

Advanced Coating Technologies: Thermal Spray, Physical Vapor Deposition, Chemical Vapor Deposition, and Sol-Gel Applications

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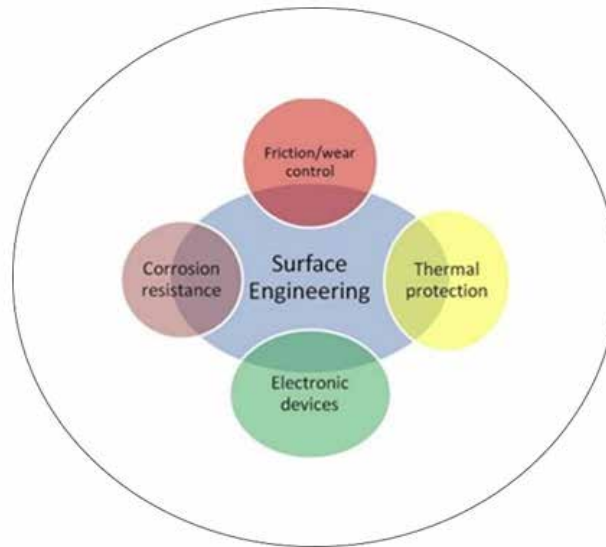
Introduction

Importance of surface engineering

In recent years, there has been significant progress in the advancement of methodologies for surface protection, with the primary objective of ensuring optimal preservation of substances. The selection of protection is dependent on the surrounding environment, the conditions of utilization, and the compatibility with the substrate's material. A multitude of surface treatment methods have been proven to be efficacious for protecting surfaces and achieving other operational objectives, and these methods are already in industrial use (El-Awadi, 2023). The term “surface engineering” refers to the methodical design of engineering components with the objective of enhancing their performance within operational contexts. This objective can be realized through surface treatments, which have the capacity to generate combinations of surface and bulk properties that are not attainable in a single material (Gawne, 1993). Surface engineering is a multidisciplinary topic that encompasses numerous branches of science related to materials science, chemistry, and physics. The present focus of multidisciplinary teams is on the research and advancement of innovative materials and coatings, with the goal of augmenting their mechanical, electrical, electrochemical and antibacterial characteristics (Rokosz, 2022). As illustrated in Figure 1, the applications of surface coatings are evident.

Figure 1

The utilization of surface engineering in diverse disciplines (Prashar et al., 2020).



Surface engineering can be broadly categorized into two main approaches: physical and chemical. Physical techniques are defined as the utilization of heat or energy in order to modify the surface. The following are examples of such techniques: thermal spray coatings, chemical vapor deposition (CVD), physical vapor deposition (PVD), and laser surface engineering. It is evident that these techniques offer significant versatility in the tailoring of surface properties. This includes, but is not limited to, hardness, adhesion, and surface texture. Consequently, they have the capacity to meet specific requirements. In contrast, a range of chemical techniques have been shown to offer a means to control surface deposition and modify the material chemically. Examples of these techniques include electroplating, electroless plating, sol-gel coatings and chemical etching. It has been evidenced that this process can lead to enhancements in a number of areas, including corrosion resistance, biocompatibility and functionalization. Surface engineering is crucial to industry. It enhances performance, protects materials against the environment and develops functionality. Considerable progress has been made in the field of surface engineering. However, challenges persist due to complex processes, precise parameter control and scalability issues for large-scale production. A number of other considerations must be taken into account, including the integration of surface engineering with other fabrication techniques and the question of cost-effectiveness. Emerging trends and technologies hold promise. The employment of sophisticated computational modelling and simulation techniques has the capacity to expedite the conceptualization of engineered surfaces that demonstrate customized properties. The exploration of new materials, such as graphene, opens up possibilities for advanced coatings and functionalized surfaces (Ramezani et al., 2023).

In order to comprehend and appraise the efficacy of surface engineering processes, a range of characterization methods is utilized. The application of microstructural characterization

methodologies, incorporating scanning electron microscopy, X-ray diffraction, and transmission electron microscopy facilitates the exploration of surface morphology, phase composition, and crystallographic structure. The analysis of surface topography can be facilitated by a variety of instruments, including atomic force microscopy (AFM), scanning tunnelling microscopy (STM), and surface profilometry. The utilization of these instruments facilitates the accurate measurement and visualization of surface characteristics, including but not limited to roughness, texture, and feature dimensions. Mechanical and tribological characterization methodologies (e.g. hardness, wear and friction, scratch and indentation testing) reveal how surfaces perform mechanically. (Ramezani et al., 2023). In this context, coating technologies represent a significant application area of surface engineering.

Coating technologies and their classification

The field of tribology and wear protection of coatings has seen considerable research activity and rapid progression in recent years. The impetus for this development has chiefly arisen from the advent of innovative coating materials, structural configurations and manufacturing technologies. The evolution of coating techniques has been a gradual process, with various methodologies being developed over the course of several decades. In conclusion, it is evident that coating technologies constitute a pivotal component within contemporary manufacturing, offering a wide variety of applications across various industrial sectors. It covers and involves many research fields. Continued innovation within the field of coating technology, driven by advancements in coating materials and deposition methods, is anticipated to have a transformative impact on industry and academia alike, giving rise to novel products and applications. It is therefore vital that investigation and advancement in this domain is pursued in the future; any significant advance in this area will merit close attention from all research communities. (Ma, 2023).

The field of coating technology represents a significant and encouraging area of research in the domain of surface engineering, with considerable potential for application in future industrial contexts. The development of coating techniques has resulted in coatings becoming an integral component of industrial manufacturing. These coatings possess a range of advantageous properties and characteristics, including super hydrophobicity and self-cleaning capabilities, augmented biological antibacterial properties, and enhanced corrosion resistance (Chen et al., 2024).

Evidently, the utilization of coating has undergone a significant transformation, becoming a pivotal technique for enhancing the efficiency and value of materials. The process of surface coating is both reliable and cost effective. It finds application in the fabrication of various instruments, materials, and components of machinery. The requirement for the desired surface properties, including resistance to corrosion, erosion, and wear,

is pivotal in this process. The primary objective of coating application is typically categorized into two broad categories: decorative and functional. The enhancement of surface characteristics, including adhesion, erosion, corrosion and wear resistance, can be achieved through the utilization of functional coatings. In the contemporary era, a plethora of coating methodologies are employed to attain the desired functional or decorative characteristics (Pattankude & Balwan, 2019).

The process of applying a coating to an object surface is known as ‘coating’, with the object itself being designated as the ‘substrate’. The coating may be applied in a manner that ensures comprehensive coverage of the substrate, or alternatively, the substrate may be coated in a selective manner, with specific regions of the substrate receiving the coating and others remaining uncovered. Coating may be delineated as the application of a protective layer to the surface of an item. The application of coatings is a common practice that is employed for the purpose of modifying the surface characteristics of the substrate. The overarching goals of the process are threefold: firstly, to modify the substrate’s appearance; secondly, to enhance adhesion; and thirdly, to augment corrosion resistance and improve wear and scratch resistance. Industrial coatings are defined by their function as a protective barrier rather than their aesthetic properties. Nevertheless, it is imperative to acknowledge their capacity to confer aesthetic value. The most common materials utilized in the domain of industrial coatings include ceramic, Al_2O_3 , acrylic, polyester, polyurethane, epoxy and silicone (Pattankude & Balwan, 2019).

A plethora of coating methodologies and materials are at one’s disposal to suit diverse coating applications, with a shared objective of safeguarding parts or structures against the detrimental effects of mechanical or chemical damage. One advantage of this protective function is that it engenders a decrease in manufacturing costs, since the fabrication of new parts is not required. Nonetheless, coating methods have a role in specific applications, depending on the desired functionality. The most significant applications are protection against corrosion and wear. It is vital to recognize that, despite the plethora of available processes, only a limited number of these have been proven to be effective and applicable in the field. The most notable methods comprise the following: PVD, CVD, thermal spray, sol–gel processes, micro-arc oxidation, and polymer coatings. The suitability of each method is dependent upon the desired application, with the options available including varying deposition methods, materials, second phases, thickness, and densities. The selection of materials is paramount to the success of coating, as they provide protection. It is acknowledged that a wide variety of materials, encompassing those of metallic, ceramic and polymeric nature, can be employed to form a protective layer (Fotovvati et al., 2019).

