



On Coating Techniques for Surface Protection: A Review

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Received: 21 February 2019; Accepted: 18 March 2019; Published: 25 March 2019



Abstract: A wide variety of coating methods and materials are available for different coating applications with a common purpose of protecting a part or structure exposed to mechanical or chemical damage. A benefit of this protective function is to decrease manufacturing cost since fabrication of new parts is not needed. Available coating materials include hard and stiff metallic alloys, ceramics, bio-glasses, polymers, and engineered plastic materials, giving designers a variety freedom of choices for durable protection. To date, numerous processes such as physical/chemical vapor deposition, micro-arc oxidation, sol–gel, thermal spraying, and electrodeposition processes have been introduced and investigated. Although each of these processes provides advantages, there are always drawbacks limiting their application. However, there are many solutions to overcome deficiencies of coating techniques by using the benefits of each process in a multi-method coating. In this article, these coating methods are categorized, and compared. By developing more advanced coating techniques and materials it is possible to enhance the qualities of protection in the future.

Keywords: surface modification; sol-gel; thermal spray; vapor deposition

1. Introduction

Mechanical parts and structures are designed for specific applications. Prior to fabricating these parts, some extensive material selection constraints have to be met. These constraints include body materials, mechanical properties (e.g., tension, compression, yield, torsion, fatigue, bending, and creep), desired functionality (e.g., friction properties, hydrophobicity, wear resistance), thermal properties (e.g., thermal expansion and conductivity to transfer heat flux), electrical conductivity, dynamic load bearing (e.g., vibrations, high-speed rotation), and corrosion resistance. In addition, other parameters such as availability, cost of materials, safety, and toxicity of these materials must be considered. The latter category plays an important role in finalizing the material selection processes in advance to manufacturing mechanical parts and structures. For instance, silver is known to offer high electrical conductivity values, but fabricating a huge bulk of silver for electrical conductivity applications is too costly [1]. NiTi alloys are well-known for showing the shape memory effect (SME) and superelasticity (SE), which are useful in designing new actuators. Moreover, these alloys provide high biocompatibility as they are used as bone implants that could be combined with SME, SE, or both, to develop new biomedical devices for micro-surgeries inside the human body. However, the corrosion process of NiTi in physiological environments releases Ni ions as byproducts, which are a toxic and harmful category of materials for living organs [2]. Copper is a material with high thermal and electrical conductivity with many applications such as brazing advanced materials; however, it suffers from low stiffness

and wear resistance. In the case of copper rotary cooling fins, the durability of the mechanical parts decreases significantly due to the high susceptibility of copper to wear mechanism [3]. To overcome these issues and to enhance material properties for specific applications, there have been different methods offered, such as heat treatment, alloying processes, and coatings. Among these solutions, coating processes have the highest portion of material enhancement since coating layers can reduce the cost and neglect scarcity of materials as the thickness of coating layers rarely pass micrometers. This means less material is needed to form coating layers on a bulk of substrate materials. Coatings can offer different properties such as corrosion/wear resistance, enhanced surface hardness, modified surface texture, thermal/electrical insulation, enhanced wettability, hydrophobicity, etc. [4].

Coating methods are available in a wide variety due to the enormous diversity of applications and needs in different fields. These processes consist of many different on-line/off-line parameters while giving way to many different outcomes in the form of material microstructure, effectiveness, suitability, and durability. However, coating methods are useful in specific applications according to the desired functionality among which corrosion and wear protection are the most important [5]. Mechanical properties of the materials decrease by corrosion process whereas the corrosion products are released in different forms that may cause a more extreme corrosive environment or harmful side effects in different applications [6]. Coating materials have deferent deposition mechanisms that needs to be investigated for the revelation of their pros and cons for the desired application. There are many processes available, but only a few are among the most effective and applicable, including physical vapor deposition (PVD), chemical vapor deposition (CVD), micro-arc oxidation (MAO), sol-gel, thermal spray, and polymer coatings. Each of these methods is suitable for different applications as they offer different deposition methods, different materials, second phases, different thicknesses, and densities. As a result, mechanical stability, corrosion properties, biocompatibility (for biomedical applications), and enhancement of material behavior for a specific type of coating have to be considered carefully [7]. Although coating processes are applied to provide the abovementioned benefits, they suffer from disadvantages that degrade their reliability. Of these adverse effects, negative thermal effects (e.g., distortion, crack, delamination, etc.), destructive effects of loose atmospheric protection (e.g., penetration of inclusions and contaminations into the substrate) and coating materials properties (e.g., melting point, availability in different forms of foils/powders/rods, biocompatibility, etc.,) are the most crucial ones to be considered.

Materials selection is the key parameter in having a successful coating as they provide all protection purposes. Many different materials, including metals, ceramics, and polymers, can be used to form a protective layer [8]. However, the diversity of coating processes and material properties may cause difficulties in choosing the best composition of the deposited layer. To overcome this issue, the most popular candidates such as Al, Ti, Hf, Zr, Ni, Co, Pt, MgO, ZrO₂, Al₂O₃, Y₂O₃, BeO, PEEK, and PTFE must be considered while any probable new candidates should not be neglected. Although each of the feedstock materials offer corrosion or wear resistance properties, they possess different melting points, mechanical behavior, and chemical properties. Combined with their availability in different forms of powders, rods, plates, and wires for specific uses, these parameters keep the material selection in a narrower range. This review briefly covers common coating methods, materials, and their surface modification quality whereas there are plenty of other protection processes such as heat treatment, mechanical treatment, mechanical/chemical finishing, and polishing, which have not been covered in this review.

