

Review

Thermal Spray Metallization of Polymers: A Review of Hybrid Polymeric–Metallic Coatings

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Highlights

What are the main findings?

- Thermal spray enables robust metallic coatings on polymer composites.
- Stand-off distance and particle velocity strongly dictate coating quality.
- Thermal damage to polymers can be minimized by parameter optimization.

What are the implications of the main findings?

- Expands polymer use in aerospace and automotive by adding conductivity.
- Enhances wear resistance and electromagnetic shielding of composites.
- Provides a scalable, single-step alternative to chemical plating.

Abstract

In recent years, the quest for advanced materials has intensified, driving the exploration of innovative coating systems to enhance material properties. Polymeric materials, renowned for their adaptability, have found extensive use across various industries. However, their inherent limitations in mechanical strength, wear resistance, and thermal stability have prompted researchers to seek enhancement avenues. Hybrid polymeric–metallic coatings have emerged as a promising solution, employing thermal spray techniques to metalize polymeric substrates. This amalgamation utilizes the versatility of thermal spraying methods, ranging from cold spraying, flame spraying, arc spraying, to plasma spraying, to achieve robust adhesion between metal and polymer layers. These techniques yield durable composite structures, fortifying surfaces against corrosion and wear while enabling dimensional restoration. Cold spraying, in particular, stands out among thermal spray methods due to its effectiveness in metalizing various materials. This comprehensive review delves into recent advancements in hybrid polymeric–metallic coatings via thermal spray processes. Emphasis is placed on analyzing critical factors influencing coating properties, including various thermal spray parameters. Furthermore, the paper scrutinizes the challenges and future potentials inherent in thermal spray techniques, with a focused exploration of cold spray technology. Understanding these methodologies is pivotal for optimizing the design and durability of structural materials made of polymers or composites.



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1. Introduction

Polymers and composites are extensively utilized in diverse industries, including aerospace, automotive, electronics, and sports, due to their inherent lightweight properties, cost-effectiveness, and ease of processing [1,2]. While exhibiting commendable mechanical strength and corrosion resistance, most neat polymers are fundamentally electrical insulators [3,4]. Consequently, they face constraints in regulated sectors due to low operational temperature limits, a lack of inherent thermal and electrical conductivity, and potential flammability [5,6]. Varying flammability regulations across industry sectors compound these challenges. Inherent surface imperfections further limit their durability and functionality, resulting in deficiencies in wear resistance, thermal and electrical conductivity, adhesion, erosion resistance, bioactivity, reflectiveness, and photochemical resistance [7–9]. In current materials research, integrating conductive polymers with reinforcements such as graphene, noble metals, and their compounds, typically in the form of nanoparticle-infused polymer hybrid coatings, represents an innovative approach. This method is envisioned to significantly improve several critical material attributes, including corrosion resistance, durability, and conductivity, with the overarching objective of prolonging the operational lifespan of the resultant materials [10]. To address the inherent limitations of nano-reinforced polymers, such as inadequate conductivity and vulnerability to surface degradation, and to further broaden their applications, exploring hybrid polymeric–metallic coatings is a promising approach. This approach aims to metallize polymer substrates without causing damage or distortion, thereby improving their functional properties for use in more demanding and challenging environments [11]. By applying a protective metallic layer via thermal spray deposition over fiber-reinforced polymer composites (FRPC) [12], polymer matrix composites (PMC) [9], and neat polymer substrates [13,14], these duplex structures gain significant mechanical and wear resistance owing to the intrinsic hardness of the metallic layer [15–17]. These coatings not only exhibit barrier performance but also showcase multifunctionality, such as electromagnetic shielding, erosion protection, and radiation protection, thereby broadening their applications in demanding engineering environments [18–20].

Methods for polymer surface metallization vary, each with distinct advantages and limitations. Physical vapor deposition (PVD) involves vaporizing a metal and condensing it onto the polymer surface under vacuum, producing thin, precise coatings. However, PVD requires expensive equipment and offers limited coating thickness, making it less suitable for applications needing thicker layers. Similarly, chemical vapor deposition (CVD) uses reactive gas vapors to form a metal coating through chemical reactions on the polymer surface, ensuring uniform coatings with strong adhesion. However, it involves high processing temperatures, which may degrade polymer substrates [21,22]. Electro-forming [23] builds up metal layers on a mold to create freestanding structures with high precision, but it is time-consuming and relies on hazardous chemicals. Electroplating [24–26], which deposits metal from an electrolyte solution onto a polymer substrate via electric current, provides controlled coating thickness but struggles with adhesion on non-conductive surfaces, and poses environmental hazards due to the generation of toxic waste. Direct polymer-metal bonding involves surface treatments or adhesives to enhance adhesion, but it requires complex processing and surface modifications, increasing costs and time [27–29].

In contrast, thermal spray (TS) techniques, including cold spraying, flame spraying, plasma spraying, and electric wire arc spraying, offer significant advantages over conventional metallization methods [30,31]. These processes propel molten or semi-molten metal particles onto polymer surfaces, forming a coating with strong adhesion and enhanced mechanical properties [7]. Compared to PVD and CVD, thermal spray methods provide higher deposition rates, making them suitable for large-scale applications [7]. They are also

more cost-effective, as they require less specialized equipment and have lower operational costs [32]. Furthermore, thermal spray is eco-friendlier, producing minimal hazardous waste compared to the environmental hazards, high cost, and lengthy production cycles of electroplating and electroforming [33]. Additionally, these techniques are highly scalable, allowing coating of large or complex-shaped substrates with ease [34]. While thermal spray coatings may exhibit higher porosity and roughness than those produced by PVD or CVD, their unparalleled efficiency, affordability, and versatility make thermal spray a preferred choice for metallizing polymeric surfaces in various industries [11,35]. This review critically examines thermal spraying methods for polymer metallization, encompassing cold spray, plasma spray, flame spray, and electric arc wire spray. Building on the need to overcome the inherent limitations of base polymers discussed above, this comprehensive overview aims to consolidate fragmented research on polymer metallization methods and evaluate their capabilities within the additive manufacturing landscape.

To fully contextualize the necessity of this comparative framework, it is imperative to situate this work within the current landscape of thermal spray literature. While foundational reviews have outlined the broad feasibility of polymer metallization [31], recent high-impact syntheses have predominantly narrowed their focus to the low-temperature kinetic deposition mechanisms of cold spray additive manufacturing [11,34]. As a result, a substantial knowledge gap persists regarding the systematic comparison of cold spray with high-temperature alternatives, such as flame, wire-arc, and plasma spraying, across diverse polymer matrices. By critically evaluating these four major techniques side by side, this manuscript transcends conventional literature aggregation. Its distinct contribution lies in establishing a unified, cross-method framework that weighs operational parameters (e.g., gas temperature, particle velocity) against the thermal limitations of specific polymer classes, thereby offering a comprehensive, missing guide for selecting optimal metallization strategies in advanced engineering applications.

