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New trends in metallic alloys / Alliages métalliques : nouvelles tendances

# Emerging processes for metallurgical coatings and thin films

## *Procédés émergents de revêtements métallurgiques et de films minces*

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ABSTRACT

Innovation in thin-film deposition processes, thermal spraying and cladding technologies mostly rely on evolutions of their previous iteration. Along with other examples, five case studies of emerging elaboration processes for metallurgical coatings are described coupled with their applications. In the frame of the lifetime extension of components exposed to aggressive media or their functionalization, this article depicts all the developments of the detailed processes. Physical vapor deposition (PVD) of coatings with exceptional properties is possible thanks to sources generating highly ionized metallic vapors. The control of the average energy per incident species and particularly metallic ions strongly influences the characteristics of the deposited layer obtained, for example, with HiPIMS (High Power Impulse Magnetron Sputtering). While PVD techniques are mainly directive regarding the growth of the coating, chemical vapor deposition (CVD) processes manage to homogeneously coat complex 3D shapes. The use of specific precursors in DLI–MOCVD (Direct Liquid Injection – MetalOrganic CVD), carefully selected from the whole metalorganic chemistry, allows one to efficiently treat heat-sensitive substrates and broadens their application range. The third detailed example of emerging technology is suspension plasma spraying (SPS). Projection of various solutions containing nanoparticles leads to the growth of unusual morphologies and microstructures and to the generation of porous coatings with multi-scaled porosity. On the other hand, cold-spray uses metallic powders with higher granulometry and does not modify them during the deposition process. As a result, high-purity and dense materials are deposited with properties similar to those of wrought materials. Whereas cold-spray is suitable only for ductile metals, laser cladding can be applied to ceramics, polymers and of course metals. Laser cladding is a key technology for advanced metallurgical engineering and alloy development due to its capability for functionally graded materials production and combinatorial synthesis.

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## RÉSUMÉ

L'innovation dans les procédés de dépôt de couches minces ou épaisses et la projection thermique repose principalement sur les évolutions de leurs versions précédentes. Cinq études de cas de procédés émergents d'élaboration de revêtements métallurgiques avec leurs applications sont proposées. Les développements des procédés sont détaillés dans un contexte d'amélioration de la durée de vie de composants exposés à des milieux agressifs. Ainsi, des revêtements aux propriétés exceptionnelles sont obtenus par des procédés de dépôt physique en phase vapeur (PVD) grâce à des sources de vapeur métallique fortement ionisée. Les propriétés des couches sont contrôlables par exemple en HiPIMS (pulvérisation magnétron par impulsions de forte puissance) via l'énergie moyenne des ions métalliques. Alors que les techniques PVD sont plutôt directives, les procédés de dépôt chimique en phase vapeur (CVD) parviennent à revêtir uniformément des formes complexes. L'utilisation en DLI-MOCVD (Direct Liquid Injection – MetalOrganic CVD) de précurseurs soigneusement sélectionnés au sein de la chimie organométallique permet de traiter efficacement des substrats thermosensibles pour élargir le domaine d'application de ces revêtements. Le troisième exemple de technologie émergente est la projection plasma de suspensions. Ces dernières contenant des nanoparticules, leur projection mène à la croissance de structures inhabituelles et à des revêtements à porosité multiple. La projection à froid utilise quant à elle des poudres métalliques avec des granulométries supérieures. Celles-ci ne subissant pas de transformations pendant leur projection, des matériaux denses et de haute pureté sont déposés avec des propriétés comparables à celles de matériaux corroyés. Alors que la projection à froid convient aux métaux ductiles, les revêtements laser peuvent être appliqués aux céramiques, polymères et bien sûr aux métaux. Cette technologie est essentielle pour une ingénierie métallurgique avancée et le développement de nouveaux alliages en raison de sa capacité à produire des matériaux à gradient et à utiliser la synthèse combinatoire.

## 1. Introduction

Metallurgical coatings and thin films have been developed in the field of high-performance metallurgy for a very long time. They often rely on the implementation of quite old processes, but emerging technologies are regularly involved. As surface functionalization steps are increasingly integrated from the beginning in the conception and life cycle of a component, it is then possible to produce efficient architectures capable of addressing complex and extreme environments. The coatings generally operate under combined stresses such as mechanical loading with corrosion or irradiation in addition to oxidation or corrosion. Thus, the main driver for the development of surface engineering in the metallurgy field is about improving component lifetimes.

For most applications, the coating design has to be done on the basis of precise specifications when the elaboration method is dictated by a certain number of scientific, technological, economic, and environmental criteria. Materials efficiency, especially when it comes to the use of critical metals for example, as well as the recyclability of scarce resources can also in some cases become a major criterion.

This paper does not aim at making a comprehensive list of surface engineering processes for metallurgy but, on the contrary, to illustrate with a few well-targeted examples the innovation in terms of materials and processes through industrial applications. The latter is often the result of technological progress made by existing processes usually known for a long time.

Surface treatment processes fall into four main categories: thin-film deposition processes with, in particular, PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition) as well as their hybridized technologies, thermal spraying processes in the broad sense (plasma high velocity oxy-fuel, cold spray...) leading to thick coatings, diffusion processes (among them pack cementation and derivative processes, implementation of powder slurries, liquid metals. . . ), and welding processes. Conversion processes and post-treatments also need to be considered. They can confer or modify particular properties to treated surfaces (recrystallization of extreme surface for example, by laser or electron beam treatment).

The purpose of this article is to illustrate potential vectors of process innovation through several examples, successively PVD, CVD, thermal spraying, and more specifically plasma spraying and cold spraying, and finally laser cladding, which belongs to welding processes. The complementarity between these processes is illustrated in Fig. 1 in terms of substrate temperature, ranging from 0 °C to 1000 °C, and coating thickness, ranging from 0.1 μm to 10 mm. Regarding PVD technologies, the main route for innovation is the development of new power supplies leading to metallic vapors with a high ionization rate that results in specific properties, for instance the control of microstructure and interfaces. In the case of CVD, the appropriate choice of metalorganic precursors allows us first to lower the deposition temperatures, making the process compatible with heat-sensitive substrates, and second to access the entire diversity of chemistry in terms of compositions

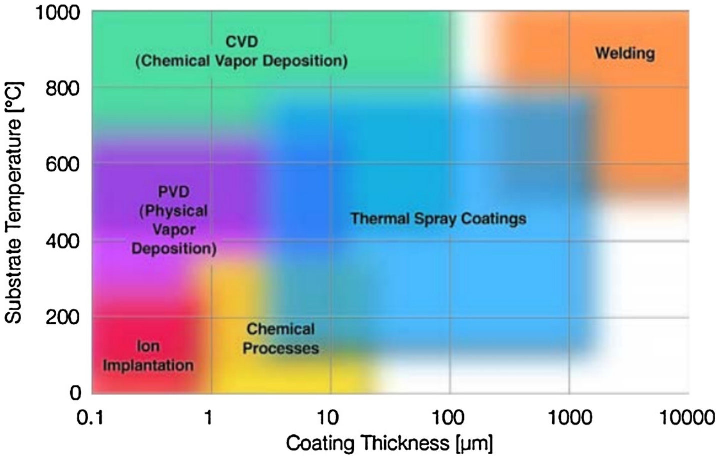


**Fig. 1.** Coating process comparison (reproduced from [1]).

and compounds. Finally, when dealing with thermal spraying technologies, it is very clear that the access to innovative and on-demand powders constitutes one of the main vectors of technological rupture. It is, for instance, the case with the possibility to produce gradient coatings or via a controlled implementation of nanopowders use through the form of suspensions or aggregates.