2. Reliable Coating Methods

Coating processes provide protection to a specific part or area of a structure exposed to harsh and corrosive environments in different fields ranging from aerospace and the automotive industry to tiny biomedical devices and implants inside the human body.

2.1. Physical Vapor Deposition (PVD) Coating

PVD process is famous for offering corrosion and wear resistance and thin protective films on the surface of the materials that are exposed to corrosive media, and its applications range from decorative objects to industrial parts [9]. The advantage of this method is that the mechanical, corrosion, and aesthetic properties of the coating layers could be adjusted on demand. In general, PVD is a process that takes place in a high vacuum and the solid/liquid materials transfer to a vapor phase followed by a metal vapor condensation, which creates a solid and dense film. The most known types of PVD are sputtering and evaporation. Since the coating layers created by PVD are thin in nature, there is always a need for multilayered coatings while the materials selection should be considered carefully. Apart from its decorative applications, many PVD-coated parts serve as components that undergo a high rate of wear that causes abrasion on the surface and removes the coating layer. This phenomenon reduces corrosion resistance properties of the parts and makes them more susceptible to a corrosive media. Figure 1 represents a schematic view of different types of electron beam PVD machines. In this method, the coating growth is dominated by a physical evaporation process. The thermal energy needed for evaporation may be supplied by different supply units, such as electron beam, heating wire, laser beam, molecular beam, etc. [10]. This thermal energy heats the atoms of the source material, which can be in the form of solid or liquid, to its evaporation point. The vaporized atoms travel a distance through the vacuum and deposit onto the substrate.



Figure 1. Schematic view of a physical vapor deposition (PVD) machine using electron beam as the heat source.

In different studies, the material composition of PVD coatings was investigated and they claimed that the base material of the coating significantly affected corrosion properties of the coated parts. As an example, Mathew et al. [11] investigated the corrosion properties of two different compositions of single-layered Ti-based (TiC_xO_y) and Zr-based (ZrC_xO_y) coating layers. They claimed that the Ti-based group provides better corrosion resistance compared to the Zr-based, one and in the Ti-based group, the highest corrosion enhancement was provided by samples with 0.55-0.79 fractions of oxygen in the coating composition. In other research related to the food industry by Damborenea et al. [10], the effect of the acidic environment of artificial casings in an acidic range of 1–3 pH was investigated. They reported that the PVD coating of TiN on the surface of stainless-steel equipment increased corrosion resistance and protected the equipment from corrosion failure for a significantly longer time. In addition to material selection for PVD coating compositions, many researchers investigated the effect of coating quality, porosity, and adhesion on different substrates such as stainless steel, Ti-based alloys, and ceramics [12–15]. In summary, PVD coating can be utilized in many applications such as aerospace, automotive, biomedical instruments, optics, and firearms. It provides the advantage of flexibility in using any organic and inorganic material as a deposition layer while the coating layer offers high hardness and corrosion resistance [16]. The PVD process for polymeric materials is challenging since the deposition leads to degradation of the polymer that reduces the molecular weight of the film. PVD has been used for polyethylene (PE), polyvinylidene fluoride (PVDF), and

conductive π -conjugated polymers such as poly(2,5-thienylene) (PTh), and poly(pyridine-2-5-diyl) (PPy) [17,18].

2.2. Chemical Vapor Deposition (CVD) Coating

Another type of vapor deposition is called CVD. This process undergoes a high vacuum and is widely used in the semiconductors industry providing a solid, high quality, and a high resistance coating layer on any substrate [19–22]. CVD can be used for mechanical parts in constant contact, which need protection against corrosion and wear. In this process, the substrate, known as a wafer, would be exposed to a set of volatile material precursors where a chemical reaction creates a deposition layer on the surface of the material. However, some byproducts of these chemical reactions, which are removed by constant airflow of the vacuum pump, can remain in the chamber. A schematic of the CVD setup is shown in Figure 2. The vaporized CVD materials are pumped from the right side and the heaters keep the temperature high enough to facilitate the chemical reaction between the substrate and vaporized materials.



Figure 2. Schematic chemical vapor deposition (CVD) setup, mechanical parts, and operation mechanism [23].