2. Background

2.1. Thermal Spray Metallized Polymeric Coatings

Thermal spray metallization involves depositing metal onto a polymer substrate, such as embedding or adhering metal particles onto a polymer-based surface, as depicted in Figure 1. Over the past three decades, thermal spraying has evolved as a versatile technique for depositing a wide array of materials onto diverse substrates. This procedure entails spraying metallic powder onto a solid surface to form a coating layer. In conventional thermal spray processes, particles typically soften or melt during flight and flatten on impact. In cold spray, by contrast, particles remain solid and bond through high-velocity impact, plastic deformation, and mechanical interlocking. Different methods harness electrical, chemical, or kinetic energy sources to soften the sprayed powder (Figure 1) [7]. Depending on the process, the feedstock is melted, softened, or accelerated by an electric arc, combustion flame, plasma jet, or preheated gas stream, propelling it toward the target. Coating precursors, available as metals, plastics, or ceramics in powder, wire, or rod forms, disintegrate into particles within a plasma jet and adhere upon impact with the target. As incoming particles envelop the target, subsequent particles adhere to one another, forming the coating layer.

Thermal spray metallization processes for polymer substrates broadly fall into four categories based on the primary energy source for particle acceleration and heating [36,37]: (i) cold spray, which deposits metal or metal alloy particles at low temperatures driven by kinetics; (ii) flame spraying, using combustion flame jets for particle deposition; (iii) electric arc wire spraying, generating thermal jets via electrode discharges within a carrier gas stream; and (iv) plasma spraying, employing ionized gas jets powered by DC currents or

radio frequencies. Different thermal spray processes, using diverse heat sources to heat and accelerate particles during deposition, yield varying energy levels. As shown in Figure 1, the gas is preheated using different energy sources: electrical (gray), chemical (orange), and kinetic (blue).

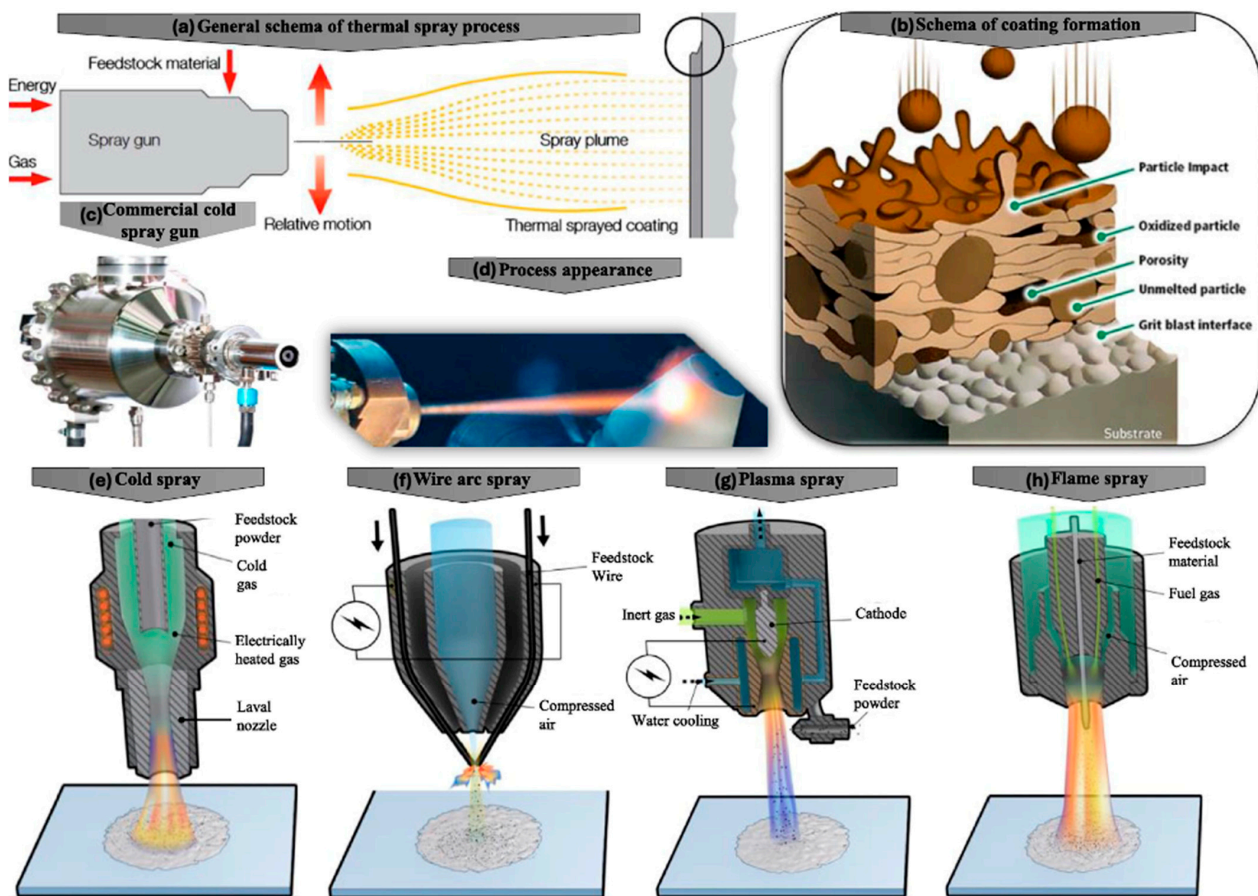


Figure 1. Comprehensive schematic of the thermal spray metallization on polymeric substrates: (a) overview of the thermal spray process, (b) coating formation via particle deformation, (c) a commercial thermal spray gun hardware, (d) real-time thermal spray process appearance, and (e–h) fundamental working principles comparing the cold, flame, arc, and plasma spray methods. Reproduced from Ref. [7] under the terms of the Creative Commons CC-BY license.

In thermal spray metallization, a critical consideration revolves around preserving the workpiece's integrity during coating application at operating temperatures [35]. Despite the workpiece's low steady-state temperature, localized temperature increases can occur due to impacts from individual particles, posing a threat to underlying polymers. While most polymers tolerate substrate temperatures below 150 °C, the impact of supersonic particles generates substantial localized heat, reaching thousands of degrees per impact [38]. This thermal effect fosters metallurgical bonds between particles and the metallic substrate but adversely affects the polymeric substrate, potentially altering the mechanical properties, particularly when the powder undergoes melting during spraying [35]. Mechanistically, when the localized heat flux from the spray jet and particle impact exceeds the polymer's glass transition (T_g) or melting (T_m) temperatures, it triggers rapid thermo-oxidative degradation and macromolecular chain scission. This highly localized degradation forms a brittle, carbonized boundary layer at the interface that not only prevents effective mechanical interlocking but also drastically compromises the long-term stability of the hybrid structure by serving as an initiation site for delamination under cyclic loads. The kinetic energy of sprayed particles and the temperature of the entraining gas stream, a typical gas environ-

ment, exhibit a strong correlation, influencing the microstructure and physical attributes of metal coatings on polymer substrates [37,39]. As depicted in Figure 2, distinct thermal spray metallization methods exhibit a broad spectrum of gas temperatures and particle impact velocities [37,40]. This graphical mapping is critical for polymer metallization: methods operating in the high-temperature, low-velocity regime (such as flame spraying) pose the greatest risk of polymer degradation and rely heavily on thermal softening for adhesion. Conversely, methods in the low-temperature, high-velocity regime (such as cold spray) rely strictly on kinetic energy to drive plastic deformation, thereby preserving the polymer's thermal stability. Figure 1 further schematically illustrates these distinctions, highlighting how the primary energy sources—electrical, chemical, and kinetic—dictate the severe thermal loads transferred to the thermosensitive substrate during the coating formation process.