## 2. Innovation in thin films technologies

In the first part of the review, two innovative vapor deposition technologies are presented, i.e. the HiPIMS and the DLI–MOCVD. Since they are quite different in terms of physical chemistry, they are described separately in two distinct sections.

### *2.1. High-power impulse magnetron sputtering for more efficient PVD*

If the phenomenon of sputtering was highlighted in the middle of the 19th century by W. R. Grove, it is in the second half of the 20th century, and more particularly from the work of P. Sigmund during the 1960s [2], that the understanding of the physical and physicochemical phenomena involved and the technological progress led to the industrial development of sputtering. The microstructure and properties of the films being related to the average energy per incident species (Fig. 1), many studies were conducted from the 1980s on highly ionized discharges (i-PVD) likely to lead to the sputtering of metal ions. During the 1990s, the Induced Coupled Plasma (ICP) technique involving the addition of a radio frequency polarized antenna and the exploitation of electron–cyclotron resonance (ECR) from a cavity submitted to microwave radiation allowed one to partially ionize the sputtered metal vapor. However, it is only from the work of W. M. Posadowski et al. [3] on the effect of the increase of power dissipated on the target that V. Kouznetzov et al. [4] published the first work on high-power impulse magnetron sputtering (HiPIMS) in 1999, paving the way for innovative applications in the field of physical vapor deposition processes.

Diode sputtering consists in establishing an electric discharge in a rarefied atmosphere (1 Pa) of rare gas, generally argon, by applying a potential difference (1 kV) between the target, consisting of the material at the origin of the coating, and the walls of the reactor connected to the mass. The $Ar^+$ ions are then attracted by the negative electric field applied to the target and their impact causes the sputtering of metal atoms by ballistic effect. The metal vapor thus created condenses on the substrate to form a coating. The synthesis of dense coatings requires to reduce the deposition pressure to around 0.1 Pa, which is incompatible with the possibility of carrying out a diode discharge due to a mean free path of electrons close to that of the target-to-substrate distance (10 cm). Maintaining a stable low-pressure discharge then requires concentric magnets placed behind the target, generating field lines that close within the gas phase, trapping the electrons, which can then create ionizing shocks in the immediate vicinity of the gas phase. This is called magnetron sputtering. The introduction of a chemically active gas simultaneously with argon allows the synthesis of ceramic coatings from metal targets, but the instability of the discharge requires the implementation of closed-loop control systems to allow the high rate deposition of stoichiometric ceramic coatings. High Power Impulse Magnetron Sputtering (HiPIMS) technology consists in supplying the target with pulses of 10 to 200 µs at frequencies of the order of 100 to 500 Hz. The instantaneous power dissipated during the pulses can reach about 1 MW, which corresponds to currents of a few thousand amperes for a bias voltage of 600 to 1000 V. However, the average power remains close to a few kW in order to preserve the integrity of the target. Such conditions make it possible to ionize the sputtered metal vapor according to two main mechanisms: by impact of the electrons of the discharge or by Penning ionization, produced by the collision with the excited metastable argon atoms.

The advantage of having a highly ionized metal vapor results in:

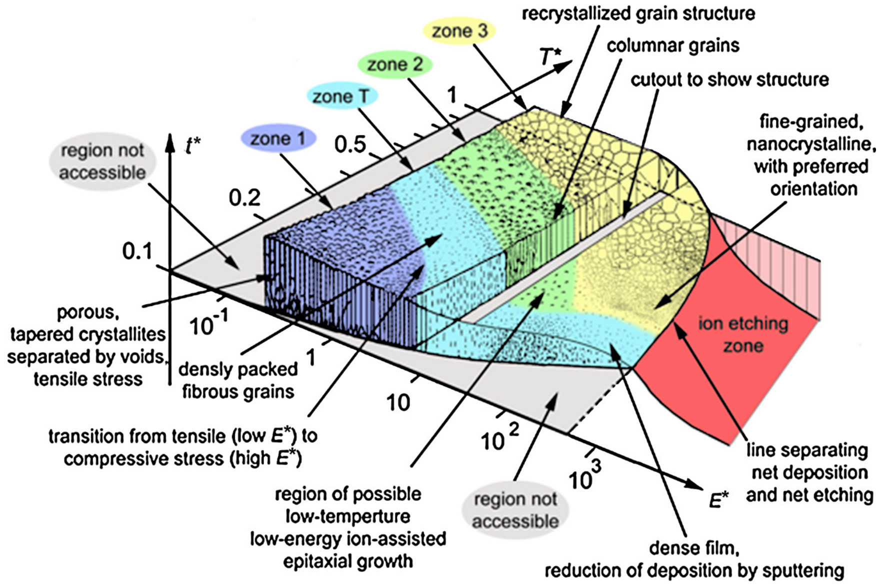


**Fig. 2.** Schematic morphology of coatings as a function of the generalized temperature ($T^*$), which considers the temperature shift caused by the potential energy of the particles arriving on the surface, and normalized energy of impinging species ($E^*$), which describes the displacement and heating effects caused by the kinetic energy of the bombarding particles, see Ref. [5] for an explanation (reproduced from [5]).

- excellent adhesion of the coatings obtained for limited etching times of the surface to be coated,
- a microstructure and a density of the layers associated with a level of adjustable internal stresses through the bias voltage of the substrates, which makes it possible to perfectly manage the average energy per incident species,
- greater homogeneity of coatings deposited on surfaces of complex geometry,
- the possibility of synthesizing stoichiometric layers for reactive gas flow rates lower than the critical flow rate at which this instability occurs,
- the possibility of crystallizing phases, including metastable ones, at temperatures lower than those defined by thermodynamic equilibrium and/or obtained by conventional magnetron sputtering methods.