The engineering components have been utilized in a variety of applications, encompassing, but not restricted to, the domains of aircraft, power generation, the marine industry, the

chemical industry and the paper industry. These components have demonstrated a high degree of reliability when employed in a range of extreme environmental conditions. The principal concerns that emerge in the context of performance wear, such as corrosion and erosion, or their combinations, result in a reduction in the components' service life. Coating techniques are utilized to prevent surface degradation through either overlay or diffusion processes, with compositions tailored to meet specific functional requirements. A plethora of coating methodologies are at one's disposal for the purpose of averting the deterioration of surfaces (Pradeep et al., 2022).

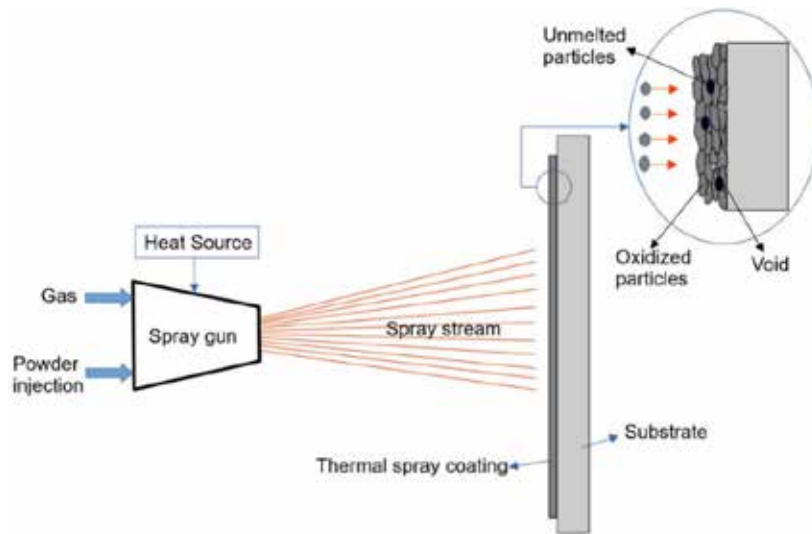
The present study examines the coating methods in question in terms of their basic principles, materials used, application areas, and advantages and disadvantages. The aim of the present study is dual: initially, to provide practical information for engineering applications, and secondly, to furnish in-depth technical content for researchers. Consequently, the current study makes a notable contribution to the advancement of the field, facilitating the selection of suitable advanced coating technologies and ensuring their effective application.

Thermal Spray Coating

Thermal spray processes constitute a significant and rapidly expanding category of surface modification technologies. A broad range of solid feedstock materials is employed, encompassing metals and alloys, hard metals, ceramics, and polymers, predominantly in the form of particulate matter, wires, and suspensions. Hard metals constitute a substantial category of materials that undergo processing by thermal spray processes in order to be applied as coatings. The formation of coatings is contingent on plastic deformation of the feedstock particles at the instant of impact, which is preceded by acceleration within or without the spray gun. The majority of thermal spray processes are accomplished through the partial or complete melting of the feedstock material. During the spraying process, the substrate remains unmelted. The splats adhere to the substrate primarily through mechanical bonding. The utilization of thermal spray technology facilitates the realization of the functional properties of hard metals on the surface of large components, which are not feasible through powder metallurgy processes due to technical and economic constraints (Berger, 2015). Figure 2 provides a schematic representation of the thermal spraying technique.

Figure 2

Schematic depiction of the thermal spray coating process (Ramezani et al., 2023).

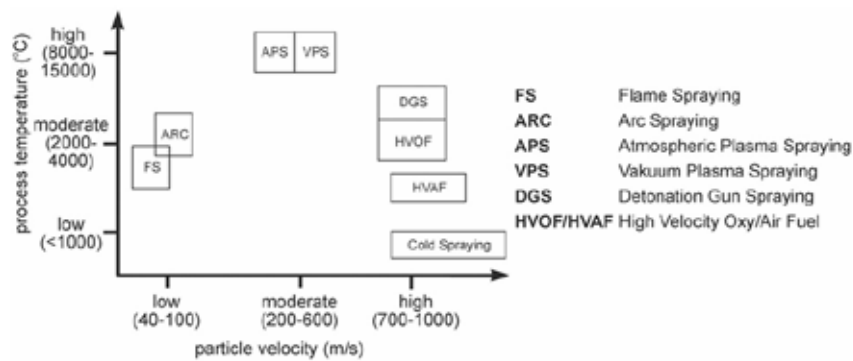


A plethora of materials are utilized in thermal spray processes for the purpose of developing coatings on solid substrates that demonstrate resistance to elevated temperatures. Thermal spray coatings characteristically possess a rough and porous texture. In comparison with conventional surface treatment technologies, they exhibit enhanced reliability, particularly with regard to mechanical properties and their applications in protection. Thermal spray processes are classified based on their energy source (electrical or chemical) and are employed in a variety of fields (aviation, energy, medicine, marine etc.) to develop coatings with different properties. In the field of additive manufacturing, specific thermal spray methodologies have proven effective in the creation of standalone components and the remediation of damaged elements. The high-velocity techniques of HVOF (High-Velocity Oxygen Fuel) and HVAF (High-Velocity Air Fuel) are characterized by their classification as high-velocity techniques, in conjunction with moderate temperatures ranging from 2000 to 4000 °C. Conversely, cold spray technology is contingent on the mechanical deformation characteristics of metallic powders operating at low temperatures, often below 800°C and approaching recrystallisation temperatures. It is mostly used on ductile materials. In contradistinction, plasma spray is a high-temperature process that has been demonstrated to yield dense coatings. This method is highly applicable to ceramics. Arc and Flame Spray (FS) are relatively slow processes. Arc can produce large throughputs/thick coatings. Thermal spray processes are also used for surface repair, rebuild, and clearance control, as well as to change the friction factor. Manufacturing items like prostheses and gas turbines heavily rely on thermal spray technologies. For example, plasma spray is used to apply hydroxyapatite ceramic coatings for bone bonding on prostheses. The utilization of thermal barrier coatings is of paramount importance in the context of high-temperature operations, wherein their function is to ensure the effective management of clearance within gas turbines. It is evident that thermal spraying is employed in a variety of

materials (Guduru et al., 2022). The various thermal spray processes can be delineated in relation to parameters such as particle velocity and process temperature, as demonstrated in Figure 3. (Berger, 2015)

Figure 3

Schematic depiction illustrating the interrelation between process temperature and velocity for the various spray processes (Berger, 2015)

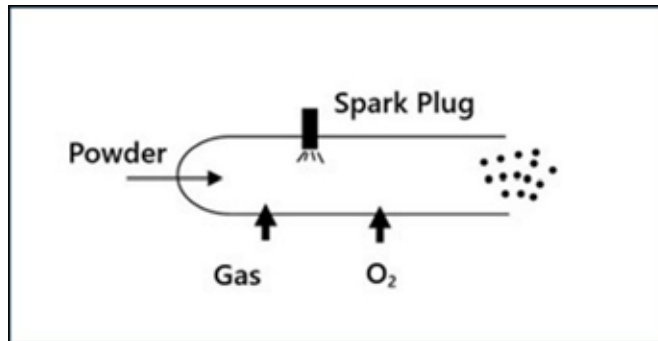


Various thermal spraying processes

A. Detonation Gun: Gas detonation has been evidenced as a means of producing optimal levels of velocity, pressure, and density within the gas flow, thus outperforming other spraying techniques in these regards. Consequently, the coatings resulting from this process are distinguished by their markedly high density and microhardness, in addition to their low porosity. It is evident that the aforementioned properties render the coatings optimal for utilization in scenarios necessitating the most stringent quality standards. For instance, they are particularly well-suited to the fabrication of aircraft engine components. The process of coating materials onto the substrate surface using the detonation gun (D-gun) involves the combustion and subsequent expansion of the fuel (normally oxygen and acetylene) to generate a jet which, in turn, melts and propels the coating materials. The initiation of detonation is affected by the spark ignition of gas in a gun. This procedure is distinguished by its comparatively reduced operational expense when juxtaposed with more prevalent HVOF and plasma spray methodologies. Within the specified parameters of the configuration, the gases are introduced into the chamber of combustion at a pressure that is marginally higher than the standard atmospheric pressure. The overarching objective of this process is to deposit coatings with a thickness of approximately 250 μm or less, with a view to enhancing the wear resistance of components that are subjected to extreme service conditions (Talib et al., 2003). As demonstrated in Figure 4, this occurrence can be observed empirically.