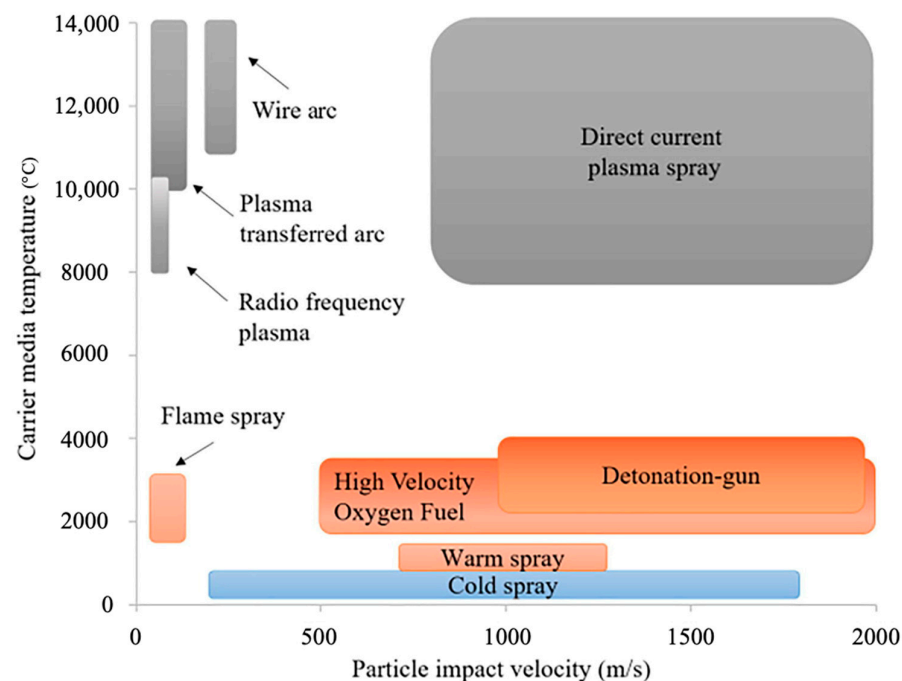


Figure 2. Operational mapping of thermal spray methods, illustrating the comparative parameter windows based on the gas-temperature versus particle-velocity plane to highlight the distinct thermal and kinetic regimes. Reproduced from Ref. [7] under the terms of the Creative Commons CC-BY license.

Thermal spraying involves three primary categories of process parameters: jet energy, feedstock materials, and spraying parameters. The electrical settings of an arc or plasma, coupled with gas type, pressure, and temperature, govern the jet's energy. This energy significantly affects the temperature, velocity, impact energy, and deformability of the spray powder, resulting in an overall deposition efficiency of around 70%, with the remaining powder reclaimed by the target. The selection of feedstock materials, typically soft, low-melting-point metals, considers factors such as powder size (ranging from 10 to 100 micrometers) and particle shape (spherical, angular, dendritic) [41]. Spraying parameters include nozzle diameter (1 to 3 mm), distance between the nozzle and the substrate (10 to 200 mm), gun travel speed, and the number of passes, offer control over powder impact energy, workpiece heating, and the coating area. The wide variability in deposition parameters enables diverse coating characteristics [7].

2.2. Advantages and Disadvantages of Thermal Spraying Technology on Polymeric-Based Structures

Thermal spray coating stands out among various coating methods due to its unique characteristics and application capabilities, offering several advantages [31,37]:

- A wide range of materials, including metals, ceramics, polymers, alloys, and plastics in different forms (powder, wire/rod), can be used without decomposing during melting.
- Metallization enhances the strength and durability of polymeric materials, making them resistant to wear, abrasion, and impacts.
- Coating polymers with metal layers through thermal spray techniques enhances their resistance to environmental factors like moisture, chemicals, and UV radiation, thereby improving their corrosion resistance.
- Metalizing fundamentally insulating polymer surfaces introduces surface electrical conductivity, making them valuable for electrical grounding and electromagnetic shielding applications.
- Thermal spray metal coatings improve the thermal conductivity of polymeric materials, enhancing heat dissipation efficiency.
- Strong bonds between metal coatings and polymers prevent delamination or peeling.
- The flexibility of the spray gun allows for processing workpieces of any size or shape, with the potential to scale using multiple gun assemblies and particle acceleration systems.
- On-site coating applications find utility in various industries such as offshore oil and gas platforms, oceanographic stations, and military equipment.
- High coating deposition rates, reaching up to 100 m/s, enable efficient application.

However, thermal spraying methods also have limitations that restrict their potential [36]:

- Directly sprayed coatings are primarily suitable for soft metals, necessitating the use of soft interlayers for hard metal spraying.
- The deposition process typically operates at a spatial resolution in millimeters.
- Coatings generally exhibit lower structural, mechanical, and electrical properties compared to bulk materials due to their particle-based formation, resulting in porous and rough coatings.
- The process generates dust and noise, requiring the use of a cabinet for containment.
- Empirical knowledge about thermal spray coating for polymeric materials remains limited, with a lack of comprehensive reference books, manufacturer guidelines, or extensive publications.

Optimizing the polymer-spraying process requires pilot experiments and a further understanding of the relationship between the process and material properties to achieve optimal results.

3. Thermal Spraying Metallization Technology of Polymeric Materials

3.1. Cold Spraying

The cold spraying process involves accelerating solid particles through a nozzle at high velocities ranging from 300 to 1200 m/s at relatively low temperatures, causing plastic deformation and interlocking upon impact with the substrate [37,39]. Notably, the past four years (2018–2022) have seen a surge in studies focusing on Powder Metallization (PM) using cold spraying [11], with recent literature reviews emerging in the last year [34,42]. Advancements in cold spray technology have now enabled the metallization of polymer-based materials. This process entails introducing a preheated gas, such as helium, nitrogen, or air, into a converging-diverging nozzle to elevate gas velocity, which then mixes with a metallic powder before exiting the nozzle. Momentum from the gas motion accelerates the powder to supersonic speeds, imparting extreme kinetic energy upon impact. This

kinetic energy is converted entirely into severe plastic deformation upon impact, facilitating solid-state mechanical interlocking and bonding the particles to the target strictly without melting [43]. Originally discovered during the examination of high-speed solid-particle erosion in the 1990s, cold spray essentially repurposes sandblasting by using metallic particles and a hot gas medium, shifting the process from erosion to material deposition [44]. Unique among thermal spray methods, cold spray relies on a low-temperature preheated gas to propel solid metallic powder onto the target, thereby reducing powder oxidation and mitigating thermal damage [33,45,46].