However, it is necessary to emphasize the preponderant effect of the magnetic configuration of the magnetron on the performance of the HiPIMS process, particularly in terms of deposition rate and propensity to maintain a sufficient ionization rate of the metal vapor in the vicinity of the substrate to be coated.

The control of the average incident ion energy associated with HiPIMS technology allows the optimization of the properties of thin films in many areas compared to the same coatings deposited by conventional methods, or even by the method of vacuum cathodic arc deposition in the field of hard and ultra-hard coating. As presented in Fig. 2, HiPIMS allows one to access to film-growth regimes such in zone such as in zone 3.

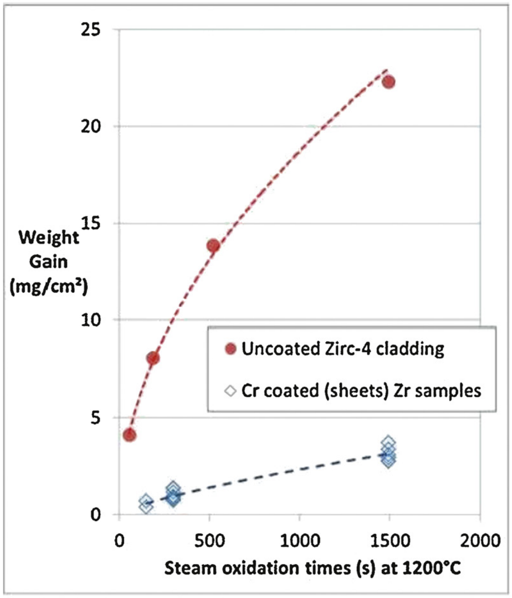
In the field of transparent conductive oxides, the improvement of the conductivity of n-type coatings such as ZnO: Al is believed to be related to epitaxial effects. In the aeronautical field, increased performances have also been observed with regard to erosion by sand or water of AlTiN coatings compared to the same coatings deposited by alternative processes. Finally, exceptional performance has been obtained with respect to the protection of nuclear fuel cladding with chromium coatings, both under nominal conditions and under loss-of-coolant accident conditions (LOCA) [6]. For these last two applications, the performances obtained are associated with excellent adhesion of the layers and compactness that conventional or alternative methods do not achieve.

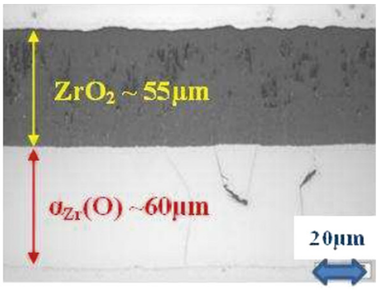
Concerning the protective coatings on Zr-based cladding, an enhanced high-temperature steam corrosion resistance is measured after 300 s in the 1000–1200 °C range if compared with the uncoated Zr-based cladding as presented in Fig. 3. Moreover, for an extend oxidation times up to 6000 s under the maximum LOCA's (Lost-of-coolant accident) temperature (1200 °C), it has been observed that the clad segment is able to resist to the final water quenching down to room temperature.

The upscaling process on Framatome's M5® claddings for a further industrialization is currently in progress [5]. The latter is the solution chosen by Framatome in the frame of the enhanced accident tolerant fuel (EATF) competition [7,8].

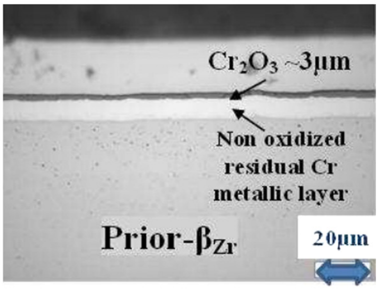
The HiPIMS technology allows one to improve the coatings' adherence and the microstructure's density on zirconium-based substrates; it was demonstrated that Cr–Si–N nanocomposites systems present a promising behavior when they are submitted to high-temperature oxidation (Fig. 4) [10]. This type of nanocomposites coatings will lead to an increase of the performances of classical chromium coatings [11].

Moreover, other interesting HiPIMS products are Ti–Si–N nanocomposites hard coatings that present an enhanced oxidation resistance at high temperatures [12]. These coatings are usually processed by HiPIMS coupled and DC-pulsed magnetron





(a) Uncoated Zirc-4 after steam oxidation for 300s at 1200°C



(b) Cr coated Zirc-4 after steam oxidation for 300s at 1200°C

**Fig. 3.** Comparison between the respective high temperature steam oxidation behaviors at 1200 °C of uncoated vs. Cr coated Zircaloy-4 samples (reproduced from [9]).

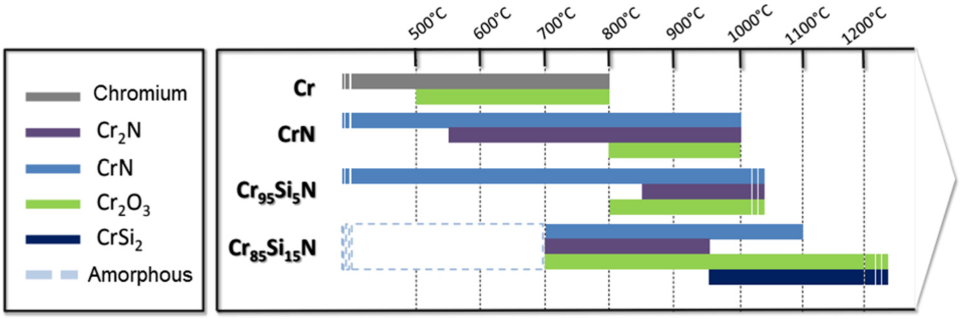


**Fig. 4.** Phase content evolution of Cr–Si–N HiPMS PVD coatings as a function of the oxidation temperature (reproduced from [10]).

sputtering (PDCMS). The hybridization of these techniques permits an accurate control of the silicon content in coating, thus allowing one to add an optimal silicon content which allows one to retain the mechanical properties under extreme conditions.

Among the properties required for the development of coatings for the enhanced ATF, a good behavior under irradiation in nominal conditions is required. The work achieved by Mamour Sal [13] on the study of the behavior under ion irradiation of Cr–Ta multilayered systems provides interesting and promising answers. Indeed, in this context, Cr–Ta nanolayered systems with a respective period of 15 nm and 50 nm were irradiated in the Jannus accelerator with the aim of simulating their behavior when they are submitted to neutron irradiation. The first results show that multilayered structure remains intact, even after a radiation dose of 250 dpa[2] (Fig. 5).

Furthermore, regarding the response to heavy ions and helium implantation, the most significant results show that the Cr–Ta interfaces are good traps for helium, the post-implantation diffusion is very limited in systems with a high density of interfaces. Cr–Ta systems with a period of 15 nm allow 20% of helium accommodation, which induces a self-healing behavior of these coatings under irradiation. The Cr–Ta interfaces act as defect traps that allow a recovery efficiency of above 80% for the 15-nm period systems.