Figure 4

Detonation Gun (Talib et al., 2003).



B. Atmospheric plasma spraying (APS): The APS process employs thermal plasma as the heat source for the deposition process. These plasmas are produced by means of direct current arc or radio-frequency discharge. It has previously been established through empirical observation that such conditions permit temperatures in the flames to exceed 8,000 K, with peak values of up to 14,000 K at the jet core. The velocities of particles range from 20 to 500m/s, contingent upon the distribution of the particles' sizes. The elevated temperatures of the process cause a significant percentage of the material to melt, which, in combination with the comparatively high velocities, results in the production of coatings that exhibit superior deposition densities, bond strengths and reduced porosity when compared to the majority of thermal spraying processes. The utilization of APS has been demonstrated to yield coatings that exhibit a high degree of cost-efficiency and quality. This facilitates their successful implementation in multiple industrial domains (Tejero-Martin et al., 2019).

C. Vacuum plasma spraying: The development of plasma spraying in controlled environments can be traced back to the late 1960s, with the primary objective of mitigating the deleterious effects engendered by the interaction of the in-flight heated particulate matter in the surrounding environment. Such adverse effects comprise oxidation and unwelcome contaminants in the coatings. The employment of low and very low pressures has been evidenced to be conducive to the advancement of thermally sprayed coatings of a high quality. The pressure levels employed in these processes vary considerably. In the case of low-pressure plasma spraying (LPPS), pressures are typically in the range of 4,000 Pa to 40,000 Pa; however, in the domain of very low plasma spraying (VLPPS), pressures can reach as low as 100 Pa. In the event of a value falling below this threshold, the designation employed is that of vacuum plasma spraying (VPS). This approach has been evidenced to produce coatings with porosity levels as low as 1%, exhibiting columnar structures comparable to those attained through physical vapor deposition (PVD). Moreover, it has been established that this method engenders an enhanced deposition rate in comparison with PVD techniques (Tejero-Martin et al., 2019).

D. Cold spraying: The process of kinetic or cold spraying, as the nomenclature suggests, is predicated on the transfer of elevated levels of kinetic energy into the constituent particles of the feedstock. The purpose of the process is to achieve the required bond strength upon impact at the surface of the substrate. This is an antithetical phenomenon to the customary usage of heat transfer evident in alternative thermal spray technologies. The process under discussion allows deformable powder particles of a ductile nature to be deposited without the need for the conventional melting process, followed by a rapid impact step, with subsequent solidification of the resultant material. This method of powder deposition effectively reduces residual stresses and also reduces the incidence of in-flight oxidation of the particles. The fundamental principle of the process entails the utilization of pressurized gases with diminished oxidation potential, such as helium or nitrogen. The gases are exposed to moderate heating, typically below the melting point of the feedstock particles (up to 1000K), in order to enhance gas flow velocities, as opposed to heating the particles themselves. Once the required pressure and temperature conditions have been met, the gas is guided through a de Laval nozzle, thereby accelerating it to velocities that surpass the speed of sound (up to 1,200 meters per second) as it undergoes an increase in temperature during the process of expansion. It has been deduced that this process facilitates the achievement of temperatures that are lower than ambient temperature on occasion. The resulting coatings exhibit the same phase content as the powder feedstock, devoid of oxide contamination and characterized by low porosity. The coatings demonstrate a propensity for compressive residual stresses, a notable deviation from the tensile stresses typically observed in other thermal spray technologies. Additionally, the coatings exhibit low ductility, a consequence of the extensive work hardening that occurs during the deposition process (Tejero-Martin et al., 2019).

E. Flame spray: Flame spraying is an industrial process that has existed for over a century, during which time its technology has remained relatively unchanged. In essence, the process involves the injection of oxygen and fuel (acetylene or propane) through a nozzle. The combustion of the gaseous mixture occurs prior to the occurrence of a flame by the nozzle. The flame temperature fluctuates within the range of 3000 to 3300 °C, contingent upon the oxygen-to-fuel ratio. The feedstock materials utilized can be in powder or wire form. The process under discussion involves the deposition of materials such as nickel- and cobalt-based alloys, certain refractory metals, ZrO_2 , Al_2O_3 , TiO_2 , and Cr_2C_3 , all of which are deposited in a NiCr matrix. The spray process is adaptable, portable, and has a low capital cost. The implementation of this methodology is a prevalent technique in the synthesis of coatings characterized by elevated levels of porosity. As demonstrated in previous research, the flame spraying process has been shown to require less energy and to be more economical than other thermal spray processes. Nonetheless, it has been shown to lack corrosion resistance. Conversely, the pre-oxidized portion exhibited no

discernible response to air oxidation. The porosity of the finishes exhibited a marginal effect on the oxidation of the air. It has been proven that elevated levels of in situ oxides and pores in flame-sprayed coatings have a deleterious impact on the efficacy of the process when it is employed in high-temperature applications (Qadir et al., 2024).

F. Arc Spray: Arc-Spray (Wire-Arc) involves the utilization of direct current arc between two conducting wires for the purpose of melting consumable wires. The wires in question are found to be electrically charged, exhibiting opposing polarities. They are then fed into the arc gun. The wires are motorized and fed into the spray torch. It has been established through documented evidence that the presence of opposing charges on the wires has the capacity to generate sufficient heat to cause the melting of the wire tips. This phenomenon is a consequence of continuous exposure to the heat generated. The subsequent process of atomization, involving the use of gases such as air, argon and nitrogen, propels the droplets towards the substrate surface. This process has been demonstrated to exhibit higher deposition rates in comparison to HVOF and plasma spray (Talib et al., 2003).

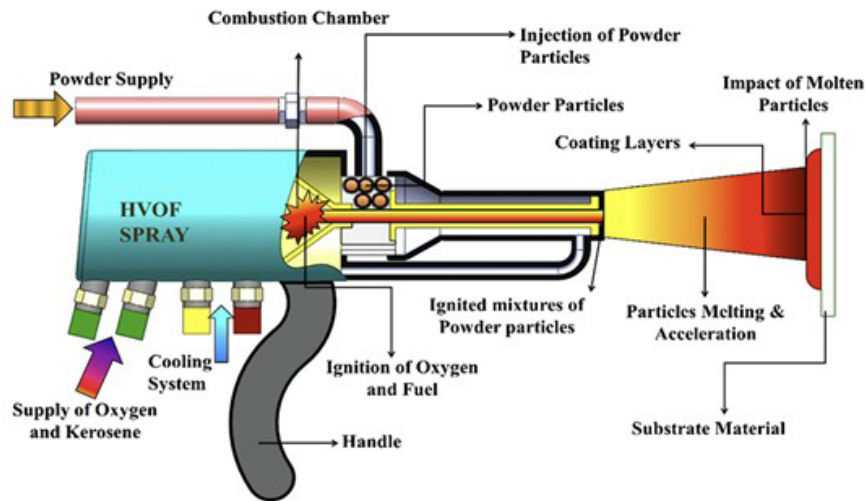
G. High-Velocity Oxy-Fuel (HVOF): In the HVOF coating technique, the particles are initially dispersed into a stream of combustion gases, whereas they are subsequently sprayed and deposition occurs onto the surface of the base material. The fabrication of this HVOF spray gun was undertaken with the specific purpose of withstanding the multiple shocks that are typically present during the combustion process. Subsequently, the flame exits the nozzle, undergoes unimpeded expansion, and produces a supersonic jet characterized by elevated kinetic energy. The HVOF coating has the following properties. Firstly, it possesses low porosity and high hardness. Secondly, it exhibits strong adhesion due to its high impact particulate speeds. Thirdly, the process temperature is comparatively low when it is compared to the flame and plasma spraying process. Furthermore, HVOF spray methods have the capacity to deposit a variety of materials, including ceramic powders, polymers, composites, metals and alloys, such as Inconel, Tribo-alloy and Hastelloy. The HVOF technique is distinguished from conventional thermal spray deposition processes through its utilization of lower temperature heating and the discharge of powder molecules at extremely high velocity over the substrate to form coatings that are both thicker and more dense. As illustrated in Figure 5, the working principle of the HVOF thermal spray process is schematically represented.