CVD technique provides a wide selection of materials in different compositions and forms such as carbides, nitrides, oxynitrides, a composition of Si with O and Ge, carbon in forms of fluorocarbons, diamond, polymers, graphene, fibers/nanofibers/nanotubes, Ti, and W. In addition, these materials could be provided in different microstructures such as monocrystalline, polycrystalline, and amorphous [24,25]. Moreover, CVD of polymers has been shown to be a reliable process in applications such as biomedical device implants, circuit boards, and durable lubricious coatings [26]. CVD process performs in three different categories of atmospheric pressure CVD, low-pressure CVD, and ultra-high vacuum CVD, and the last two methods are the most common ones [27]. There are many other classifications related to the CVD process based on substrate heating, material properties, and types of plasma utilized in vaporizing the materials. These second-hand categories often include aerosol-assisted CVD, direct liquid injection CVD, plasma-enhanced CVD, microwave-plasma-assisted CVD, hybrid physical-chemical CVD, and photo-assisted CVD [28,29]. There are arguments on the advantages and disadvantages of CVD over PVD based on the applications. In the CVD process, the substrate is heated up to 900 °C, which cannot be used for temperature-sensitive materials. PVD provides a solution for materials of this kind. On the other hand, CVD has the advantage of less waste of materials since only the heated area can be coated. In order to enhance this capability, computer-controlled lasers could be utilized to selectively heat the preferred areas [30,31].

2.3. Micro-Arc Oxidation (MAO) Coating

MAO process is known as a flexible process of coating regarding the composition of coating layers. The schematic of the process is illustrated in Figure 3. In general, MAO utilizes a high voltage difference between anode and cathode to generate micro-arcs as plasma channels. When these arcs hit

the substrate, they melt a portion of the surface, depending on the intensity of the micro-arcs. At the same time, plasma channels release their pressure, which assists the deposition of coating materials in the working electrolyte on the substrate surface. The existing oxygen inside the electrolyte causes a chemical reaction of oxidation and provides oxides deposited on the surface of the substrate materials. The versatility of this process lies in the flexibility of combining desired elements and compounds as a solute in the working electrolyte. To date, the materials most commonly coated with MAO are Al, Mg, Ti, and their alloys [32]. High corrosion resistance is the most important characteristic of a MAO-treated layer. In addition, being a porous structure, this coating layer provides high bone ingrowth while formed on biomedical implants and fixations [33].



Figure 3. Schematic view of micro-arc oxidation (MAO) process.

Advantages of MAO can be a coating surface with high hardness and adherence properties while it has different scales of porosity throughout its structure. This type of multi-structural nature comes from the coating itself. Figure 4 illustrates a MAO-treated surface under different frequencies resulting in porous structures with different porosities. At the first steps of coating, a solid layer of metallic oxides covers the substrate called barrier inner layer. The porous structure is created on top of this layer during the next steps of coating with a reported thickness of up to 100 μ m [34]. This porous structure is the reason for increased surface adhesion in bio applications. The parameters affecting the coating quality are voltage, current density, electrolyte type, process time, pulsate current, and current type, i.e., AC or DC [35,36]. However, many researchers utilized different process parameter ranges and it has been claimed that in all the studies, corrosion properties of the coated samples improved while metallic ion release decreased significantly [37–39]. The only disadvantage of the MAO process might be its limitation in substrate materials that are mostly valve metals such as Al, Mg, Ti, Zr, Nb, and Ta [35].



Figure 4. SEM micrographs of MAO coating structures under different frequencies of (**a**) 60 Hz, (**b**) 500 Hz, (**c**) 1000 Hz, and (**d**) 2000 Hz [40].

2.4. Electrodeposition Coating

Electrodeposition of materials is considered a type of protection utilizing the deposition of metallic ions on a substrate. In this process, a difference in potential between anode and cathode poles causes an ion transfer in the unit cell. After a while, a coating layer forms on the submerged sample by receiving ions from the other electrode. Extensive studies have been done on popular electrodeposition materials. The common group of metals that have been intensively studied includes, but is not limited to, Ni-P, Ni-P/Sn, Ni-P-W, Ag/Pd, Cu/Ag, Cu/Ni, Co/Ag, and Co/Pt [41–43]. According to these studies, the electrodeposited coatings significantly enhance the corrosion properties of the substrate. Moreover, this technique has been shown to be promising in producing superhydrophobic polymeric coatings such as polythiophene [44]. In general, electrodeposition is categorized into two processes known as electrolytic deposition (ELD) and electrophoretic deposition (EPD), which are discussed more in the following sections.

2.4.1. Electrolytic Deposition (ELD) Coating

ELD is an electrochemical process employed to form a dense metallic coating with a uniform thickness distribution on conductive substrates. Substrate and deposition materials are selected as cathode and anode while placed inside an electrochemical unit cell. Figure 5 illustrates a general overview of the process. By applying a potential difference between anode and cathode poles, metallic ions move toward working electrolyte and from there toward the substrate. The deposition phase requires super-saturation of electrolyte, which occurs due to charging current in the circuit. In this technique, the concentration of metallic ions of electrolyte remains constant during the coating process [45]. Although this method is mostly used for decorative and low-corrosion/wear applications, there have been reports of development of other applications such as optics, electronics, biomedical, high-temperature, and solid-oxide fuel cells [46,47]. By further increasing the potential difference in electrolytic unit cells, ceramic materials can be deposited on metallic substrates that is more similar to the MAO process. Tian et al. [48] deposited Ni-Co-Al₂O₃ on steel pipes and reported a notable enhancement of corrosion of substrate exposed to oil sand slurry. Yang et al. [49] deposited Ni-Co-SiC on carbon steel pipes exposed to oil sand slurry and reported significant corrosion and erosion-enhanced corrosion resistance. The same results were reported by Fayomi et al. [50] on a Zn-Ni-Al₂O₃-coated mild steel substrate. In addition, Redondo et al. [51] deposited a corrosion resistant polypyrrole (PPy) coating on a copper substrate from a dihydrogen phosphate solution.