As shown in the previous examples, HiPIMS is a processing route that opens many possibilities in terms of advanced metallurgy. Recently, MAX phases have been synthesized by HiPIMS in one single step [14,15]. These types of coatings

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[2] Displacements per atom.

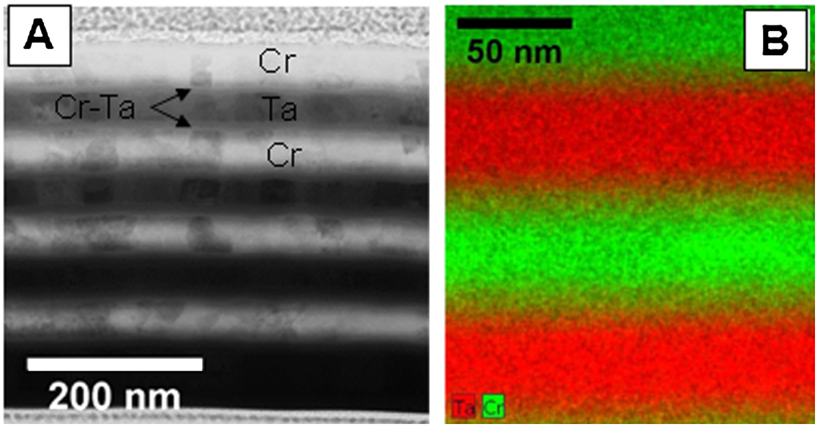

**Fig. 5.** Cr–Ta nanolayered system after a 250-dpa irradiation dose: (A) transmission electron microscopy and (B) energy dispersive X-ray spectrometry micrographs (reproduced from [13]).

present an enhanced erosion resistance. Because of their high temperature resistance and self-healing properties, some researchers are focusing the studies on MAX phases as potential candidates for the next generation of EATF [16].

Finally, HiPIMS recently permitted to deposit new metallic compounds such as high-entropy alloys (HEAs). Some researchers have shown that these materials have high strength, excellent corrosion resistance, good thermal stability, and a superior wear resistance [17].

HiPIMS is an innovative technology that is attracting considerable academic interest because of its ability to manage the average energy per incident species that conditions the properties of thin films. This enthusiasm is also shared by generators manufacturers who have multiplied over the last decade. Its tricky implementation, in particular because of the considerable influence of the magnetic configuration of the magnetron sources on the performance of the process, and the cost of the generators mean that the industrial developments remain confidential. Nevertheless, this technology is approaching a maturity that should lead to an amplification of industrial applications over the next decade.

### *2.2. DLI–MOCVD to take advantage of the diversity and richness of organometallic chemistry*

The Chemical Vapor Deposition (CVD) processes have many industrial applications, in particular in the field of cutting and forming tools due to (i) their high productivity, (ii) the wide range of advanced coatings that can be deposited (carbides, nitrides, oxides…), (iii) the performance of these coatings optimized thanks to specific compositions, microstructures or architectures (multilayers, nanocomposites, compositional gradient…), and (iv) the good conformal coverage on complex shapes and geometries. In the field of functional thin films, CVD is also an industrial technique, for instance for epitaxial growth of semiconductors in microelectronics or for depositing functional layers in solar cell fabrication and glass industry.

For decades, CVD processes were operating at high temperatures because they were based on the chemistry of the halides, which considerably slowed their development. The increasing demand for highly diversified and high-performance coatings leads to process developments for which scale-up, low deposition temperature, and uniform thickness are permanent and stringent requirements. In this context, new processes are emerging.

The family of CVD processes is based on the generation and transport of a reactive vapor phase that upon its decomposition in a process chamber produces the growth of a coating on the surface to be covered by heterogeneous chemical reactions. The energy required for the activation of both the gas phase and the heterogeneous decomposition can be mainly thermal, photonic or electric discharge (plasma). Plasma-enhanced CVD processes are undergoing important developments for surface engineering, but they are not discussed here. We only cite, as an example in mechanical engineering, diamond coatings that are industrially deposited by microwave plasma CVD as wear resistant coatings [18].

Once overcoming low-temperature and scale-up constraints, thermal CVD processes can achieve challenges that are not feasible or difficult to demonstrate by other techniques. Therefore, they can be implemented into manufacturing in-line or roll-to-roll CVD reactors to deposit protective coatings (BN, TaC…) on substrates moving at constant speed [19] or for continuous deposition of functional layers at an industrial level as graphene [20] and photovoltaic Si [21]. Also, mass production of ceramic composite materials is performed by low-pressure CVD in porous bodies, namely by chemical vapor infiltration (CVI) [22].

A recent challenge is the development of a process capable of uniformly covering the inner wall of long tubes with a protective coating a few microns thick. Atomic-layer deposition (ALD) belongs to the family of CVD, and was initially developed principally for manufacturing metal oxide functional thin films. ALD is extremely conformal and it has been recently used for the deposition of $HfO_2$ on the interior surface in a complex cooling circuit for corrosion mitigation by the cooling fluid [23]. However, ALD still suffers from very low growth rates to be a viable process for developing protective coatings.

DLI–MOCVD is an emerging process that combines the use of metalorganic (MO) precursors and direct liquid injection (DLI) of the reactive sources in an organic solvent. This innovative process is developed for different applications including the internal protection of long tubes. It benefits from most of the advantages of the CVD techniques mentioned in the introduction. Here we highlight its promising prospects and its potential for industrial transfer. Indeed, although CVD is primarily a chemical process, there is more in this process than just chemistry, since gas flow and heat and mass transfer play also a key role. As a result, modeling of the process is a suitable approach for this objective.

The main advantages of DLI–MOCVD are a significant reduction of the deposition temperatures thanks to the metalorganic precursors and the feeding of the reactor by high vapor flow rates generated by the DLI system, which is necessary both for obtaining high deposition rates and for operating in large-scale reactors. Due to the thermal fragility of metalorganic compounds, a limitation of MOCVD process with conventional devices of precursor evaporation is its prolonged heating throughout the duration of deposition; this can affect the reproducibility of coatings. An advantage of the DLI system is that it keeps the precursor at room temperature and under inert gas throughout the run, and only micro-amounts are injected into a flash evaporation chamber.

The versatility of this process is related to the vastness of the materials that can be deposited thanks to molecular engineering achievable in metalorganic chemistry for designing suitable precursors, many of them being now commercially available.