HVOF coating techniques have a proven record of superiority over other thermal spraying techniques and are especially suitable for the application of cemented carbides and associated coatings. It has been demonstrated that high-speed particles impacting upon a substrate surface can lead to the formation of coatings exhibiting a high degree of density and uniform distribution. The presence of condensed splats is a hallmark of these coatings. The primary advantages of HVOF thermal spraying over other methods

are its high particle velocity and relatively modest thermal energy dissipation during the spraying process (Sathish et al., 2023).

Figure 5

Schematic illustration of the HVOF thermal spray process (Sathish et al., 2023)

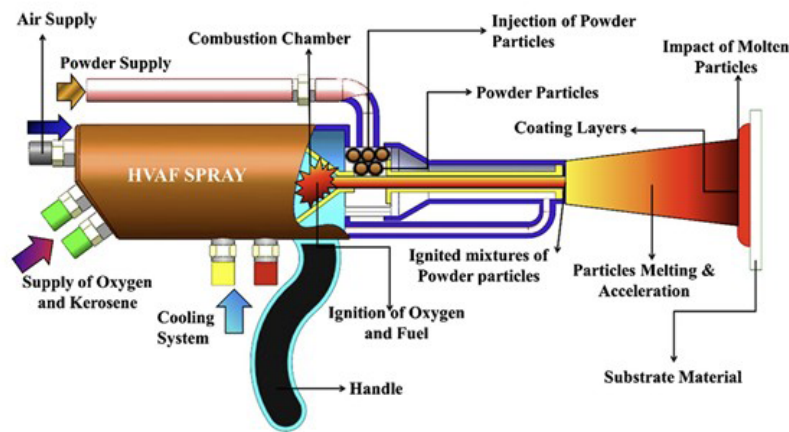


H. High-Velocity Air–Fuel Process (HVAF): The HVAF process represents a thermally sprayed coating approach that operates at a lower combustion temperature due to its utilization of compressed air. This method incorporates a streamlined design, obviating the need for water-cooling mechanisms, and consequently results in reduced running costs. It is within the combustion compartment that the HVAF process is initiated, with the objective of combusting a mixture of compressed air and fuel gas. The HVAF coatings process exhibited significantly superior adhesion properties in comparison to conventional spraying methods, thereby underscoring its efficacy in scenarios where bonding strength is paramount. The utilization of high-velocity spraying technologies, including HVOF and HVAF, has become a prevalent method for the application of hardened coatings. This approach functions as a substitute for the utilization of environmentally detrimental hard chrome, thereby contributing to the promotion of eco-friendly manufacturing practices. These hardened coatings possess wear-resistant properties and enhance the lifespan of the components, thus offering considerable benefits in the context of environmental production. The gas-fuel and liquid-fuel HVOF spray methods both employ the purest oxygen, resulting in a significantly higher ignition temperature in comparison to the HVAF spray process, which functions under highly compressed air. It has been ascertained that, due to the diminished oxygen concentration levels inherent to the HVAF process, the observed particles exhibit a substantially lower temperature in comparison to that of the conventional HVOF process. As illustrated schematically in Figure 6, the HVAF thermal spray process functions in the manner

depicted. In the HVOF process, the temperature of the particulate remains below 1600 K. It is imperative to acknowledge that this is lower than the melting point of stainless steel. It has been hypothesized that controlled oxidation of the coating is an effective method of enhancing chemical homogeneity. In the HVOF process, the particle velocity is typically approximately 700 m/s, which results in minimal porosity and strong adhesion strength in the coating (Sathish et al., 2023).

Figure 6

Schematic view of working principle of HVOF thermal spray process (Sathish et al., 2023)



Physical Vapor Deposition (PVD) Coating

Physical vapor deposition (PVD) is described as the process of extracting atoms from a solid or liquid state via physical processes, which are then deposited on a nearby surface, leading to the formation of a thin film or coating (Gudmundsson et al., 2022). The process referred to as PVD is conducted under vacuum conditions. PVD processes encompass a variety of methodologies, including but not limited to electron beam physical vapor deposition, cathode arc deposition, ion plating, evaporative deposition, sputtering, and enhanced sputtering. The PVD method involves the evaporation of solid coating material using thermal or ion bombardment, the latter process being referred to as sputtering. Concurrently, reactive gas is also introduced, forming a compound with metal vapor and depositing a thin film of highly adherent coating on the substrate. Such coatings are utilized in a plethora of diverse applications. They include the following: the aerospace industry; the automotive industry; the surgical industry; the medical industry; dyes; molds for a range of materials; cutting tools; optics; firearms; textiles; and thin films. It has been established that all PVD methods are effective when it comes to coating surfaces facing deposition flux. The selection of the most appropriate deposition method necessitates consideration of various factors. These factors include, but are not limited to, the substrate type, the thin film material, the necessity for uniformity, and the requirement for thickness control (Shahidi et al., 2015)PVD has the capacity to produce dense and crystalline films at substantially reduced temperatures. It is particularly beneficial in configurations where the interdiffusion of elements between adjacent layers

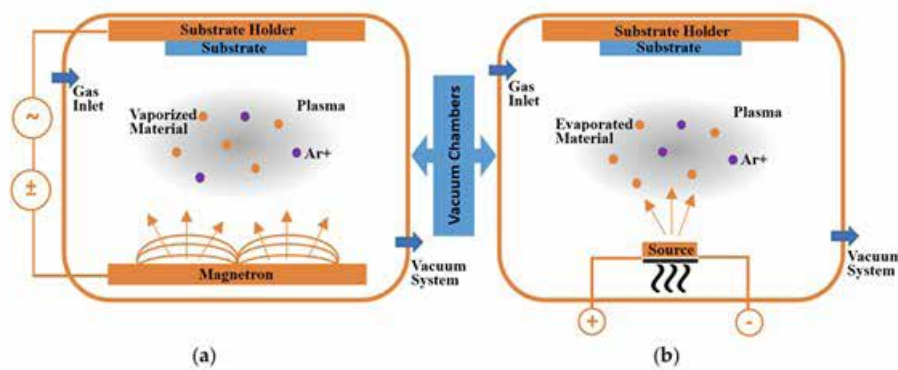
is detrimental and must be prevented. A notable illustration of this is provided by model systems employed to study interfacial phenomena. To illustrate, a sintering temperature of a minimum of 1400 °C is required to achieve the densification of screen-printed yttria-stabilized zirconia, whereas layers of comparable density are attained at 800 °C by PVD (Lobe et al., 2021).

The accumulation of coating materials in the form of molten or semi molten splats is an inherent property of thermal spray processes, a fact that is widely recognized within the scientific community. The processes of PVD are distinct from the thermal spray technology in that they construct a coating from the vapor phase at low environmental pressure ($\sim 10^{-4}$ mbar). The process of applying hot coating material necessitates elevated temperatures, thus ensuring that droplets do not solidify rapidly on a cold surface. The coating material is instead deposited onto the substrate from the vapor. This approach has yielded coatings that exhibit properties heretofore unattainable through conventional thermal spray processes. PVD coatings have been evidenced to manifest a high degree of homogeneity, characterized by a thin, dense, hard, and gas-tight composition. Alternatively, these coatings can be designed with a specially engineered microstructure, offering distinct advantages in specific applications (Von Niessen et al., 2010). The utilization of said techniques facilitates the extraction of particles from the designated target material under conditions of minimal pressure, thus enabling their subsequent conveyance and deposition on the substrate. The reactor utilized in the evaporation process necessitates elevated vacuum pressure levels. It has been established that these characteristics and parameters typically yield reduced atomic energy and diminished gas adsorption within the coating deposition. This outcome indicates that the movement of particles with larger grains leads to a noticeable decrease in the adhesion of these particles to the substrate compared to the sputtering technique. It has been established that during the process of deposition, contaminant particles are released from the melted coating material and subsequently move onto the substrate. The extant literature indicates that this phenomenon has the capacity to engender a diminution in the purity of the resultant coatings. Evaporation is typically utilized for the deposition of films and coatings of greater thickness, with minimal constraints imposed on the surface morphology. Nonetheless, it is imperative to recognize that the evaporation process exhibits enhanced deposition rates in comparison to the sputtering process. Consequently, the sputtering process is regarded as a viable option for applications where the surface quality is of paramount importance, with considerations such as roughness, grain size, and stoichiometry being of greater significance than the deposition rate. As has been shown, the deposition process is contingent upon the presence of certain temperature limitations in specific applications. It can be posited that this occurrence may be attributable to the generation of stress that transpires during the cooling process. The cooling process is dependent on the decrease in temperature or the substrate (polymer) melting point. This has resulted