Figure 5. Schematic setup for electrodeposition of copper metal particles over aluminum oxide [52].

2.4.2. Electrophoretic Deposition (EPD) Coating

EPD is another form of electrodeposition that provides thicker coating layers with a colloidal nature. Using an electric field in a unit cell, similar to that of ELD, thin films form on substrates by coagulation of colloidal particles. EPD is a multi-phase technique, in which:

- 2. The moving particles gather in one electrode and form a larger coagulated particle.
- 3. The larger particles deposit on the surface of the electrode, which is a to-be-coated substrate.

Finally, a thick coating layer will be created on the substrate having a powder-shaped structure. Figure 6 represents a schematic of the working mechanism of the EPD process. Densification processes (e.g., furnace curing, light curing, sintering, etc.,) are recommended to increase the quality of the protective layer. Up to now, numerous applications have been introduced for EPD that include coating, selective deposition, graded material deposition, porous structure deposition, and biomedical applications [53,54]. The materials used in EPD are commonly borides, carbides, oxides, phosphates, and metals [53,55]. Castro et al. [56] reported fabricating corrosion resistant coatings by sol-gel and EPD on stainless-steel AISI 304 and reported two and four times increases in corrosion resistance for each of these processes, respectively. In another study by Gebhart et al. [57], an AISI 316 L stainless steel was coated with chitosan for biomedical applications. They reported positive effects of this coating on corrosion behavior of the substrate. They also asserted that the applied electric field in EPD is the key factor in controlling coating features, such as hydrophobicity, thickness, and structure. TC4 Ti-alloy orthopedic implants were coated by graphene by Chen et al. [58]. They reported that the graphene-coated artificial joint implants show a considerable increase in life span. They found that the reason any corrosion on substrates occurred was micro-cracks in coating surfaces. Fei et al. [59] studied the wear resistance of EPD coatings and successfully deposited SiC particles on paper-based friction materials and achieved an excellent wear enhancement of this material. Table 1 summarizes ELD and EPD processes regarding their characteristics and components.



Figure 6. Sketch of the electrophoretic deposition process [60].

Table 1	Characteristics	of	electrode	position	techniques	[61]	í.
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Property	ELD	EPD
Coating elements	Ions	Solid particles
Surface charge	Medium	High
Preferred electrolyte	Water	Organic
Ionic electrolytic strength	High	Low
Electrolytic conductivity	High	Low
Approximate rate of deposition	$0.1 \mu m/min$	1000 μm/min

Sol-gel coating is one of the most successful coating processes of biomedical devices. The wide range of investigations on this process and its applications can ease the setup and performance of experiments while keeping the outcomes reliable [62]. On the other hand, sol-gel is capable of enhancing previously existing coating layers from corrosion and ion release point of view. Due to its liquid-permeating nature, sol-gel can easily seal porous coating structures or damaged layers. Calcium phosphorous (CaP) precursors dissolved in ethanol/distilled water are used to make the solution called as Sol. In order to make a gel phase out of the solution, the prepared mixture undergoes heating at different temperatures to facilitate the aqueous portion of the solution and increase the viscosity to the desired level. This phase, which transforms it from a liquid solution to a gel phase, is where sol-gel gets its name. After preparation, the parts or devices are dipped in the sol-gel medium at a constant and controlled speed. This process may be repeated to achieve a multilayered coating or thicker coating of the same material. In addition, the coated samples can be baked to dry out faster or to provide intentional dehydrating cracks on the surface of the coating layer for next processing steps. Figure 7 represents a schematic of an example of a sol-gel coating process.



Figure 7. Schematic sol–gel coating process from solution preparation to the final solid structure formation.

Advantages of the sol-gel process include high adhesion of the coating layer, ability to coat complex geometries, flexibility in the composition of the coating layer, and lower cost than other similar coating processes. Additionally, there is no need to have a conductive material as a substrate as there is no extreme heating or vacuum applied to the parts meaning that the substrate will be virtually untouched during the coating process. Sol-gel coating is done in different forms such as dip-coating, spraying, and spinning [63,64]. Figure 8 shows a sol-gel deposited coating layer with a rough and porous microstructure. One disadvantage of this process could be that a constant speed of dipping and withdrawing is needed to maintain a uniform thickness of coating throughout the substrate surface. There is also always a possibility of coating failure during heat treatment on multilayered coating structures. Sol-gel coating for industrial applications is considered a slow process and is not cost effective in high production rates [65]. All these being said, the sol-gel process performs well when it comes to protecting a substrate against corrosion and decreasing ion release, as reported in many scientific studies [66,67]. Moreover, in a study by Faustini, et al. [68], models were proposed in order to explain and predict sol-gel behavior and the effect of dipping/withdrawing steps on the final quality of the coating layer. Likewise, many other studies investigated and proposed continuum-based/numerical models that could be implemented in predicting sol-gel mechanisms during the process and characteristics of the coating layers [69–73]. Hybrid network materials were generated using sol-gel process when either organic moieties or polymeric categories chemically bonded to an inorganic component. The chemical bond between the organic and inorganic network

can be addressed through introducing functional groups into the polymeric part by silane, silanol, etc., using pre-introduced functional groups in the polymer, and exploiting alkoxysilanes precursors. Poly(dimethylsiloxane) (PDMS), poly(ether ketone) (PEK), and polycarbonate are among numerous polymeric materials that have been used in the sol–gel process [74–77].