Initially DLI–MOCVD has been developed and has grown rapidly for the growth of functional oxide thin films for optical and electronic devices [24]. For oxide deposition, carbon contamination of the films originating both from the precursor and the organic solvent was prevented by adding an $O_2$ partial pressure, which involves both combustion and pyrolysis reactions. The pioneering work on DLI–MOCVD of carbides [25], nitrides [26] and metals [26] from bis(arene)M precursors, where M is a transition metal in the oxidation state zero (Cr, Mo, W, V...), has revealed a great potential for applications as metallurgical protective coatings. Further work on SiC [28] and HfC has confirmed the interest of this process, for instance to produce nanostructured multilayer coatings by readily controlling the gas phase [26].

The main disadvantages of the DLI–MOCVD process result from the use of highly reactive and sometimes toxic precursors, and from the implementation of a complex chemistry that can be difficult to control, in particular for upscaling the process.

However, both a recent experimental results demonstrating the possibility of closed-loop recycling of effluents [29] and a modeling approach [30] contribute to the burgeoning industrialization potential of this DLI–MOCVD process. Furthermore, obtaining increased performance of advanced coatings sometimes requires the realization of specific nanostructures or architectures such as multilayers or nanocomposites. As a result, complex coatings sometimes have to be made by several techniques, and it is obvious that there is a considerable interest for hybrid processes implemented in a single deposition chamber. The DLI–MOCVD method, just like its parent MOCVD technique, has a good potential for hybridization. For example, III-nitride tunnel junctions were fabricated by a hybrid MOCVD/MBE (Molecular Beam Epitaxy) process combined in a single chamber [31]. Also, plasma-enhanced DLI–MOCVD was used for the growth of phase change materials (GeTe) [32], and a novel hybrid MOCVD/ALD reactor has been implemented to fabricate $SnO_x/TiO_2$ multilayers [33].

The Cr–C–N system allows a remarkable flexibility. It is both a model for analogous M–C–N systems ($M = Cr, V, Nb, Mo$) where similar precursors exist, and a basic system for many metallurgical protective coatings. Bis(arene)chromium precursors decomposition through DLI–MOCVD process results in the growth of amorphous $a$-$CrC_x$ coatings between 623 and 773 K [29]. These organometallic molecules have a sandwich structure with a center Cr atom characterized by a zero oxidation state. Consequently, no Cr(VI) derivative is involved in this REACH (the European regulation about Registration, Evaluation, Authorization and restriction of CHemicals) compatible process. The addition of a carbon inhibitor leads to the deposition of crystallized metallic Cr [27] while cubic CrN (and $Cr_2(C, N)$ intermediate nitride) can be grown by controlling a $NH_3$ partial pressure [26]. Nanostructured CrC/CrN multilayer coatings can be readily obtained as shown in Fig. 6a. The Cr(0) chemistry implemented in this process allows a loop-recycling of effluents until their entire decomposition, leading to a conversion yield close to 100%, which significantly decrease both the economic and the environmental impacts of the process [28].

The dense and amorphous $a$-$CrC_x$ coatings exhibit a glassy-like microstructure without grain and grain boundaries. They have a high hardness (20 to 25 GPa) and a good abrasive wear resistance. Thermally stable up to about 873 K, they crystallized above this temperature to form chromium carbides. Si-doping (2 at. %) increases the temperature of this amorphous-to-crystallized structural transformation to 1023 K. Finally, the excellent high-temperature oxidation resistance of $a$-$CrC_x$ coatings makes them an efficient barrier to protect the inner-surface of Zr-based nuclear fuel claddings in accident conditions (Fig. 6b) [34].

Numerical modeling and multi-scale simulation of the process are essential approaches for upscaling. A DLI–MOCVD pilot is currently capable of internally protects a bundle of 1-m-long fuel cladding segments with a uniformly thick $a$-$CrC_x$ coating of several micrometers, as shown in Fig. 1c. Many evaluations specific to nuclear applications are currently in progress. By continuing the coupling between modeling and experimentation, the scaling progresses towards its final extent, i.e. full-length nuclear claddings of 4 m. This would be a first transfer of a DLI–MOCVD process in the metallurgy field.

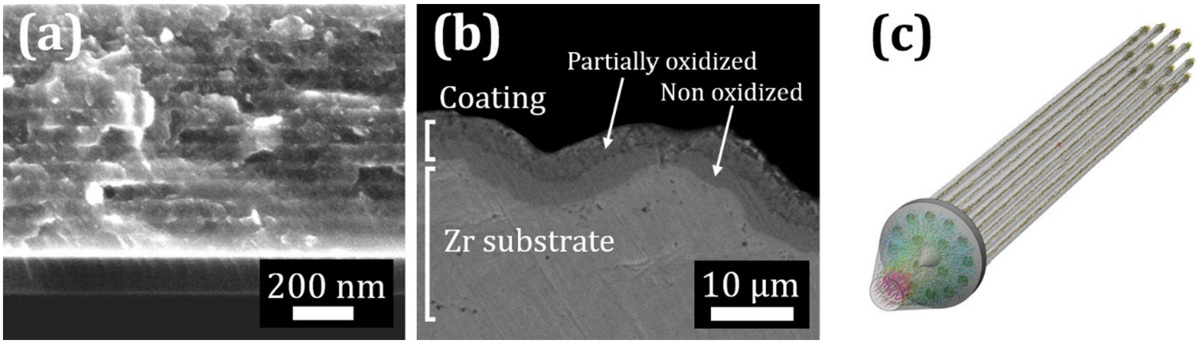

**Fig. 6.** Scanning electron microscope (SEM) cross-section (a) of a $CrC_x/CrN$ multilayer coating grown by DLI–MOCVD constituted of 30 layers with a period of 53 nm, (b) of a protective *a*-$CrC_x$ coating after oxidation at high temperature as described in [18], and (c) computational simulation of a deposition in a bundle of 16 clad segments 1 m in length, validating the design of the gas-phase distributor.

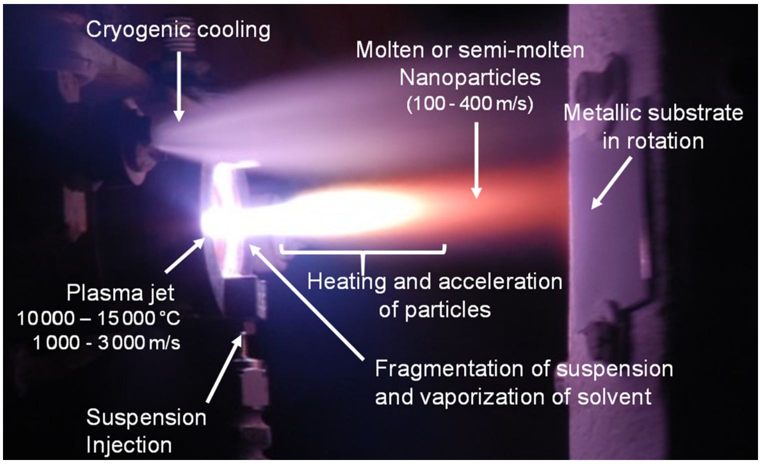

**Fig. 7.** Illustration of a nanoparticles suspension sprayed by SPS (courtesy of CEA).

## 3. Innovation in thermal spraying and cladding technologies

While the first part of this review dealt with processes belonging to thin films deposition techniques, the second part presents three technologies capable of coating components with thicker layers. They consist in suspension plasma spraying, cold spray, and finally laser cladding.