in the sputtering process becoming increasingly pertinent within the domain of PVD deposition techniques. Furthermore, innovative techniques derived from the sputtering process have been developed to address the constant increase in market demands. The advent of novel coating properties has been precipitated by the emerging of new systems derived from conventional processes, thus aligning with the requirements of both the market and researchers (Baptista et al., 2018). As depicted in Figure 7, the schematic representation of two traditional PVD methodologies.

Figure 7

Schematic representation of two traditional PVD methodologies: (a) sputtering and (b) evaporating utilizing ionized Argon (Ar^+) gas (Baptista et al., 2018)



The capacity to demonstrate flexibility and adaptability in response to market demands has resulted in the development and refinement of techniques for a variety of processes. This has consequently resulted in the proliferation of multiple variants. These techniques are subject to constant evolution and continue to serve as a rich source of inspiration for numerous academic studies. A substantial corpus of literature, encompassing books and articles, has been published which disseminates information regarding these variants. This has resulted in a state of affairs in which it is challenging to quantify all extant techniques. PVD methods are the most frequently employed for the deposition of thin films, with sputtering and evaporation being the most common (Baptista et al., 2018).

Different types of PVD

A. Cathodic arc deposition: The process involves high-power electric arc discharge, which is directed towards the target (source) material, resulting in the blasting away of a portion of the material in the form of a highly ionized vapor that is subsequently deposited onto the workpiece (Shahidi et al., 2015).

B. Electron beam physical vapor deposition: In order to attain the requisite outcomes, the material to be deposited is exposed to an electron beam within a high vacuum environment. It has been demonstrated that this process results in a significant increase in the vapor pressure of the material. Following this process, the material is transported via diffusion and subsequently deposited by condensation onto the cooler workpiece

(Shahidi et al., 2015).

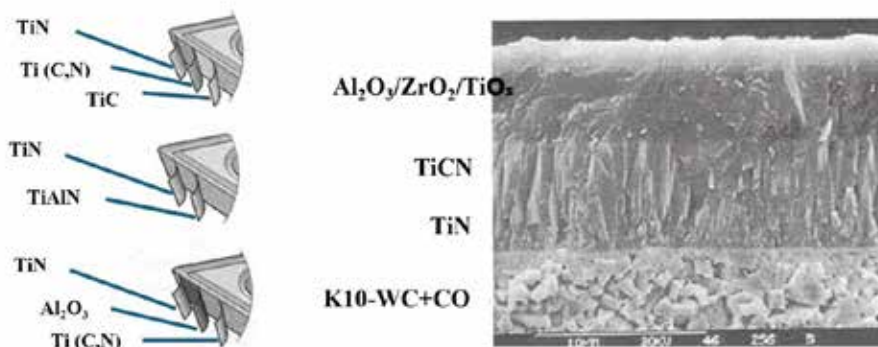
C. Evaporative deposition: The material to be deposited is exposed to an elevated temperature in a state of high vapor pressure, achieved through the utilization of electrically resistive heating within a vacuum characterized by a low pressure level (Shahidi et al., 2015). D. Pulsed laser deposition: The process involves the utilization of a high-power laser, which serves to ablate material from the target, thereby converting it into a vaporous state (Shahidi et al., 2015).

E. Sputter deposition: The plasma discharge, which is characterized by its tendency to emit a glow (and which is typically confined to the area around the “target” by means of a magnet), is responsible for bombarding the material, resulting in the sputtering of some of it away as a vapor for subsequent deposition (Shahidi et al., 2015).

PVD coatings applied to cutting tools offer significant advantages in terms of cutting accuracy, wear resistance, and surface quality. PVD coatings typically consist of hard ceramic or carbide compounds such as TiN, TiAlN, CrN, and AlTiN, which enhance tool wear resistance, thermal stability, and reduce friction coefficients. Coating thickness has been found to range between several hundred nanometers and several micrometers. It is worthy of remark that it remains stable at elevated temperatures; this property improves tool life, cutting force, and drilling efficiency during the machining of challenging materials, such as aluminum, hard metals, and stainless steels. For good adhesion, surface cleanliness, proper dip coating, and anti-wear parameters are important; the coating also improves appearance, chemical resistance, and corrosion protection. However, coating choice depends on tool geometry, workpiece material, and cooling conditions; in some cases, the coating can affect conductivity or brittleness, so a careful design analysis is required during the planning phase. As illustrated in Figure 8, the samples of coatings applied to tungsten carbide cutting tools and microstructure.

Figure 8

Samples of coatings applied to tungsten carbide cutting tools and microstructure (Sandvik Coromant, 2025)



Chemical Vapor Deposition (CVD) Coating

The Chemical Vapor Deposition (CVD) was initially conceived as a pioneering manufacturing process, with the objective of producing a range of engineering products, including nanocomposite ceramic coatings and critical components within multiple industrial domains, such as the semiconductor industry, the ceramic industry and the mining industry. In recent times, the scope of the CVD technique has expanded significantly beyond its original parameters, particularly within the domains of semiconductor and microelectronics industries, as a consequence of extensive research activities across a range of disciplines. The reasons for the uniqueness of the chemical vapor deposition (CVD) technique are manifold. These include the ability to produce highly versatile layers, the possibility of applying nanocomposite ceramic coatings to metals, the ease of semiconductor fabrication, and the opportunity to fabricate layers with organic and inorganic substances. The layers that are produced by the CVD technique are typically crystalline or amorphous in nature. These layers possess a range of properties that can be tailored by means of controlling the production parameters. Indeed, the CVD technique is but one of several ceramic coating deposition techniques that have undergone rapid development in recent years. As is widely accepted within the relevant scholarly community, the CVD process results in the creation of a solid layer on the substrate. This phenomenon can be attributed to a chemical reaction occurring within the vapor phase. As is apparent from the evidence presented, the formation of soot, a by-product of incomplete combustion, has been a persistent phenomenon throughout history. This occurrence has been identified in the context of the CVD technique, thereby indicating a possible correlation between the two processes (Sabzi et al., 2023).

The significance of CVD can be ascribed to the broad spectrum of elements and compounds that can be deposited by this method. It has been determined that such deposits may be formed at comparatively lower temperatures and at ambient atmospheric pressure. The process of depositing films with a high degree of purity is applicable to the following types of films: amorphous, epitaxial, polycrystalline and uniaxially oriented polycrystalline films. CVD includes the chemicals that react, how they react, and how heat and movement work in the reactors. It also includes how materials and energy move in and out of the reactors (Frey, 2015). One of the major benefits of CVD is the capacity to create pure, high melting-point substances at fairly low temperatures. A further benefit of CVD is its considerable throwing power, which facilitates the coating of hidden surfaces, provided diffusion or convection can transport reactants to the area in question. CVD has also been shown to achieve high material deposition rates of tens of micrometers per hour or more (Weimer, 1997).