Figure 8. SEM of sol-gel-deposited CaP microstructure in different magnifications of the same area [78].

2.6. Thermal Spray Coating

Thermal spray coating is a general term for a series of processes that utilize a plasma, electric, or chemical combustion heat source to melt a set of designed materials and spray the melt on the surface in order to produce a protective layer. These are reliable types of corrosion- and wear-resistant coatings. In this process, a heat source, which is mostly provided by chemical combustion or plasma discharge, heats up the materials to a molten or semi-solid phase and sprays them on the substrate with a high speed of a jet. The thickness achieved in thermal spray coating techniques can range from 20 µm to several millimeters which is significantly higher than the thickness offered by electroplating, CVD, or PVD processes [79]. In addition, the materials that can be used as feedstock of thermal spray coatings range from refractory metals and metallic alloys to ceramics, plastics, and composites and can easily cover a relatively high surface area of a substrate [79]. Thermal spray coatings are categorized into different types based on their characteristics and process specifications. The most popular categories are plasma, detonation, warm/cold, high-velocity air fuel (HVAF), high-velocity oxyfuel (HVOF), flame, and wire arc spraying [80,81].

2.6.1. High-Velocity Oxy-Fuel Coating (HVOF)

Figure 9a represents an HVOF coating process in a schematic format. A mix of fuel, such as acetylene, propane, methane, hydrogen, or natural gas, and oxygen in gas or liquid phase undergo continuous combustion in a designed combustion chamber to provide a high-pressure steam of hot gas. The combustion chamber releases the combustion products into a nozzle to create a spray with a speed of more than 1000 m/s [82]. After combustion, coating materials in powder form are injected inside this hot jet stream to get partially melted accelerated while they are leaving the nozzle tip. The hot jet pushes the semisolid particles against the substrate and creates a coating layer with varying thicknesses up to several millimeters. The advantage of this process is that the coating layer has a high density and adheres to the substrate well, while it is able to utilize coating materials such as hydroxyapatite (HA), W, Cr, Al, Zr, and their oxides/carbides or polymeric materials such as nylon 11/silica nanocomposites to deposit corrosion- and wear-resistant layers [83,84]. Figure 9b represents a multilayer coating provided by HVOF. The coating layer could be performed on non-conductive materials such as polymers and ceramics that are able to undergo high velocity and temperature of the jet stream and the particle [85]. To date, many researchers have investigated corrosion and wear resistance of HVOF coatings in various applications and corrosive environments. Based on these studies, coating layers made by this technique served well and improved corrosion-wear properties of substrates [86–88]. A summary of these studies is listed in Table 2.



Figure 9. (a) Schematic setup of a high-velocity oxy-fuel (HVOF) coating system [89] and (b) cross-section SEM micrograph of HVOF-sprayed multilayer coating on Al7075-T7351 plates [87].

 Table 2. Electrochemical corrosion measurements of different coating composition provided by HVOF [90].

Coating Composition		Corrosion Rate (mm/y)	
	0.1M NaOH	0.1M H ₂ SO ₄	Sea Water
WC-Cr ₃ C ₂ -Ni	0.38	0.15	_
Cr ₃ C ₂ -NiCr	0.17	0.077	_
WC-Co	_	—	0.76
WC-Co-Cr	_	_	0.32
Cr ₂ O ₃ -Al ₂ O ₃ -TiO ₂	3.2×10^{-5}	3.6×10^{-5}	_
Cr ₂ O ₃	7.6×10^{-3}	1.5×10^{-3}	_

2.6.2. Plasma Spray Coating

Figure 10 illustrates a schematic view of a plasma spray coating setup. This process can be done under vacuum or atmospheric conditions. In this process, a plasma gun provides a high-temperature DC/induction plasma (up to 10000 K), which can easily melt refractory metals, ceramics, and polymers. The materials used in the stabilization of plasma can be gas, water, or a mixture of these two, known as hybrid plasma. The materials to be deposited are fed into this hot plasma stream and the high temperature melts the feedstock. Due to the high speed of plasma at the tip of a converging nozzle, the molten droplets are deposited instantly on the substrate against the coating setup. The flexibility of this process facilitates the utilization of different types of feedstock such as powder, slurry, suspensions, and liquids [91]. The resulting coating layer has a high corrosion and wear resistance and it is able to adhere to the substrate due to surface tension and high temperature. A significant corrosion- and wear-resistance enhancement was reported in many studies on different materials such as chromium oxide and NiCr alloys [92,93]. Plasma sprayed coating of polymers, especially PEEK, have been implemented for corrosion protection of metal substrates (nylon, PVDF), antistick coatings of papers and rollers, plastic moldings, wear-resistant coatings, moisture protection materials, and electrical barrier coatings [94]. On the other hand, vacuum plasma spraying is a low-temperature process and is mostly used for materials that cannot perform reactions in atmospheric pressure to modify the surface of the substrate. The most popular application of vacuum plasma spraying is the surface modification of engineering polymers and plastics, rubbers, metals, and fibers [95]. In this process, a material can go through cross-linking, friction decrease, adherence increase, etc. [95–97].