### *3.1. Suspension Plasma Spraying (SPS) for the best use of nanomaterials*

The Suspension Plasma Spray process was developed from the pioneer studies on liquid injection through flame (early 1970s) and plasma (1900s) for nanopowder synthesis [35,36]. If the principle remains close to the initial developments, liquid feedstock thermal spray processes and particularly suspension plasma spraying (SPS) are widely studied since the 2000s for coating production due to their various applications, as described by the following reviews [35–37].

Suspension Plasma Spraying consists in the injection of thin particles ($< 5$ µm and most generally between 0.1 and 1 µm) through a plasma jet. (See Fig. 7.) Most of the plasma gun technologies used for the SPS process are based on the ionization of plasma gases (argon, helium, nitrogen or a mixture of them) by a direct current (DC) discharge between a cathode and an anode nozzle, allowing a plasma jet at high temperature (8000–14 000 K) and velocity ranges (800–2200 m/s) [35]. The injection of such as thin particles requires a carrier medium heavier than conventional carrier gases used in Atmospheric Plasma Spraying (APS). Here, solid particles are dispersed in a liquid, used as a carrier medium. This suspension is then injected through the plasma jet using a calibrated injector (usually 0.1–0.5 mm). The liquid is fragmented in droplets before its vaporization. In order to reduce the energy consumption during liquid vaporization, alcohol-based suspensions can be used, provoking combustion with air. Free particles are then molten and accelerated similarly with the APS process before flattening onto the substrate. The use of thinner particles than for APS imposes lower standoff distances (30–50 mm) to prevent an in-flight re-solidification of molten nanoparticles [5]. The low size of the particles used for the SPS process induces new coating build-up mechanisms leading to unusual microstructures for thermal spray-like columnar microstructure [38].

Suspension Plasma Spraying is of high interest due to the following advantages:

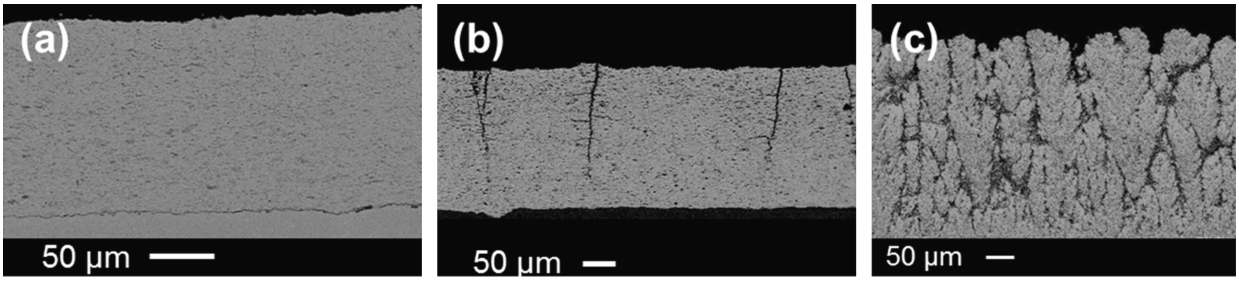

**Fig. 8.** Illustration of homogeneous (a), vertically cracked (b), and columnar (c) microstructures obtained by SPS (courtesy of CEA).

- SPS allows us to perform various morphologies of coating microstructures: homogeneous, vertically cracked, dense and columnar (see examples in Fig. 8);
- SPS features porous coatings with multi-scaled porosity;
- SPS can create thin film coatings (a few micrometers);
- SPS can spray various compositions of materials by using a solution of precursors or powders in suspension.

On the other hand, the Suspension Plasma Spraying process presents also some drawbacks:

- the deposition rate is significantly lower than conventional plasma spray processes (2–3 times lower);
- the lower standoff distance could induce an overheating of the coated component part, requiring a specific cooling system (for example, cryogenic cooling), and also could limit the movement of the plasma gun in front of a complex coated component.

The ability of SPS to perform porous coating (usually 10–30%) with multi-scaled porosity appears to be interesting for energy and biomedical applications. For example, SPS coatings could improve the performances of Solid Oxygen Fuel Cell (SOFC) as an electrolyte and enhance their biocompatibility for medical prostheses.

In the aeronautic field, SPS is close to its industrial expansion with SPS thermal barrier coatings (TBCs) and/or SPS environmental barrier coatings (EBCs) used for the protection of hot section parts of gas turbine engines. Indeed, the unusual columnar structure obtained by SPS is particularly interesting for the protection of Nickel-based super alloy turbine blades and vanes. The main aeronautic OEMs (Original Equipment Manufacturers) develop TBCs using SPS for improved properties (thermal lifetime, thermal insulation) at low cost compared to the standard coatings performed by EB-PVD (Electron Beam-Physical Vapor Deposition).

Suspension Plasma Spraying is close to become a mature coating process, mainly supported by aeronautical developments on TBC. Indeed, this process allows various coating morphologies and can be easily added to industrial thermal spray facilities. These technical developments are supported by plasma spray manufacturers with plasma gun and suspension delivery systems as well as thermal spray powder manufacturers with commercial suspensions ready to use.

### *3.2. Cold Spray for dense ductile coatings*

The Cold Spray (CS) process was developed in the mid-1980s by scientists from the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences (ITAM of RAS) in Novosibirsk, Russia [39]. The goal was to deposit a large range of ductile materials onto different substrates in an economic way. The principle is still the same, while the devices have been improved during these nearly forty years. Readers who want to go further can refer to the following references [38,40,41].

Cold Spray is a kinetic spray process, utilizing supersonic jets of compressed gas to accelerate particles to high velocities. Fig. 9 shows the typical principle.

Issuing from the powder feedstock, the particles (typically 5–50 μm) are injected in a high-pressure low-temperature gas flow (nitrogen, helium or mixture from 0.4 – low-pressure device – to 5 MPa – high-pressure device – from 300 K to 1400 K) before traveling to a de Laval type nozzle. At the nozzle exit, the solid ductile particles, in motion at velocities between 300 and 1500 m/s, plastically deform on impact with the substrate, and consolidate to create a coating. However, it implies that particle velocities at impact are higher than a so-called critical velocity (see Fig. 10), which depends on particle material, size, and morphology.