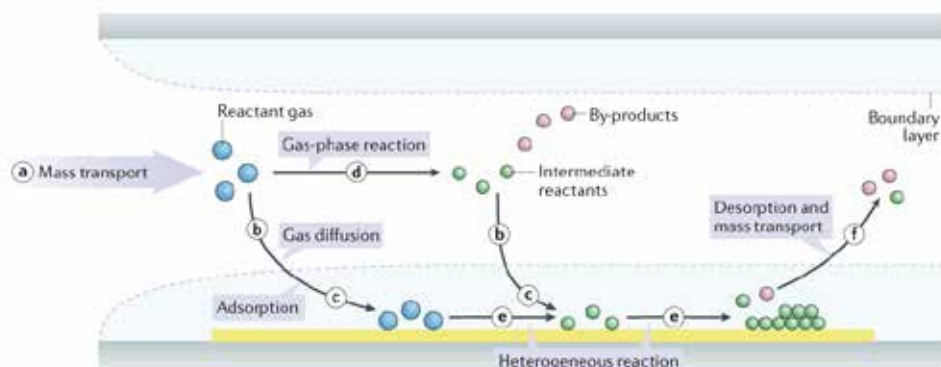
In contradistinction to physical vapor deposition techniques, like evaporation and sputtering, the chemical vapor deposition confers a distinct advantage by virtue of

its reliance on chemical reactions that facilitate the modulation of deposition rates, in addition to the fabrication of products of exceptional quality with unparalleled conformality. CVD facilitates the calibration of the configurations and characteristics of the ensuing artefacts, and a plethora of sophisticated CVD systems and their derivatives have been cultivated, such as plasma-enhanced CVD and MOCVD (metal organic CVD). The requirement of high-vacuum working environments is not a feature of CVD, a factor that leads to its popularity in electronics, surface modification, optoelectronics, and biomedical applications (Sun et al., 2021).

Notwithstanding the variations observed among different CVD types, the fundamental process remains similar in essence and consists of the following common elementary steps (Figure 9). Initially, the reactant gases are conveyed into the reactor. Subsequently, it has been demonstrated that these reactant gases undergo gas-phase reactions to form intermediate reactants and gaseous by-products via homogeneous reactions. Alternatively, they diffuse directly through the substrate's boundary layer. Adsorption and diffusion of reactant gases and intermediate reactants onto and along the substrate's surface is clear. Subsequently, heterogeneous reaction phenomena occurred at the interface where the gaseous state and solid phase met. These reactions led to continuous thin film formation via three processes: nucleation, growth, and coalescence. These were also the processes through which reaction by-products were formed. As a consequence, the desorption of gaseous byproducts and unreacted reactants from the surface of a reaction zone is a well-documented occurrence. It is crucial to recognize that the occurrence of gas-phase reactions is contingent upon elevated temperatures or the introduction of additional energy, such as that which is inherent in the form of plasma. Moreover, in scenarios where the deposition process is contingent on surface catalysis of the underlying substrate, it is crucial to acknowledge the inherent heterogeneity of the reaction. This principle may be illustrated by the process of catalytic growth of graphene on a metal surface (Sun et al., 2021).

Figure 9

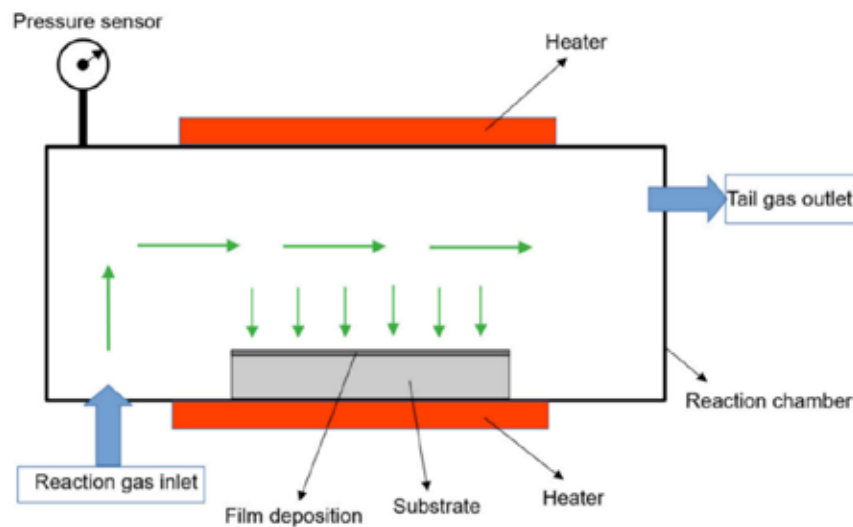
Schematic of general fundamental steps of a typical CVD process (Sun et al., 2021)



Firstly, reactant gases, indicated by blue circles in the schematic representation, undergo transportation to the reactor, which is step a in the process. It is evident that two possible routes are delineated for the reactant gases. Firstly, direct diffusion through the boundary layer is a possibility (step b). Secondly, adsorption onto the substrate is an alternative (step c). Another hypothesis to be considered is that intermediate reactants (green symbols) and by-products (red symbols) could be formed through gas-phase reactions (step d). The subsequent deposition of the reactants and by-products onto the substrate is facilitated by two mechanisms: diffusion (step b) and adsorption (step c). The process of surface diffusion (step e) and heterogeneous reactions are both initiated on the substrate surface. Evidence suggests that these reactions take place prior to the formation of thin films or coatings. In conclusion, the process of desorption of by-products and unreacted species is initiated from the surface, and the subsequent forced extraction of these elements as exhausts is executed (step f). CVD, chemical vapor deposition (Sun et al., 2021). As depicted in Figure 10, the CVD coating process is schematically represented.

Figure 10

Chemical vapor deposition coating method (Ramezani et al., 2023)



In order to satisfy the mounting demands of contemporary technologies, a range of specialized CVD techniques have been devised. These techniques have been customized for specific applications (Heydari Gharahcheshmeh, 2025).

CVD categories and variants

A. Horizontal CVD and vertical CVD are both based on the configuration of the reactor or the direction of gas movement. The horizontal tube reactor represents the most prevalent configuration, wherein the substrates are mounted in a horizontal, vertical, or tilted orientation, with the objective of adjusting the gas movement. The vertical reactor is typically equipped with a showerhead mixer, a configuration that is advantageous for

ensuring material uniformity and enhancing the growth rate (Sun et al., 2021).

B. Atmospheric pressure CVD and low-pressure CVD are dependent on the working pressure. In circumstances pertaining to low-pressure CVD, the utilization of a vacuum pump is imperative to ensure the effective regulation of gas flow. By way of contrast, atmospheric pressure chemical vapor deposition does not generally require the utilization of a pump and typically engenders a slow flow rate for the reactive gas. (Sun et al., 2021).

C. The terms “hot-wall CVD” and “cold-wall CVD” refer to the heating methods employed in thermal CVD. In the context of hot-wall CVD, the reaction chamber is subject to the application of thermal energy from an external furnace, ensuring the maintenance of a consistent and uniform temperature throughout the chamber. In the procedure of cold-wall CVD, the substrate and the substrate’s immediate vicinity are the only components that are heated. It is imperative to note that the reactor wall is maintained at a low temperature, thereby facilitating expeditious cycles of heating and cooling. In the field of cold-wall CVD, the employment of resistance heating, hot plates and induction heating methods has emerged as a predominant approach (Sun et al., 2021).

D. It is evident that photo-assisted CVD, plasma-enhanced CVD, and laser-assisted CVD are distinct variations on the theme of thermal CVD. These variants involve the incorporation of supplementary components and the utilization of alternative forms of energy to facilitate the CVD reaction. In the process denoted as plasma-enhanced chemical vapor deposition, plasma is defined as being a partially ionized high-energy gas. This plasma is produced by direct current, radio-frequency voltage or microwave sources and is subsequently coupled to the reactor, thereby leading to a significant decrease in the reaction temperature. In the process of photo-assisted/laser-assisted Chemical Vapor Deposition (CVD), light from either a high-intensity lamp or a laser is utilized with the objective of promoting the desired deposition (Sun et al., 2021).

