples of substitute materials are the Fe-based coating materials, in which the expensive Ni or Co matrix has been replaced with Fe-based alloy, generally with an austenitic and/or ferritic structure with high chromium content, and the embedded hard carbide particles are

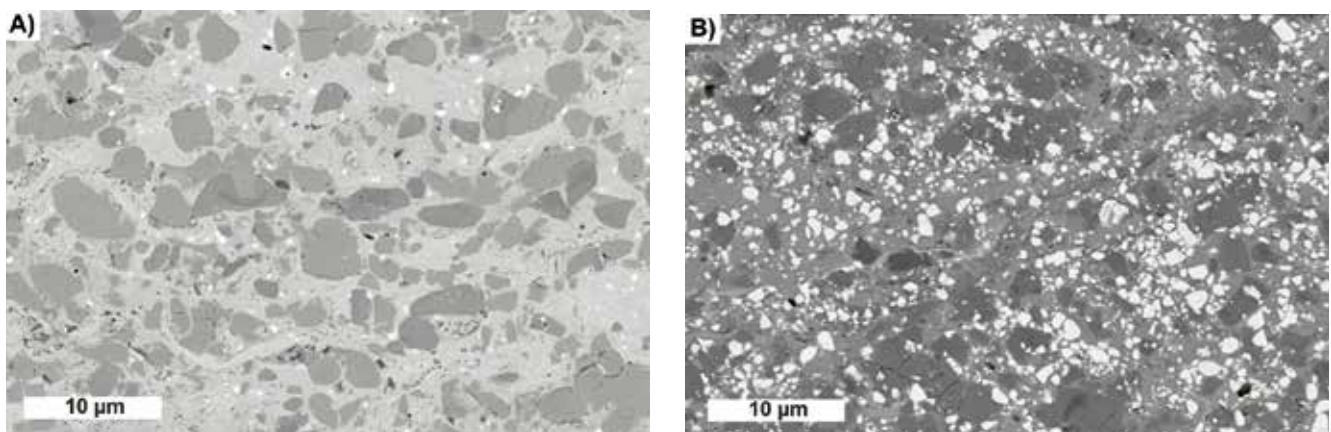


Figure 7. Microstructures of the HVAF sprayed coatings with Cr_3C_2 carbides A) embedded in Inconel 625 type metal alloy matrix and B) with fine WC addition to improve the hardness and wear properties [2].

replaced with hard carbide or boride precipitates within the Fe-based alloy. Even though the Fe-based coatings cannot provide as high abrasive wear resistance as the novel WC-CoCr coatings, they possess competitive sliding wear resistance and significantly improved cavitation erosion resistance with lower material costs (**Figure 8**). Furthermore, Fe-based coating materials have been acknowledged as environmentally friendly and health safe coating solutions which makes them even more promising as substitutive materials. Fe-based materials and their performance have been extensively studied at TUT during the past few years. Besides the development of alternative coating material compositions, it is crucial to generate by experimental

with HVOF and HVAF processes, Proceedings of 28th International Conference on Surface Modification Technologies, 16-18 June, 2014, Tampere, Finland, to be published.

[3] A. Milanti, H. Koivuluoto, P. Vuoristo, G. Bolelli, F. Bozza, L. Lusvardi, Microstructural Characteristics and Tribological Behavior of HVOF-Sprayed Novel Fe-Based Alloy Coatings, Coatings, 4, 2014, p. 98-120. ▲

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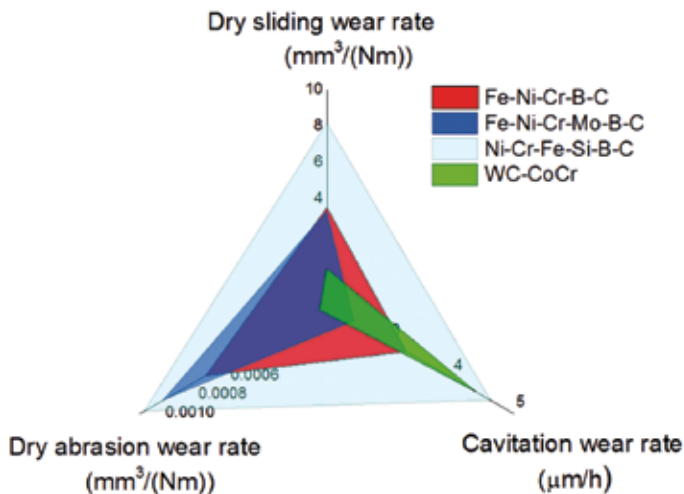


Figure 8. Radar wear rates diagram of HVOF-sprayed Fe-based, Ni-based and WC-CoCr coatings [3]

research a sufficient amount of information on the thermal spray processability and properties of the alternative and substitute materials.

Strengthening research collaboration improves competitiveness, expertise and expert training

Tampere University of Technology and VTT Technical Research Center of Finland are starting in 2015 close collaboration in the field of thermal spray coating processing by establishing a new research platform entitled "Thermal Spray Center Finland" (TSC Finland) located in Tampere. Through joint research collaboration these two organizations with their long term experience in thermal spray technology will form a noticeable research platform with world-class expertise and competitiveness in the field of thermal spraying. ▲

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