Figure 10. Schematic plasma spray coating setup and its parts [98].

2.6.3. Cold Spray Coating

Cold spray coating is a technique that relies on impact and solid mechanics of particles. Unlike HVOF and plasma spray coating methods, this process does not utilize a heat source to perform coating on substrates. The general working mechanism of cold spray coating depends on particle size, the temperature of the target, material properties of coating particles, and a critical velocity [99]. Powder materials are fed to a stream of high-velocity mediums (helium and nitrogen) to achieve the desired kinetic energy. After particle-substrate impacts take place, this energy deforms the particles and bond them to the substrate. Another mechanism of this process can be penetration of the particles inside the substrate. Using a high flow rate of accelerated particles, the surface is coated with desired materials. The most-used powder materials consist of a wide range of plastics, metals, ceramics, composites, and metallic alloys [100,101]. In addition, the most-studied substrate materials include soft metals such as Al and Cu, while in literature, the coating of some hard materials such as W and Ti has been reported [102,103]. In some studies, the temperature of the accelerating medium has been increased in order to enhance process efficiency [104]. Although this process is simple and cheap compared to the other thermal spray methods, the operation range is very limited. Figure 11 shows SEM micrographs of cold spray-treated surfaces and a schematic view of cold spray coating process.



Figure 11. Top: SEM micrographs of cold spray-coated AA6061 substrate by (**a**) as-received and (**b**) heat-treated AA7075 particles with a mechanical interlocking between the coating and the substrate [105]. Bottom figure: a schematic view of cold spray coating process [106].

2.6.4. Warm Spray Coating

Figure 12 (left) shows a schematic representation of the warm spray coating method. As stated about cold spray coating, low working temperature decreases efficiency and reliability of thermal spray coating methods. However, high temperatures melt feedstock and introduce new chemical reactions, which may cause oxidation or change of properties due to extreme heating of particles and substrates. In order to overcome this problem, a new technique was introduced as a warm spray coating. This is a modification of HVOF coating that enjoys reduced temperature in the combustion chamber by introducing nitrogen to the fluid mixture. As a result, this method is categorized somewhere between cold spray coating and HVOF coating and provides a high efficiency of the coating process [107]. However, as reported in the literature, the achieved coating layer contains many impurities relative to the other two processes due to low temperature and existence of oxygen in the accelerating stream. These porosities and oxide phases are illustrated in Figure 12 (right). Advantages of using this process rise in the coating of materials, which are sensitive to oxidization in high temperatures or the materials that cannot withstand high working temperatures such as bio-metal-glasses, Ti and its alloys, engineering plastics, and polymers such as PEEK [108,109]. Cold/warm spray coatings are not used for extremely harsh environments, however many research studies investigated corrosion properties of this type of coating on different materials such as Ti, bio-metal-glasses, WC-Co cermet, etc., under different corrosion conditions and they claimed an enhancement in corrosion resistance of substrates [110,111].

2.6.5. Arc Wire Spray Coating

Another type of thermal spray coating technique is called arc wire spray coating (Figure 13a). In this process, two consumable metallic wires, which are charged with a DC supply, generate an arc between them resulting in a melting process of the feeding wires. The products of this melting process are then pumped out of a converging nozzle tip toward the target with the supplied pressure of compressed gas. Although the flexibility of this process allows for the use of many metallic alloys as coating layers, this process is limited to conductive wires and materials. In order to solve this issue, a modified version of arc wire plasma was introduced having one consumable wire, which makes an arc with a non-consumable metallic cathode [112]. The remaining steps of the process are the same as the original version. This method is well-known for applications of an internal surface coating such as engine blocks, etc., that offers a lighter metal as the whole block while the internal surfaces are coated with a wear- and corrosion-resistant metallic alloy. This flexibility can significantly reduce production cost. Almost all of the conductive materials such as Al, Zn, Mo, Ni, and other metallic alloys such as Ni and Ti alloys can be used as feedstock in this process [79,113]. In addition, utilization of cored wires is reported in the literature [114]. Figure 13b represents the microstructure of an arc wire spray-coated substrate. To this point, many of the popular thermal spray coating techniques have been introduced. However, there is no doubt that other processes could be investigated regarding their working mechanisms, coating efficiency, coating quality, speed of process, and ease of applications.



Figure 12. Left: A schematic of warm spray coating technique and its setup [115]. Right: Cross-section BSE micrographs of warm spray-deposited Ti-6Al-4V on low-carbon steel substrate processes spray pressure and nitrogen flow rates of (a) 1 MPa and 0.5 m3/min, (b) 1 MPa and 1 m3/min, (c) 1 MPa and 1.5 m3/min, (d) 4 MPa and 0.5 m3/min, (e) 4 MPa and 1 m3/min, and (f) 4 MPa and 1.5 m3/min, respectively [116].