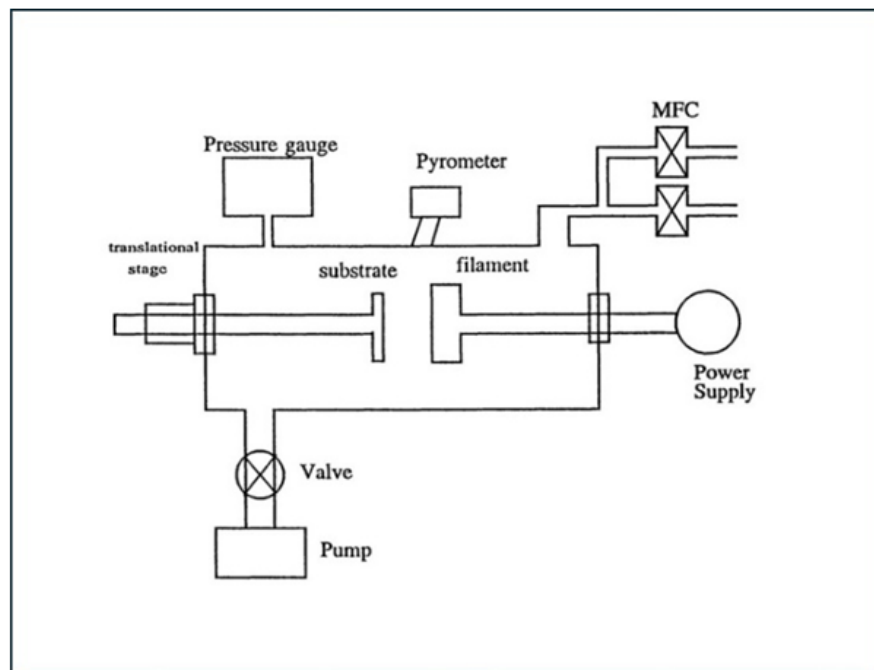
E. Metal organic chemical vapor deposition (MOCVD) is described as the process of utilizing metal-organic precursors, which are generally volatile liquids, in a controlled manner. These precursors vaporized to form thin films. The MOCVD (Molecular-Beam Epitaxy) technique represents a pivotal method in the fabrication of III-V compound semiconductors and high-temperature super fluids, along with epitaxial layers. The significance of this technique is paramount in the context of manufacturing advancements in electronic and optoelectronic devices (Heydari Gharahcheshmeh, 2025).

F. Hot filament CVD chamber is fabricated from stainless steel and incorporates a tungsten wire filament. The filament is arranged in a vertical orientation. The lower terminal is attached to a braided copper wire, whilst the upper terminal is firmly fixed in position. It is imperative that a stainless-steel substrate holder is utilized in order to facilitate the execution of thin-film deposition. The temperatures of the filament are

generally measured at a range of between 2000°C and 2200°C, with filament currents ranging from 50 A to 60 A. The substrate temperature is generally determined within the 950 °C–1,000 °C range during the course of CVD diamond thin film deposition. The feed gases consist of 99.999% hydrogen and 99.8% methane. The pressure within the chamber is meticulously regulated within the 30–100 Torr range. The schematic representation of the hot-filament CVD process is depicted in Figure 11 (Manawi et al., 2018).

Figure 11

Schematic representation of the hot-filament CVD chamber (Manawi et al., 2018)



G. Initiated CVD (iCVD) technique entails the utilization of vapor-phase reactants, encompassing an initiator and monomers. These reactants undergo a process of chain-growth polymerization subsequent to their adsorption onto a substrate that has been subjected to temperature control. The utilization of an initiator enables the attainment of considerably lower filament temperatures, thereby ensuring the preservation of the monomer's organic functional groups. The retention of functional groups enables precise control over the wettability and surface reactions of the film. Meanwhile, iCVD has been evidenced to facilitate the deposition of polymer films which exhibit controlled thickness and composition. This has resulted in an expanded use of CVD, encompassing surface coatings, biomedical applications, and nanostructured materials (Heydari Gharahcheshmeh, 2025).

H. Oxidation chemical vapor deposition (oCVD) process is a one-step approach that directly converts vapor-phase monomers and oxidant vapors into thin conjugated, conducting and semiconducting polymer films. It is at the substrate surface that a

combination of step-growth polymerization and simultaneous doping occur within a single deposition step. Precise control of the properties of oCVD-derived thin films is achievable through meticulous adjustments to the flow rates of the reactants in the vapor phase. This process involves the modulation of other crucial parameters such as the deposition temperature and chamber pressure. The oxidant saturation ratio (OSR) in the oCVD method is a critical process parameter with significant implications for the texture and nanostructure of the deposited thin films, and thereby the electrical conductivity of the resultant material. In the event of multiple monomers being introduced, the flow rate ratios of these monomers can be modified to allow for the precise calibration of the composition and characteristics of the ensuing copolymer films. One of the most advantageous features of oCVD is its versatility as a deposition technique. Some of the benefits of oCVD include the ability to form conformal coatings, process at low temperatures, and carry out solvent-free synthesis. Other advantages include the capacity for uniform film growth, mechanical flexibility, scalability for industrial applications, and substrate independence (Heydari Gharahcheshmeh, 2025).

oCVD is a process that is contingent upon the spontaneous reaction between oxidant gases and monomer vapors upon their adsorption to the substrate, thereby producing step-growth polymerization, which, by and large, results in the formation of conducting or semiconducting polymer films. The process of organic chemical vapor deposition (oCVD) has been established as a facilitating factor in the fabrication of conjugated, conducting and semiconducting polymers. This development presents novel opportunities for the realization of flexible electronics and organic optoelectronics (Heydari Gharahcheshmeh, 2025).

I. Molecular layer deposition and atomic layer deposition are two similar variants of CVD for the deposition of inorganic and organic thin films correspondingly. The process of molecular and atomic layer deposition involves the introduction of precursors sequentially. The deposition of high-quality thin films by the layer-by-layer method is known to be characterized by self-limiting absorption and surface reactions of the precursors. Subsequent to the deposition of each stratum, the residual precursor is eradicated by the carrier gas (Sun et al., 2021).

Sol-Gel Coating

Sol-gel protective coatings have exhibited remarkable properties with regard to chemical stability, oxidation control, and improved corrosion resistance for metal substrates. Furthermore, the sol-gel method constitutes an ecologically sustainable technique of surface protection. It has been evidenced that the substance under consideration has the capacity to substitute for the noxious pretreatments and coatings that have traditionally been employed to enhance the corrosion resistance of metals (Wang & Bierwagen, 2009). It has been evidenced

that the sol-gel method is a highly effective process for the production of adherent and chemically inert oxide or hybrid films. These films can be produced at relatively low temperatures (Hegde et al., 2024).

A plethora of techniques can be utilized to facilitate the process of applying coatings to metallic surfaces. A number of processes are worthy of note, including electrochemical deposition, PVD, CVD, plasma spraying and sol-gel processes. The utilization of sol-gel coatings is beneficial for a number of reasons. The following list enumerates several of the most significant features (Wang & Bierwagen, 2009):

- The temperature at which sol-gel processing is generally conducted is low, frequently approximating room temperature. It is therefore evident that the process of thermal volatilization and degradation of entrapped species, such as organic inhibitors, is minimized (Wang & Bierwagen, 2009).
- The utilization of liquid precursors in the casting process enables the fabrication of coatings with intricate geometries and the production of thin films, obviating the necessity for conventional machining or melting techniques (Wang & Bierwagen, 2009).
- The formation of sol-gel films is achieved through the utilization of “green” coating technologies: The method is distinguished by its utilization of compounds, a process which prevents the introduction of impurities into the end product during the preliminary phase of the procedure. This approach is notable for its waste-free nature and the elimination of the washing stage, which are major benefits in terms of efficiency and environmental impact (Wang & Bierwagen, 2009).