While cold spray is a promising technique for coating polymers, it faces distinct hurdles; creating the initial layer is vital, yet substrate erosion can frequently occur, especially with epoxy resins [47]. While successful coatings have been achieved on thermoplastics such as polyetheretherketone (PEEK) and polycarbonate, high processing temperatures can degrade the underlying material. Therefore, carefully chosen parameters are essential for successful cold spray deposition on polymers [48]. In recent years, cold spraying has emerged as a preferred coating method for thermally sensitive substrates due to its operational temperature reduction [33]. The low-pressure cold spray system stands out as a cost-effective and straightforward means of realizing cold spray, catering to various PM requirements across diverse applications [31].

Extensive studies have explored PM through cold spraying as a means to mitigate the impact of lightning strikes on polymeric composites [49–52]. Typically, polymer composites exhibit conductivity levels below 5 MS/m [53]. Applications of cold-sprayed coatings have effectively shielded Carbon Fiber Reinforced Polymer (CFRP) components from lightning strikes, generating 200 A current C-waveforms [51]. Beyond chemical plating, electroconductive Sn layers can also be cold-sprayed onto polymers [54,55], offering a greener, single-step alternative to the labor-intensive 14-step chemical plating process. While spray coatings often present a rough, matte appearance, electropolishing can transform them into decorative, glossy finishes. Furthermore, cold-sprayed copper coatings have demonstrated an 85% reduction in biofouling on marine structures [56]. The versatility of cold spraying is used to mitigate biofouling on seawater piles, inlets, underwater cables, ropes, buoys, polymer-hulled ships, and fish farm equipment. An advantageous feature of cold spraying lies in its on-site applicability, notably on oceanographic and oil platforms, offering significant technical benefits. However, it is important to note that embedded metallic powders, unlike continuous coatings, do not significantly impact the bulk polymer properties beyond altering color. Erosion complicates the formation of coatings above the embedded layer, especially on thermoset composites. Nevertheless, coatings formed through particle embedment possess distinctive properties suitable for a wide array of applications.

A critical evaluation of the cold spray literature reveals that feedstock density and carrier gas selection are the primary factors governing the narrow operational window between successful deposition and substrate erosion. For instance, the use of helium as a carrier gas provides sufficient kinetic acceleration to yield highly dense, environmentally stable Al coatings on carbon fiber reinforced polymers (CFRP) that resist delamination even under severe thermal cycling and humidity exposure [57]. When using nitrogen, which imparts lower kinetic energy, precise control of parameters becomes paramount to prevent interfacial defects. Under optimized nitrogen flow, cold spraying can successfully yield defect-free Al and bimetallic Al/Cu coatings on polymer matrix composites, with the kinetic bombardment of Cu particles actively enhancing the microhardness of the underlying Al bond-layer [9]. However, achieving this robust adhesion is heavily dependent on the specific weight and critical velocity of the chosen metal. High-density particles, such as Cu and hard Al alloys, frequently induce substrate erosion rather than plastic deformation upon impact with softer thermoplastics (e.g., PC/ABS, polyamide-6,

and polypropylene). Consequently, to mitigate erosion and initiate the necessary plastic deformation for multi-layered coating growth, it is often critical to utilize lower-density metals with more favorable mechanical deformability, such as tin (Sn), which can yield highly conductive coatings up to 100 µm thick without the need for extensive substrate pre-treatment [54].

Furthermore, cold-sprayed metal coatings can provide additional benefits for structural materials made of thermosensitive polymers, such as carbon fiber-reinforced polymer composites (CFRPs) [14] used in aerospace applications, as well as in surface protection and bonding engineering [9,58]. An alternative approach involves reducing the temperature of powder particles by adjusting the carrier gas, thereby enhancing the plasticity of the metal particles [13,58]. This adjustment may lower the critical velocity for cold spray deposition and particle adhesion [39]. A survey of previous studies outlined in Table 1 [31] demonstrates a prevalent trend of utilizing low carrier gas temperature for cold spraying metals onto thermoplastic substrates, including Al deposited on polyamide 66 (PA66) [59], copper (Cu) and silver (Sn) coatings on polyvinyl chloride (PVC) [1], aluminum coatings on polycarbonate (PC) [41], and titanium on polyetheretherketone (PEEK) [60].

Table 1. Comparative Synthesis of Thermal Spray Methods for Polymer Metallization.

Feature	Cold Spray	Flame Spray	Electric Arc-Wire Spray	Plasma Spray
Gas Temperature	150–350 °C	2000–3000 °C	≤5000 °C	~14,000 °C
Particle Velocity	300–1400 m/s	<100 m/s	<100–300 m/s	160–2000 m/s
Suitable Polymers	PEEK, PC, PVC, CFRP, PP, PU, HDPE	PU, Polyester, GFRP, ABS	CFRP, PMC, Polyimide	PMC, CFRP
Coating Materials	Al, Cu, Sn, Ag	Al, Al-12Si, Zn-Al, NiCrAlY	Zn, Al	Al, Zn, Cu, Al ₂ O ₃ , TiO ₂
Adhesion Mechanism	Mechanical interlocking, severe plastic deformation	Mechanical (often requires garnet sand interlayer)	Mechanical (requires sandblasting or bond coats)	Chemical affinity/roughness (requires intermediate bond layer)
Key Advantages	No thermal degradation, low oxidation, dense coatings	Cost-effective, deposits low-melting-point metals easily	High deposition rate, highly scalable, cost-efficient	Deposits refractory metals/ceramics, high shear adhesion
Key Limitations	Substrate erosion (especially thermosets), high gas cost	High thermal load, high porosity (~20%), polymer warping	Thermal damage can lower substrate strength	Highest risk of thermal degradation; strict active cooling required
Primary Applications	Aerospace lightning strike protection, antifouling	De-icing systems, heating elements	Anti-corrosion on large civil and marine structures	Wear-resistant multilayered coatings

Tables 1 and 3 in Ref. [7] list the successful applications of cold spray technology across the polymers and composites, predominantly centered on PEEK and CFRP. When impact energy is directed into thermoplastics, plastic deformation within the substrate occurs [61]. In contrast, thermosets are prone to undergo micro-fracturing rather than plastic deformation, leading to reduced deposition efficiency [18]. Addressing this challenge involves coating thermosets, such as PLA, prior to cold spraying [62,63]. Ideal feedstock materials for both thermoplastics and thermosets should be soft metals with low yield strength and high ductility, such as Sn, Cu, Zn, Al, or their combinations, to facilitate severe plastic deformation without melting. The presence of hard particles such as Fe and Cu often leads to surface erosion of the substrate, embedding the coating layer without complete deformation [13,64,65]. Reported particle sizes predominantly fall within the range of 20 to 40 µm (Table 3). The difficulty of depositing hard metals can be mitigated by using lighter materials such as Sn [58,66] or Al [38] as interlayers. Subsequent deposition involves layers

of iron oxide, titanium oxide, or copper oxide powder. The type of gas employed affects particle velocity, oxygen content, and the composite's structural integrity [66,67]. Helium notably enhances the acceleration of metallic powders, thereby improving deposition efficiency, coating hardness, and density. However, its high cost significantly increases fabrication costs. Among the available options, inert nitrogen stands as the most prevalent choice (Table 3). Determining suitable parameters for cold-sprayed PM, particularly for dense metallic powders such as Cu and Fe, remains a significant challenge. Many studies, as shown in Table 3, primarily focus on particle embedding. The challenge lies in forming coatings over embedded layers, especially in thermoset composites, due to erosion. In contrast to cold spraying parameters on metallic substrates [11], polymeric substrates require a narrower range of parameters to avoid erosion and thermal damage and ensure uniform particle bonding. Temperature field simulations during single-particle impact have been the subject of theoretical studies and simulations [68,69]. However, due to various assumptions, errors may exceed the narrow range of process parameters for polymeric substrates. Future studies should focus on identifying particle velocities, masses, and other bonding factors during cold spraying.