Figure 13. (a) Schematic arc wire spray coating setup and mechanism of operation [117]. (b) SEM micrograph of arc wire spray-coated surface by Tafa's steel (95MXC) cored wire feedstock. The substrate material is not mentioned in Reference [114].

3. Summary

In order to have a successful coating deposition on a substrate, there are several affecting parameters including deposition materials, substrate materials, feedstock form (powder, wire, rods, precursors, etc.), and deposition methods. However, the deposition processes are the most important ones as they deal with chemical alteration of materials and alloying of composition elements in the coating layer. In addition, based on the characteristics of different feedstock and substrate materials, one can easily choose the best option for deposition. The processes that are the most successful and the most investigated deposition means are physical/chemical vapor deposition (PVD/CVD), micro-arc oxidation (MAO), electrodeposition (i.e., electrolytic deposition (ELD) and electrophoretic deposition (EPD)), sol–gel, and different types of thermal spraying processes (i.e., HVOF, plasma, cold, warm, and arc wire spraying). The mentioned processes utilize different mechanisms in order to deposit specific types of materials on substrates making the material selection important in order to have the highest efficiency of the coating. Some of the processes use thermal sources to change the state of feedstock to liquids and semisolids in forms of particles, droplets, and clusters. Some others use the difference between electrochemical changes between poles and some deposit materials without chemical change of state. Depending on the substrate materials, feedstock, and means of deposition, the coating layers

are different in thickness, microstructure, and functionality. In addition, some processes are specific to metallic feedstocks, which are conductive, while the rest can deposit polymers, ceramics, and metallic alloys regardless of their physical properties.

In summary, the thermal processes, such as various types of thermal spray coating, implement high temperatures and high speed of plasma jets in order to have a higher material deposition rate. In these methods, the high temperatures and high-speed jets allow feedstock deposition and eliminate the adverse effects of high melting point on ceramics and superalloys. The obtained coating thicknesses, in these cases, are high (up to several hundred microns). However, the coating microstructure consists of oxide and carbide inclusions and provides porosity, depending on process parameters. In the vaporization-based processes, the deposited coating layer is a thin film with high corrosion/wear-resistance mostly used in tool coating and protection of sliding components of machines. The coating achieved in these types is a thin solid film with low porosity and high adherence to the substrate. Micro-arc oxidation is a high-voltage version of anodization, which is mostly implemented on biomaterials for bone implant and biomedical device applications. In addition, valve metals (Al, Ti, Zr, Hf, V, Nb) have been extensively used as substrates as well. The coating structured by MAO offers high substrate/coating adhesion with a porous structure that is crucial for biomaterial coating as the bone ingrowth increases. The porous microstructure also enhances the corrosion resistance and facilitates the engineering calculations on the lifetime of the implants, either degrading fast or staying for a longer time. Sol-gel is another type of material deposition that is significantly flexible in feedstock composition, and as the process utilizes aqueous solutions as particle carriers, the complexity of geometry does not affect the coating quality. In addition, sol-gel-deposited layers are a reliable sealant for porous substrates and coatings in order to increase their corrosion resistance. Although sol-gel offers high flexibility and capability in coating purposes, the process is relatively slow and increases the production time. Electrochemical processes are another type of aqueous deposition methods utilizing the difference between electrochemical charges of anode and cathode poles of a chemical unit cell. The flexibility in the coating composition and a wide variety of substrates used in this method make it a reliable deposition process. However, this process suffers from depending on conductivity properties of substrates (poles) for material deposition as the charges need to move freely in the circuit.

Although these processes are reliable means of material deposition and surface protection, there are disadvantages to all of them in different applications. Thus, there have been studies on combining these techniques in order to benefit from an advantageous point of each process and minimize the negative effect of each method. The most applicable way of deposition modification and protection enhancement is known to be multilayered coating deposition. The different layers deposited on top of the previous ones can have different thicknesses, compositions, and physical/chemical properties. This consideration has more importance while porous structures or thin films are deposited. As an instance, a PVD-coated substrate has a thin film with notable corrosion/wear resistance, but a higher layer thickness can increase the functional lifetime of the coated component. As another example, the porous microstructure of a MAO-treated surface can be sealed with several layers of sol-gel deposition in order to decrease the corrosive medium penetration to the substrate and increase its corrosion resistance while maintaining the porous structure. All being said, in order to have the highest efficiency and functionality of a protective layer, different aspects need to be considered carefully. Layer thickness, coating composition, suitability of the deposition technique regarding feedstock and substrate materials, and physical/chemical properties of the deposited layers are the key features changing the final protection quality. Table 3 presents a brief overview of the discussed processes and their features. In addition, pros and cons of covered coating techniques in this review are summarized in Table 4.