Preparation of sol-gel coatings

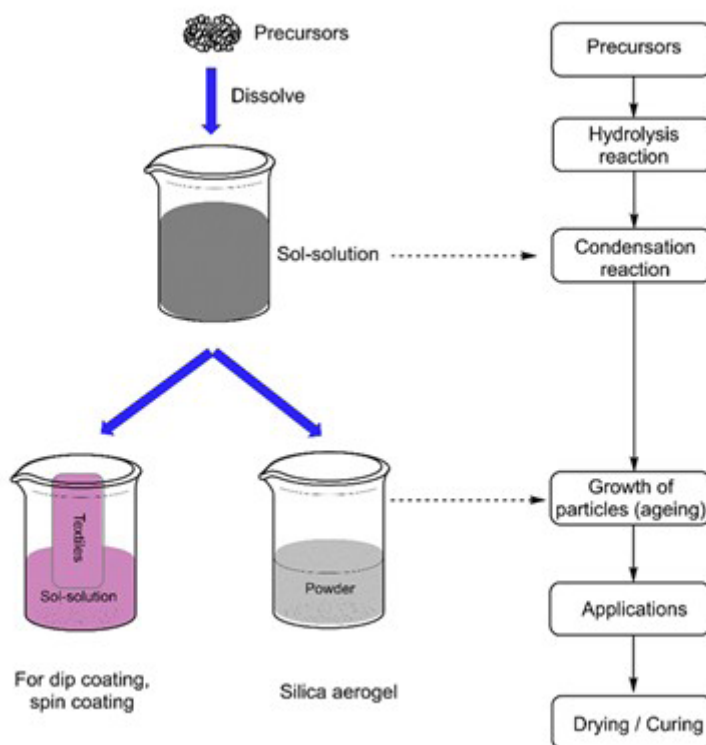
The sol-gel process may thus be delineated as a sequence of reactions between molecular precursors in a liquid medium, which results in the formulation of an oxide network. In summary, there are two fundamental methodologies that are utilized in the fabrication of sol-gel coatings. The two methodologies are the inorganic and the organic methods. The inorganic method is distinguished by the development of networks via the establishment of a colloidal suspension (typically oxides) and the subsequent gelation of the sol (a colloidal suspension of particles measuring between 1 and 100 nanometers) to form a network within a continuous liquid phase. Nevertheless, it is imperative to acknowledge that the most widely utilized methodology is the organic approach, which is typically commenced with a mixture of monomeric metal or metalloid alkoxide precursors $M(OR)_n$ in an alcohol or other low-molecular weight organic solvent (Wang & Bierwagen, 2009).

Sol-gel is a wet processing method in which a homogenous precursor solution is formed by dissolving the raw material in a solvent, whether this is water or an organic solvent.

This step, irrespective of whether the precursor material consists of an inorganic salt or a metal alkoxide, is the foremost stage in the sol-gel procedure. Sol-gel processes are categorized into five distinct stages: firstly, hydrolysis, followed by condensation (gelation), then gel aging, then the application stage and finally the curing stage (Periyasamy et al., 2020). The sol-gel process is depicted schematically in Figure 12.

Figure 12

Steps constituting a sol-gel process (Periyasamy et al., 2020)



In the majority of instances, the dissolution of inorganic or metal-organic precursor substances is carried out in an alcohol-based solvent. Subsequently, a hydrolysis process is initiated, involving the application of water and a condensation reaction. This process results in the formation of dispersed fine particles or polymers, which are collectively referred to as sol. In summary, the process of forming interconnections between sols leads to the establishment of an inorganic polymer network, which is widely recognized as 'gel'. This network contains remnants of water and solvents. It is broadly acknowledged within the scientific community that the process of formation or coating occurs during the transition period from solution to gel. This procedure is conducted prior to the removal of the residual water and solvents, and results in the formation of a dry gel. Subsequent application of heat to the gel has been demonstrated to facilitate the process of dense final product formation (Tan et al., 2021).

Irrespective of the technique used, a substantial contraction in volume and internal stress accumulation occur after deposition. This is due to substantial evaporation of solvents and water. Cracks are prone to formation due to internal stress if the conditions for film

formation are not met with the requisite degree of rigor. It is apparent that the process of curing and the subsequent heat treatment of sol–gel coatings exhibit significant variability. This variability is contingent on the presence of disparate microstructures, stringent quality requirements, and the practical applications concerned (Wang & Bierwagen, 2009). The sol–gel solution is employed in conjunction with coating techniques, including dip, spray, and spin coating. The utilization of sol–gel technology in conjunction with a substrate engenders the establishment of a robust and substantial surface that subsequently overcomes the irregularities present after being subjected to a precise temperature (Zanurin et al., 2022).

Ceramics are considered to be effective coating materials due to their favorable thermal and electrical properties, in addition to their resistance to corrosion, wear and oxidation. The process of synthesizing ceramic coating using the sol–gel method has been evidenced to exhibit several advantageous features. These include relatively low cost and simple methodology. The implementation of the sol–gel method facilitates the coating of complex geometries, with the thickness of the coating being readily adaptable for a range of applications. Ceramic coating can be categorized into two distinct classifications: oxides and non-oxides. Oxide ceramics are non-metallic and naturally inorganic compounds, including alumina, zirconia, silica and magnesia. The oxide ceramic coating exhibited favorable electrical properties, minimal wear resistance, and excellent oxidation resistance. It is evident that the non-oxide ceramic does not exhibit greater or lesser oxide properties. The most notable properties are thermal shock resistance and resilience against fractures. Typical oxides comprise alumina and zirconia, whilst non-oxides principally consist of carbides, borides, nitrides and silicides (Zanurin et al., 2022).

The necessity of regulating the interactions between materials and their immediate environment is contingent on the material’s surface characteristics. In light of this, the sol-gel process is being utilized with increasing frequency in the modification of the surfaces of a variety of materials, including metals, organic polymers, inorganic particulates, and glasses. This method allows for control of properties such as wettability, biocompatibility, porosity, corrosion, catalytic activity, and the selective adsorption of analytes, at the level required by the substrate surfaces to which these properties are applied. Consequentially, the utilization of sol-gels has garnered interest within diverse scientific and technological domains, such as metallurgy, biomaterials, analytical chemistry, and photocatalysts. A salient feature of the technique is its economic viability, making it a suitable option for large-scale applications (Carrera-Figueiras et al., 2019).

Notwithstanding, the methodology of sol-gel synthesis is distinguished by its remarkable versatility, which has engendered the fabrication of a wide variety of materials. The utilization of these materials has been observed within diverse scientific and technological

domains. The versatility of sol-gel techniques has given rise to a substantial degree of interest in their application to the field of coating development. The utilization of these coatings in analytical chemistry is driven by the objective of enhancing the efficiency and specificity of sorbents. This enhancement process serves to facilitate the concentration of desired analytes, thereby ensuring the effective analysis of chemical substances. In the domain of biomedical engineering, sol-gel coatings have garnered attention for their potential in regulating the surface interactions between medical implants and devices and biological environments. In the domain of photocatalysis, sol-gel coatings have been developed for applications such as organic compound degradation. The application of anticorrosion sol-gel coatings is a material management strategy that aims to mitigate the degradation of materials and metallic structures. This approach is employed to preserve the surface and bulk integrity of metallic materials, thereby ensuring their functionality and longevity. The sol-gel coating technique is a method of coating a substrate in a “sol” solution, followed by the vertical extraction of the substrate at a controlled speed. It is evident that a very fine coating of gel is thus formed, since there is rapid evaporation of the solvent during the extraction of the substrate. The coating’s thickness is determined by the liquid’s viscosity, surface tension, and the rate of removal; it is evident that an accelerated rate of removal will result in a greater thickness of the coating. Subsequent to the acquisition of the initial coating layer, the process can be reiterated to create a multilayer structure. The drying step also exerts influence on the final structure of the film, and thickness limits must be observed in order to prevent cracking or detachment of the film from the substrate (Carrera-Figueiras et al., 2019).

Conclusion

The progressive development of coating technologies is a consequence of the necessity to satisfy the increasing industrial requirements and the high-performance expectations that have been established. A wide range of solutions is offered by thermal spraying, PVD, CVD and sol-gel methods. The advantages of these methods are dependent on several factors, including the type of material, the application area and the cost requirements. The application of thermal spraying is particularly prominent in cases requiring high wear resistance; meanwhile, both PVD and CVD methods are preferred for the creation of both thin and high-purity coatings, as well as for controlled coatings. Conversely, sol-gel offers a viable alternative for functional coatings, attributable to its effectiveness at low temperatures and its capacity for versatility. In the future, the integration of nanotechnology with hybrid coating technologies and environmentally friendly processes is predicted to lead to substantial improvements in the performance of these methodologies. It is to be anticipated that this will pave the way for the advancement of more innovative and sustainable applications. Consequently, the utilization of advanced coating technologies is poised to not only address prevailing industrial challenges but also remains a pivotal element in the design of future generations of products.

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