3.2. Flame Spraying

Flame spraying is a process that uses the combustion of fluid fuels to generate a flame jet, melt the feedstock material, and propel it onto a substrate for deposition. Typically, acetylene and oxygen act as combustion gases, with air occasionally added for cooling purposes [70]. An inert gas, such as argon, is used as a carrier gas to propel feedstock particles toward the substrate through a nozzle. Various forms of materials, such as powder, wire, rod, and cord, can be utilized as feedstock materials. Sufficiently high flame temperatures are necessary to ensure feedstock material melting [37]. Flame spray processes commonly operate at gas temperatures ranging between 2000 and 3000 °C [71], while particle impact velocity generally remains under 100 m/s. Flame spraying encompasses a wide array of parameters that determine its process, including nozzle geometry, stand-off distance from the substrate, gas pressure, feedstock material, and gas flow ratio, for instance, the fuel-to-oxygen ratio, as detailed in Table 2 [31].

Several studies [3,72] have demonstrated enhanced polymer-based structures through flame-sprayed metal coatings, providing notable functional advantages. These benefits include improved electrical and thermal conductivity, as shown in Table 4. Despite being recognized as a highly cost-effective method for metalizing polymers through thermal spray [3], flame-sprayed metal coatings typically exhibit higher porosity and, consequently, lower mechanical strength compared to coatings deposited via cold and plasma methods [40]. Therefore, precise parameter optimization in the spraying process is crucial to developing functional metal coatings on polymer-based structures that are both effective and economical. The sensitivity of polymer-based substrates to high-temperature, semi-molten, and molten particles often limit flame spray deposition of metal coatings. Furthermore, experiments on heat transfer suggest that flame spray metal deposition on polymer-based substrates can impose significant thermal loads [73].

A critical evaluation of flame spray (FS) metallization reveals that its primary advantage—the economical deposition of low-melting-point metals like Al and Zn—is fundamentally counterbalanced by severe thermal degradation risks to the polymeric substrate and inherently high coating porosity (typically ~20%) [74]. While descriptive studies frequently highlight the functional success of FS, such as depositing Al-12Si onto polyurethane (PU) for de-icing systems [70,73], forming conductive coatings on textile fabrics [17,75], preventing ice on structures, or applying Zn-Al alloys onto ABS to achieve high electrical conductivity (2682 S/m), these applications are strictly limited to substrates that can either

endure significant thermal loads or tolerate highly porous barrier layers [76]. To mitigate thermal damage and structural erosion during deposition, particularly on sensitive fiber-reinforced polymer composites (FRPCs), researchers have had to shift away from direct spraying [15]. Instead, the implementation of protective garnet-sand interlayers and the injection of compressed cooling air into the FS torch have proven mandatory to preserve the substrate's mechanical properties [73]. Consequently, while FS is highly adaptable for fabricating functional coatings, optimizing the thermodynamic field through precise stand-off distances (typically 100–200 mm) and active cooling remains the primary critical barrier to its wider industrial application.

3.3. Electric Arc-Wire Spraying

Wire arc spray uses the heat generated by an electric arc to melt feedstock wires, forming droplets that are then accelerated in a gas stream through a nozzle onto a substrate using a water spray method [37,77]. This technique relies on two opposing polarity feedstock wires converging at a constant speed at the nozzle outlet to create the electric arc discharge. Notably, electric arc wire spraying can generate gas temperatures greater than 5000 °C [77] while maintaining particle impact velocities typically below 300 m/s [37]. Various metal or metal-cored wires can serve as feedstocks [37]. Table 2 in [31] illustrates key process parameters, including arc gun geometry, electric current input, stand-off distance, carrier gas pressure, wire material, and feed rate [77,78]. Melting wires form drop-lets at their tips, subsequently blown away by a high-velocity gas stream. During atomization, the gas stream has multiple functions: removing molten metal to create large primary droplets, atomizing these into secondary microscale particles, and propelling these particles toward the substrate [78]. Increased gas velocity results in smaller primary and secondary droplets, enhancing acceleration but potentially increasing oxidation, thereby elevating the oxide content in the coating. To mitigate oxidation, a shroud employing non-oxidizing gases like nitrogen or carbon dioxide can be utilized [78]. Elevating droplet velocity not only enhances deposition efficiency but also improves coating properties. Wire arc spraying, with relatively low production costs compared to FS [77], emerges as a promising alternative for industrial PM applications, offering nearly threefold cost efficiency.

Researchers have recently explored depositing metals onto polymers using arc spraying techniques; however, this method often presents challenges, leading to poor adhesion strength and substrate damage. Addressing this tradeoff, surface conditioning emerged as a potential solution. Liu et al. [35] applied an arc-spraying method to a CFRP substrate to establish an interlayer for wear-resistant WC-Co coatings. However, due to the high melting points of materials such as Ni and Cu, nanometer-sized interlayers were susceptible to delamination, likely caused by thermal damage. Opting for materials such as Al and Zn, with melting points higher than CFRP but lower than those of Cu or Ni, mitigates the risk of thermal degradation. However, the bond strength of arc-sprayed Al coatings was notably lower, merely half that of plasma-sprayed Al (7.5 vs. 14.2 MPa). Sandblasting, preceding arc spraying, elevated coating bond strength by almost 20% (9.4 MPa) [2]. Despite achieving a uniform Zn coating on a CFRP substrate, this method caused a significant 15% reduction in the substrate's mechanical properties [79]. Protective coatings such as epoxy overflow, copper powder, or aluminum mesh were applied prior to Zn spraying on CFRP surfaces to mitigate substrate damage [79]. A protective powder layer, while shielding carbon fibers, also weakened adhesion between the coating and the substrate, as evidenced by the loose powder layer's detachment during bending tests. Notably, substrates with protective layers exhibited over a 50% increase in adhesion strength compared to those without [79].