Deposition Process	Source	Feedstock Material	Substrate Material	Coating Thickness (µm)	Reference
PVD	Physical	TiCxOy-ZrCxOy, TiN, PE, PVDF, PTh	AISI M2 steel, SS, glass, Si, potassium bromide(KBr)-carbon-Au-Al, Ag-Au-Cu-Al	1.2–6.3, 5, 0.2, 0.2, 0.1, 0.1	[10,11,17,18,118]
CVD	Chemical	Niobium oxide(Nb₂O₅), W-TiN-WSi₂-Ta₂O₅-Cu-SiO₂, polycrystalline Si- Si₃N₄-SiO₂, PTFE. Ni₃Ti	Glass, Si, Si, Kleenex, Ni-Co-Fe	0.05–0.2, -, 0.2–0.6, 0.04–0.1–16	[24,25,119–121]
MAO	Electrochemical	Hydroxyapatite (HA)/TiO ₂ , PCL duplex, HA- HA/ZrO ₂	Ti-6Al-4V, Mg, NiT	10–20, 2–3, 7	[32,34,37]
ELD	Electrochemical	Ni-Co-Al ₂ O ₃ , Ni-Co-SiC, Zn-Ni-Al ₂ O ₃ , PPy	Steel, carbon steel, mild steel, Cu	50–200, 10–70, -, -	[48–51]
EPD	Electrochemical	bioactive glass (45S5 BG)-Cu-doped BG, SiO ₂ , chitosan, grapheme, SiC	AISI 316L SS, AISI 304 SS, AISI 316 L SS, Ti-6Al-4V alloy (TC4), Aramid-carbon-cellulose fibers composite	-, 7, 1–6, -, -	[56-59,122]
Sol–gel	Physical	TiCl ₄ -(tetraethyl orthosilicate) TEOS- (methyltriethyl orthosilicate)MTEOS, HA, PDMS, Polycarbonate	Si, NiTi, stainless steel	0.01–1, 1–4	[62,68,74,123],
HVOF	Thermal	HA, CoNiCrAlY, WC	Ti-6Al-4V, Inconel 738 metal, AISI 4340 SS	70, -, 100	[83,84,124]
Plasma spray	Thermal	Al ₂ O ₃ -ZrO ₂ - yttria stabilized zirconia (YSZ), Metco 447- Alumina/Titania 87/13- Nicrome 80/20- Hastalloy G30, TiC-NiCrBSi	SS, steel, AISI 4140 steel	-, 0.5–1, -	[91,92,96]
Cold spray	Physical	HA, AA7075, Ni/Al, mixed Ni/Al/MoO3, and Ni-clad Al	Ti-6Al-4V, Al 6061-T6, Al 6061	100–1000, 40–300, -	[103,105,106]
Warm spray	Physical	Zr-Cu _{12.3} Ni _{7.6} -Al _{3.5} , Ti, Ti, WC-Co	316L SS, steel, steel, carbon steel	400–1000, -, 400, 300	[108,110,111,125]
Arc wire spray	Thermal	MoS ₂ -TiC-Fe, Ti/Al	Carbon steel, SUS 304	1000, -	[112,113]

Table 3. Summary of coating processes and their specific feature.

Deposition Process	Advantages	Disadvantages	Reference
PVD	Corrosion and wear resistance/thin film deposition is possible/adjustable mechanical, corrosion and aesthetic properties	Requires a high vacuum/corrosion resistance is affected by abrasion/degradation control is challenging for polymer deposition applications	[9,17,18]
CVD	Corrosion and wear resistance/deposition of various types of materials with different microstructures/works with low and atmospheric pressures	Requires ultra-high vacuum/requires heat resistant substrates/small amount of coating materials waste	[24,25,30,31]
МАО	High corrosion resistance and hardness/porous structure for biomedical applications/different scales of porosity through the thickness/	Mostly applicable to valve metals	[33,35]
ELD	Decorative and low-corrosion/wear applications/high-temperature applications	Works for conductive substrates	[46,47]
EPD	Various kinds of selective, graded material, and porous structure depositions/biomedical applications/wear resistant	Works for conductive substrates	[53,54,59]
Sol–gel	Cost effective/biomedical applications/providing corrosion and ion release protection/multilayered (thick) coating/high adhesion/ability to coat complex geometries/flexibility in the composition/no need of conductive substrates	Thickness control/slow rate of coating cycle/possibility of coating failure during heat treatment on multilayered coating structures	[66,67]
HVOF	High density of coating layer and well substrate adherence/works for non-conductive substrates/corrosion and wear resistance	Requires a small range of powder size (5–60 µm) with a narrow size distribution/numerous process variable to change the coating structure/requires a heat source	[83–88]
Plasma spray	High corrosion and wear resistance/high substrate adherence/surface modification of engineering polymers, rubbers, metals, and fibers/anti-stick coatings	A low-temperature process that is mostly used for materials that cannot perform reactions in atmospheric pressure to modify the surface of the substrate/requires a heat source	[92,93]
Cold spray	Simple and cheap method compared to the other thermal spray methods	Limited operation range/mostly used for soft and hard metal substrates/low efficiency and reliability due to low temperatures/not useful extremely harsh environments	[102,103]
Warm spray	Applicable to materials with sensitivity to oxidization at high temperatures or heat sensitive materials	Impurity complications/not useful extremely harsh environments	[108,109]
Arc wire spray	Internal surface coatings such as engine blocks/wear and corrosion resistant	Limited to conductive wires and materials as the coating layer	[79,113]

Table 4. Advantages and disadvantages of reliable coating processes.

Funding: This research received no external funding.

Conflicts of Interest: The authors of this work ensure that there is no conflict of interest by any means and the study is not funded by any organization.

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