The Cold Spray (CS) process is of high interest due to the following advantages:

- CS is well suited for deposition of a large range of materials (temperature-sensitive, oxygen-sensitive and phase-sensitive materials) because of the low deposition temperature;
- CS of metals generally enhances fatigue resistance because of the micro “shot-peening” effect, with generally compressive residual stresses in the resultant deposits;

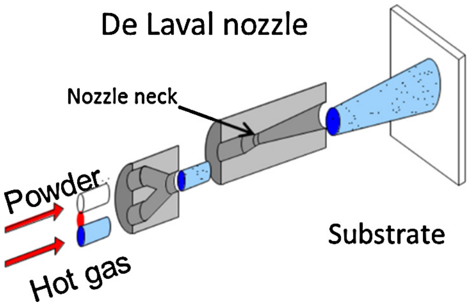

**Fig. 9.** Principle of Cold Spray, including a de Laval nozzle type.

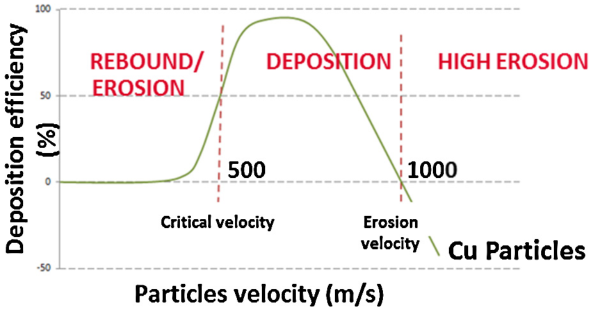

**Fig. 10.** Behavior of impacting Cu particles upon substrate depending on the velocity.

- metal CS deposits have microstructures with high degrees of consolidation similar to wrought alloys due to intrinsic high-energy low-temperature features;
- CS deposits present higher density and reduced presence of oxide phases;
- CS has significantly great deposition efficiency (DE), depending on the material properties;
- CS presents small spray beam and so offers more precise control over the area of deposition onto the substrate (less need for masking of the as-sprayed part);
- CS generally increases the possibility of dissimilar materials joining because of less heat input into the substrate, which makes the substrate material to be of lesser importance;
- a high velocity of coating building can be obtained (up to 1 mm/pass);
- a strong bonding between the metal matrix and the dispersant.

On the other hand, the Cold Spray process presents some drawbacks:

- depending on the both materials, powder and substrate, this couple can present a high level of residual stresses (due to shot peening), which requires heat treatment for tension decreasing;
- all the materials cannot be deposited due to a too high hardness, for example, leading to a too high critical velocity and so a weak DE.

E. Lugscheider [42] has emphasized the broad variety of feedstock materials used in cold spray and so the potential applications successfully used:

- against corrosion and wear;
- for repair, especially magnesium parts;
- for electromagnetic interference shielding;
- for demanding electric, electronic, or thermal applications as well as efficient deposition of soldering or brazing alloys;
- for conducting structures on nonmetal composite layers.

For some years, the Cold Spray process also appears as an attractive opportunity for free standing near-shape parts by additive manufacturing [43] (because of the high deposition efficiency, high coating-building velocity, and numerical increasing possibilities between design computer and robot).

Cold Spray processes are emerging technologies that address shortcomings of the other thermal spray processes. Their main interests lie in their ability to spray high-purity materials, with no modification of the oxide content of sprayed metallic powders, and to make coatings with properties close to those of wrought materials and localized deposits for repair purposes.

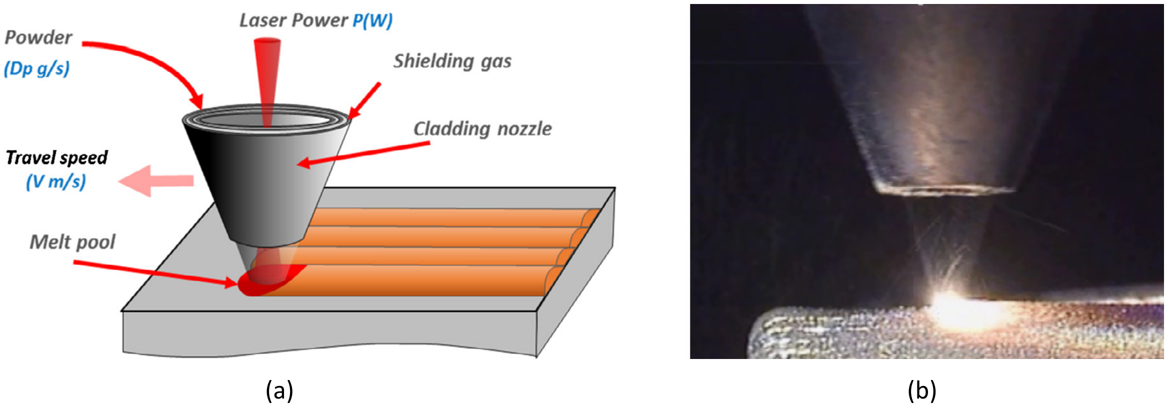

**Fig. 11.** Illustration of the laser cladding principle (a) and picture of the cladding nozzle and (b) of the melt pool during operation.

However, such processes can only spray ductile materials (metals, alloys, cermets). Since 2006, new investigations are devoted to ceramic coatings cold sprayed, achieved by spraying agglomerated nanometer-sized particles. The best results are obtained with helium as the spray gas, but the increasing cost of deposition leads to spray in a closed vessel (for recycling 90–95% of the gas used). That is why developments are also carried out with nitrogen as the working gas.

### *3.3. Laser cladding for combinatorial synthesis and graded materials*

Laser cladding was developed at the end of 1970s along with the development of laser technologies for material processing applications. With the increase in laser beam capacity enabling the melting of materials, this process was optimized and used to generate thick and dense deposits of heterogeneous material on a substrate surface. The resulting materials are characterized by improved physical properties of their surfaces as wear, corrosion resistance or thermal barriers. Initially developed for coating applications, laser cladding was extended to manufacture 3D shapes.

The laser cladding process consists of a spray of a concentrated powder flow under a laser beam on a substrate surface. The melting of the powder and of the upper part of the substrate surface layer generates a melt pool. The progressive movement of the cladding nozzle results in the production of a solidified layer of additional material with a typical thickness from 100 µm to some millimeters (see Fig. 11). Instead of powder, a filler wire can also be used as material provision.

Laser cladding has several advantages:

- fine control of the melting zone and associated fusion processes, thanks to the capability of controlling energy deposition;
- large treated zone allowing thin or thick deposits thanks to the variation of the laser beam properties;
- production of materials with very fine microstructure due to fast solidification;
- production of dense and heterogeneous materials;
- large range and type of materials (metals, ceramics [44] and polymers).