Wire arc spray has emerged as a valuable method to safeguard metal components, such as bridges, pipelines, and offshore equipment, effectively preventing corrosion and

erosion damage with a proven track record [77]. The application of a 100-micrometer-thick erosion-resistance Al coating, produced via arc spraying, significantly bolstered the thermal fatigue and erosion resistance of Polymer Matrix Composites (PMC) [2]. Thermal fatigue tests comprising 50 heat-cool cycles at 370 °C, followed by air cooling, showed no cracks in the coated samples. Subsequent testing with 43 water-quenching cycles revealed minor cracks. In erosion tests, the coated PMCs exhibited only half the mass loss and one-tenth the thickness loss of uncoated PMCs. Moreover, even when exposed to elevated temperatures (70 °C), arc-sprayed aluminum coatings showed a corrosion rate five times slower than steel under similar conditions [77]. These findings highlight the considerable enhancement in thermal fatigue and erosion resistance achieved through arc-sprayed coatings on polymeric components.

In summary, the use of low-melting-point metals such as Zn and Al in arc-sprayed coatings has proven highly effective in safeguarding both thermoset and thermoplastic polymers against erosion, corrosion, and thermal-cycling damage. To advance this technology's applicability, future research should focus on scaling up arc spray techniques to accommodate large structures and to simultaneously protect multiple structures. Electric arc-wire spraying can be cost-effective and scalable for large-area applications; however, its suitability for polymer substrates depends on thermal management, coating adhesion, and allowable substrate damage. Widely adopted across various industries, it is used to produce protective metallic coatings (e.g., Al, Zn) for diverse applications ranging from piston rings to steel buildings and bridges. The potential of wire arc spraying remains substantial, especially for forming erosion- and corrosion-resistant coatings on polymeric components in water and tidal immersion zones, thereby shielding them from these damaging effects. Further exploration in this direction holds promise for bolstering infrastructure longevity and performance.

3.4. Plasma Spraying

Plasma spraying (PS) is a thermal spraying method where a jet of ionized gas melts and propels a powder feedstock onto a substrate through a specialized spray nozzle. The plasma jet comprises ionized gases propelled through nozzles, often resulting in sub- or supersonic flow rates [80,81]. This ionized state is attained through a DC arc or RF discharge, which heats the gas to temperatures of approximately 14,000 °C [36,82]. Gases such as argon, nitrogen, helium, and hydrogen are commonly used to generate plasma jets. The particle impact velocities in plasma sprays typically range from 160 to 2000 m/s [37,40]. The plasma spray process involves several critical parameters, as detailed in Table 6, including torch geometry, input current, torch-to-substrate distance, plasma gas flow rate, feedstock material, and plasma gas type [37]. Distinguished by its exceptionally high gas temperatures, plasma spraying stands apart from other thermal spray techniques. Processes can be executed under various conditions, including vacuum, low-pressure, and inert-gas atmospheres, as well as underwater settings [83]. Among these, atmospheric plasma spraying is the most widely adopted and cost-effective method within the plasma spray domain.

PS has been less commonly employed for metalizing composite materials and polymers due to the inherent thermal instability of polymers compared to metallic or ceramic substrates. Its higher operating temperatures, in contrast to other thermal spray methods, necessitate more precise regulation of process parameters affecting substrate heating, including torch distance, gas temperature, and plasma temperature [7]. Air plasma spraying (APS) has emerged as a method for metalizing polymers by applying metal coatings. Researchers have successfully deposited Al, Zn, and Cu coatings onto Polymer Matrix Composites (PMC) parts using APS [16,35,84,85]. Comparative studies of Al and Zn bond

coats deposited via APS and electric arc wire spraying showed similar or even higher shear adhesion strengths for APS coatings. However, the high thermal load from plasma spraying can potentially degrade polymer-based substrates [35]. Strategies to enhance adhesion involve applying an intermediate thermoplastic coating as a bond layer [86]. For reliable and wear-resistant coatings, sequential spraying of aluminum and alumina powders using plasma has yielded promising multilayered coatings on CFRP [85]. Recommendations for stronger coatings include using polymers with higher thermal resistance, cooling the substrate during spraying, and ensuring proper substrate pre-treatment [87]. Affi et al. [58] utilized a combination of plasma spraying and micro-arc oxidation to deposit aluminum and alumina layers, highlighting the role of lower operating temperatures in achieving highly conductive coatings. Surface pre-treatment, such as chemical etching and grit-blasting, significantly impacts coating bond strength, attributed to enhanced surface roughness and chemical affinity between the polymer and metal splats [84]. Proper selection of parameters like initial roughness, spraying distance, layer deposition, and cooling time is critical to ensure coating interlocking and prevent thermal substrate deformation or degradation [88]. Further quantitative analysis is needed to understand the range of physical, chemical, and mechanical interactions that occur during plasma spraying between metal particles and polymeric substrates.

3.5. Critical Synthesis and Comparative Performance

While all four thermal spray methods enable polymer metallization, their industrial feasibility, scalability, and performance metrics vary significantly based on the thermal and kinetic energy of their respective deposition plumes. Cold spraying offers the most structurally sound coatings for thermosensitive thermoplastics (e.g., PEEK, PC), with exceedingly low porosity and no thermal degradation. However, its applicability to thermosets is severely limited by substrate micro-fracturing and erosion, often necessitating pre-treatments or softer metal interlayers, such as Sn, to initiate deposition.

Conversely, flame spraying provides a highly economically accessible method for depositing low-melting-point metals. However, it consistently yields the highest coating porosity—approximately 20% in aluminum-coated epoxies—and relatively low mechanical strength, limiting its use to applications where dense coatings are not strictly required, such as de-icing systems.

For large-scale industrial feasibility and scalability, electric arc-wire spraying emerges as the optimal technique. It is highly cost-efficient and allows for high deposition rates on extensive civil and marine polymer-composite structures. While arc-sprayed coatings inherently suffer from lower as-sprayed adhesion strength compared to plasma methods (e.g., yielding 7.5 MPa for Al coatings compared to 14.2 MPa for plasma spray), this limitation can be effectively mitigated through mechanical surface conditioning; sandblasting, for instance, has been shown to elevate arc-sprayed bond strength by nearly 20%.

Finally, plasma spraying delivers the highest shear adhesion strength and unique capabilities for depositing refractory metals and ceramics. However, its extreme operating temperatures (approaching 14,000 °C) impose severe thermal loads that frequently degrade polymer substrates. Consequently, its industrial application is strictly limited to highly resilient composites that employ intermediate thermoplastic bond layers or active substrate cooling systems. To provide a clear, graphical synthesis of these operational differences, Table 1 summarizes the comparative advantages, limitations, adhesion mechanisms, and suitable polymer classes for each thermal spray technique.

4. Characterization Methods for Thermal Spray Metallization on Polymer Coatings

Evaluating the quality and functional properties of thermal-sprayed coatings is pivotal in assessing their suitability for diverse applications. The comprehensive characterization of these coatings on polymer substrates is an amalgamation of materials science and engineering methodologies. Studies have demonstrated that assessing thermal-sprayed coatings on polymer-based substrates involves a diverse range of techniques, including hardness tests [89], scanning electron microscopy (SEM) [36], and X-ray diffraction (XRD) [90]. Additionally, these coatings have been evaluated for antifouling resistance [13] and thermal shock protection. The application of these diverse techniques has provided a detailed understanding of the characteristics and performance of thermal spray coatings on polymer-based substrates, serving as a crucial aspect of their comprehensive assessment.

4.1. Hardness Test

Materials undergo hardness testing, applying a localized load to assess their resistance to deformation [91,92]. Hardness evaluation is paramount in materials assessment, extensively utilized due to its wide applicability in engineering materials, notably in thermal-sprayed metal coatings [92,93]. Beyond hardness assessment, these tests offer insights into various mechanical properties like Young's modulus, bond strength, cohesion, and fracture toughness [94,95]. A range of analytical techniques and models accompany these tests to discern diverse mechanical attributes [91,93,96,97]. Following ASTM Standard E384 guidelines [89] is advised when utilizing Knoop and Vickers indenters for hardness testing across materials, including metals and polymers.

Thermal-sprayed metal coatings are often tested for hardness and elastic constants using the Vickers micro-hardness test [36,92,98]. This method employs specialized equipment featuring a pyramidal-shaped diamond indenter with a 136° angle between faces, creating square indentations on the polished coatings under specific loads and dwell time [89]. Coating hardness is measured by evaluating the distance between the indentation corners. Vickers micro-hardness testing has been employed to characterize polymer-based composites.

For instance, Zhou et al. [9] characterized a carbon fiber-reinforced PEEK coating using Vickers micro-hardness testing. After the Cu top layer was deposited, Vickers microhardness testing was performed on the Al bond coat layer. After the Cu layer was deposited, the hardness of the Al layer increased by more than 20%, from 42 to 52 HV0.1. The increase was due to the high-kinetic-energy impact of Cu particles on the Al bond coat. Following deposition of the Cu top layer, the porosity of the Al bond coat decreased from 2.9% to 1.1%. Using this data, it was determined that the Cu top layer had a hardness of 140 HV0.1, which was estimated to be approximately on the same level as the hardness of rolled copper [9,31].

The depth of the micro-hardness indentation is the same as that of the thermal-sprayed coating thickness, whereas macro-hardness indentation uses indenter loads of 1 to 100 kg [36]. Thermal-sprayed coatings have mechanical properties that may affect macro-hardness measurements [99,100]. Therefore, the top surface of thermal-sprayed metal coatings is difficult to quantify with macro-indentation [89]. ASTM Standard E384 specifies that the material should have a thickness ten times greater than the depth of the indentation [89]. A macro-hardness test would likely produce an indentation exceeding one-tenth of the coating thickness, violating ASTM E384, which requires testing thick thermal-sprayed coatings. As a result, the characterization of the macro-hardness of thermal-sprayed metal coatings is limited, and indentation measurements must be performed carefully. This limitation is severely exacerbated in polymer metallization by the "anvil effect," in which the highly compliant polymer substrate elastically yields beneath the thin, rigid metal

coating during localized loading. This results in artificially lowered hardness readings that fail to reflect the coating's true wear resistance in structural applications. The hardness of thermal-sprayed metal coatings with a thickness lower than 100 μm can also be measured with nanoindentation, as well as the local mechanical properties (i.e., individual deposited splats) within lamellar and heterogeneous microstructures of coatings. Nanoindentation measurements of thermal-sprayed metal coatings do not reveal evidence of the macroscopic effects of porosity or intra-particle bonding [101]. While thermal-sprayed metal coatings deposited onto polymer-based substrates can theoretically be evaluated using multiple nanoindentation measurements, the widespread application of this specific methodology has not been extensively reported in the current literature. Consequently, there remains a critical lack of standardized testing protocols specifically adapted to account for the stiffness mismatch inherent to hybrid polymeric-metallic structures.

In addition to measuring Young's modulus, bond strength, and fracture toughness, hardness tests can measure mechanical properties. By measuring the dimensions of the indents in the coatings and the length of the fracture cracks surrounding the indents, Besish et al. [102] evaluated the fracture toughness of YSZ coatings on a variety of materials. As long as the polymer-based substrate exhibits adequate stiffness (that is, no creeping under the force of the indenter), this technique may be applied to metallic coatings deposited onto it.

4.2. Bond Strength

Bond strength determines the mechanical integrity of thermally sprayed metal coatings, their response to compression and shear loads, and their response to temperature changes [93,103]. A coating's bond strength with its substrate is determined by a variety of bonding mechanisms [96,103,104]. Mechanical interlocking occurs when the coating penetrates into the rough surfaces of the substrate [104–107], a chemical reaction creates metallurgical bonds between coatings and substrates, and solid-state diffusion creates metallurgical bonds as well [96]. While chemical reactions and solid-state diffusion dominate metal-to-metal bonding, polymer-metal interfaces inherently lack this chemical affinity. Instead, they rely almost entirely on mechanical interlocking, achieved by inducing localized plastic deformation in thermoplastics or micro-fracturing in thermosets. Furthermore, interfacial bonding in polymers is strongly influenced by degradation mechanisms, in which excessive thermal loads cause chain scission, and by severe mismatches in the coefficients of thermal expansion (CTE) that promote spallation under thermal cycling. Due to the complexity of quantifying each mechanism's contribution to the coating's total bond strength to the substrate, the overall impact of all mechanisms is considered when measuring the coating's bond strength. In order to calculate the coating bond strength, it is necessary to analyze the integrity of the interface between the coating and the substrate, which is referred to as adhesion, as well as the internal strength of the coating itself, which is referred to as cohesion [31,36,108].

Thermal-sprayed metal coatings deposited on polymer substrates have been measured using multiple techniques to determine the bond strength between them. Typically, stud-pull tests are performed by bonding the loading element (stud) to the flat coating surface, placing it under tension, applying a controlled load, and measuring the stud's displacement until the coating delaminates [108,109]. Ganesan et al. [1] evaluated the joint strength of plasma-sprayed Cu coatings on different substrates using stud-pull tests to determine the effect of varying substrate preparation treatments on the bond strength of the layer. Surface preparation treatments were compared, including chemical, thermal, and mechanical. A universal tensile test machine was used to evaluate coating strength by pulling 6 mm aluminum studs bonded to the layers. Based on the results of this study, it can be concluded

that the chemical surface preparation treatment, with a strength of 2.6 MPa, exhibited more robust adhesion than the thermal and mechanical surface preparation treatments, which were found to have strengths of 1.7 and 2.2 MPa, respectively. The leading cause was adhesive failure, which completely removed the coating from the area in which the studs had been attached. Several studies have reported that metal coatings fail on polymer-based substrates primarily due to adhesive failures [1,86,108]. Reference [35] also reports a cohesive loss. The ASTM D4541 Standard [109] specifies procedures and guidelines for testing the adhesion strength of metallic coatings using portable adhesion testers.

In the tensile adhesion test used to estimate the bond strength of thermally sprayed metal coatings, the coatings' ultimate stress and strain are considered [35,58,110,111]. Furthermore, the peel test [112], which is one method to assess the bond strength between surfaces deposited with coatings, is another method to determine the bond strength between surfaces, as is the laser shock adhesion test [59,113,114], as well as the multilayer three-point bending test [86,93]. Despite this, it remains underexplored how these other methods can be applied to thermal-sprayed coatings deposited on polymer-based substrates. Therefore, further research is necessary in this area.