In the framework of cladding processes, laser cladding can be compared to other welding type processes as Plasma Transferred Arc Welding (PTAW), where the fusion energy is provided by an electric arc. If PTAW is a commonly used process for manufacturing thick coatings, the range of the treated zone is limited compared to laser. Moreover, the PTAW allows only high deposition rates from about 1 mm layer thickness and induces deep dilution zones. Finally, the obtained microstructure is typically coarser than the microstructure synthetized by laser process.

Thanks to the high versatility of the laser fusion energy, a large range of applications can be envisaged:

- deposition of hard facing materials for wear resistance (Fig. 12) [45,46]. Using laser cladding leads to generate coating of high quality: controlled geometry and dilution, thin microstructure, high hardness...
- deposition of near-shape geometries (Fig. 13). Laser additive manufacturing allows thin deposition and its capability to build accurate structures is adapted to repair conditions (optimization of the repair time, thermal cycles and induced stress...);
- possibility of mixing several materials with various chemical compositions. The different powders are directly injected from different powder feeders and are mixed into the nozzle before simultaneous melting. This specific process allows manufacturing metallic-matrix composite materials;
- possibility of a continuous variation of the chemical composition of the deposit by varying the feeding rate of different powders. This technique can be used to produce graded materials in 3D [48]. This is particularly interesting for difficult bounding situations, as adaption of differential dilation coefficients between the substrate and the coating materials

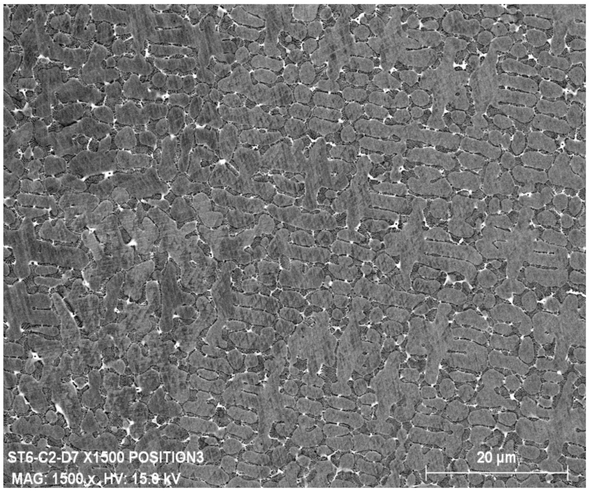

**Fig. 12.** SEM observations of thin Stellite 6 microstructure obtained by laser cladding.

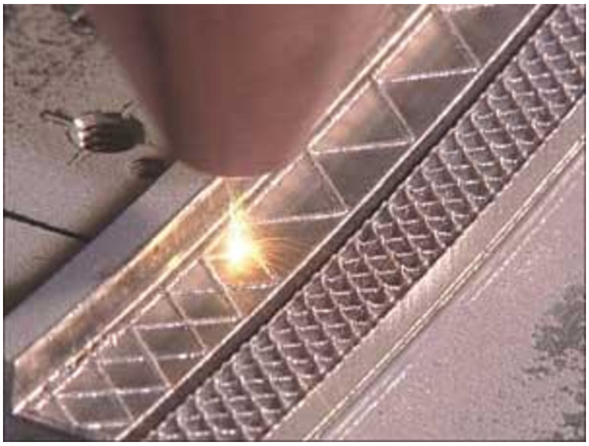

**Fig. 13.** Laser additive manufacturing is used to build the thin walls for the lattice on an aerospace component. The lattice is filled with a ceramic to form a seal against the blade that rubs against it (reproduced from [47], courtesy of Rolls-Royce).

or metallurgical incompatibilities (direct synthesis of a specific intermediate layer). By extension, the laser cladding process enables the production of metallic materials by using a combinatorial methodology. The evolution of the composition by controlling the powder flows of different powder feeders allows generating a large range of alloys in a single experimental campaign.

Although this process has been developed for about 40 years and is now a widely used process to produce material surface with improved physical properties, laser cladding has to be considered as a key opportunity in the research field dedicated to materials engineering. The adaptation of this process to the recent development performed in the metallic additive manufacturing domain allows considering a large range of potential applications as repair and 3D graded materials.

## 4. Concluding remarks

Surface engineering is emerging as a strategic discipline in the field of high-performance metallurgy. Originally developed to protect components against the aggressive environments where they work, it is more and more often used to functionalize them by activating their surface regarding specific physical or chemical phenomena. Photocatalytic, anti-bacterial or anti-biofouling surfaces are developed, for example, respectively in the fields of air and water depollution and marine energies. Surface engineering also provides low-cost metal substrates with high added value like metallic surfaces covered with thin-film photovoltaic cells for solar thermal applications.

The few examples of emerging technologies and applications presented in this article demonstrate that through the constant evolution of surface treatment processes, it is possible to propose innovative solutions, including for the most stringent industrial sectors of high performance metallurgy. The development of HiPIMS PVD processes, or the integrated use of metalorganic precursors in order to lower the CVD deposition temperatures and make the process compatible with thermo-sensitive substrates really illustrate how these technologies penetrate application sectors that were until now proscribed. This is particularly the case for nuclear energy for more efficient and robust fuel developments in an accident scenario but also in the field of fuel reprocessing with extremely severe corrosive environments.

The controlled integration of nanomaterials, as in thermal spraying technologies with the development of processes employing nanopowder suspensions, as well as deposition of nanocomposite thin films with PVD thanks to nanoparticle production cluster hybridization constitutes a strong milestone. It is now possible to produce nanocomposite thin films by choosing independently the nanoparticles and the matrix nature, which opens a very large spectrum of potential applications and new perspectives for surface engineering.

Another emerging way of innovation is about technological hybridization. Such combinations first meet economic as well as technical needs, thus allowing one to take advantage of the best of each process. Coupling arc PVD with magnetron PVD or HiPIMS, PVD with PECVD in the same device is no longer rare. However, some couplings are more innovative and lead to real breakthroughs in terms of coating performances. PVD and ALD coupling illustrates perfectly this synergy, in particular for increased performances against corrosion due to the healing effect of ALD layers.

Other drivers arise and will become accelerators in future years for surface engineering technologies. A good example is the swift development of 3D printing technologies allowing one to generate topologically optimized components, often with complex or porous alveolar architectures that must be protected from aggressive media or must be surface functionalized. The finishing technologies of additive manufacturing parts must also be developed to minimize the impact of all the defects appearing during the 3D printing step. It is for instance the case of the development of electrolytic plasma polishing technologies.

Finally, new methodologies and numerical tools enable much faster development of functional coatings and deposition processes. High-throughput approaches such as combinatorial synthesis and artificial intelligence contribution have just started to rapidly optimize complex processes, thanks in particular to the use of neural networks.

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