4.3. Chemical and Phase Composition

The phase composition of thermal-spray coatings has been evaluated by X-ray diffraction (XRD) in several studies [16,70,90,92,115]. For example, Osorio et al. [115] examined phase transformations in plasma-sprayed YSZ subjected to temperatures as high as 1100 °C for a period of 1000 h using XRD spectroscopy. XRD has also been used to assess the impact of high temperatures on phase composition during thermal spray processes [92,116]. As a result of Al particles oxidizing during high-temperature deposition, Chen et al. [116] found a higher Al₂O₃ phase content in thermal-sprayed coatings compared to Al-Al₂O₃ powder feedstock materials.

The elemental analysis of thermal-sprayed coatings is crucial, as is phase identification. An elemental composition of thermal-sprayed coatings can be determined with energy-dispersive X-ray spectroscopy (EDX), often combined with scanning electron microscopy [90].

4.4. Microstructural Analysis

Microstructural characterization provides information on the morphology of splats, voids, and cracks in thermal-sprayed coatings. This analysis involved the use of microscopy and porosimetry [117], thereby allowing us to understand how spraying parameters, substrate conditions, and feedstock properties contribute to coating porosity and lamellar splat morphology [37,40,118]. To measure porosity, techniques such as mercury infusion porosimetry, gas pycnometer, and water absorption are utilized [119], all of which involve identifying inter-splats, intra-splats, and delamination defects [36,92]. An additional level of information can be obtained by using microscopy or digital image analysis by studying pores, cracks, and coating microstructures [36]. As shown in the case of Floristan et al.'s analysis of plasma-sprayed TiO₂ coatings [120], SEM is a useful technique for qualitative splat identification, interlocking, thickness measurement, and other studies. However, simply identifying these microstructural features is insufficient; they must be directly correlated to application performance. For instance, in polymer metallization, interconnected porosity and interfacial cracks, as documented via SEM, directly correspond to the failure of the coating as an environmental barrier, allowing moisture and oxidative agents to reach and degrade the underlying polymer. Similarly, excessive inter-splat voids fundamentally disrupt electron pathways, severely limiting the coating's relevance for electrical and lightning-strike protection applications. Standardizing how these defect vol-

umes are evaluated across future studies is essential to accurately predict the composite's operational lifespan.

5. Effects of Process Parameters on Thermal Spray

Thermal-sprayed coating characteristics are intricately linked to the specific spraying parameters used during the application process. Particle velocity, particle temperature, and substrate temperature are all factors that govern the thermal spray process. In particular, the substrate temperature is of great importance when dealing with materials such as polymer-based substrates that possess a low heat capacity. The precise selection and careful optimization of spraying parameters play a pivotal role not only in determining the appearance and structure of the resulting coating but also in minimizing potential thermal damage to the polymer-based substrate during the deposition process. Furthermore, while the primary focus of this review is on polymeric substrates, the parameter optimization data presented in the subsequent tables (Tables 2–6) frequently includes traditional metallic substrates (e.g., steel, copper, and nickel alloys). The inclusion of this metallic substrate data in the subsequent tables is highly intentional; these metallic substrates are included strictly to serve as a critical comparative baseline to establish upper-limit thermodynamic boundaries, whereas polymeric substrates remain the primary focus of this review. It establishes the upper-limit thermodynamic boundaries—specifically, maximum gas temperatures, particle velocities, and kinetic energies—required to achieve dense, defect-free coatings on robust materials. By defining these extreme parameter windows, researchers can systematically down-modulate these variables to safely adapt thermal spray techniques for thermally sensitive polymer composites without inducing thermal degradation or substrate erosion.

Table 2 presents the diverse metallization process parameters required for polymer-based structures. However, these parameters must be interpreted collectively as a delicate thermodynamic balance rather than as isolated variables. For instance, while increasing the electric current in plasma and arc spraying directly enhances particle melting and deposition efficiency, it also elevates the heat flux, thereby increasing the risk of polymer warpage. Similarly, the fuel-to-oxygen ratios in flame spraying and carrier gas pressures in cold spraying dictate the critical velocity and impact temperature. Therefore, precise parameter optimization across all methods, as further detailed in the subsequent process tables, is not merely about achieving a dense metallic coating, but about maintaining the narrow thermal-kinetic window that prevents the severe thermal degradation or kinetic erosion of the underlying polymer matrix.

Table 2. Process parameters of different thermal spraying methods adopted from [31].

Thermal Spraying Methods			
Cold Spraying	Flame Spraying	Electric Arc-Wire Spraying	Plasma Spraying
Gas temperature	Nozzle geometry	Wire material	Feedstock powder
Carrier gas pressure	Feedstock powder	Electric current	Nozzle geometry
Stand-off-distance	Powder feed rate	Wire feed rate	Electric current
Feedstock powder	Carrier gas pressure	Arc gun geometry	Powder feed rate
Nozzle geometry	Compressed air pressure	Stand-off distance	Gas flow rate
	Fuel gas flow rate	Compressed air pressure	Compressed air pressure
	Stand-off distance		Stand-off distance

5.1. Effect of Processing Parameters on Cold Spraying

Optimal processing parameters affect the coating properties, thereby improving micro-hardness and reducing porosity. In the cold spray process, several parameters need to be considered: powder particle size, process temperature, spray gas pressure, spray velocity,

spray distance, and so on. Selecting optimal process parameters is crucial for improving part quality. Huang et al. [121] examined the effect of processing conditions on the characteristics of 316 L SS coating on stainless steel substrate. The study concludes that high mechanical characteristics require dense coatings that have high particle velocities. The speed of particles in flight is also elevated by increasing gas pressure and temperature. Higher particle velocity, appropriate powder size, and morphology are essential for dense, mechanically superior coatings (e.g., microhardness, tensile strength). Ganesan et al. [1] investigated the feasibility of cold spraying Cu and Sn coatings onto PVC (thermoplastic) substrates. A possible reason for this is the thermal softening of the PVC substrate, which affects the efficiency of coating deposition. Lupoi et al. [54] showed that metalizing polymer-based substrates using cold spray methods, such as PC/ABS blend, polystyrene, polyamide-6, and PP, is not suitable for Cu and Al powder particles. Cu particles have a higher impact on energy at higher gas pressures, resulting in higher erosion rates of polymer substrates. As a result of the given substrates and process parameters, it was impossible to fabricate anti-corrosion coatings for aluminum because the critical velocity for cold spray deposition of aluminum particles could not be achieved for the given substrates. However, Sn was successfully deposited on all polymer-based substrates of the same study [54] with a lower specific weight and melting temperature. In a comprehensive study by King et al. [64], copper particles were embedded into a series of thermoset substrates, namely polyamide (nylon), polypropylene (PP), polyurethane (PU), HDPE, PTFE, PC, and polypropylene (PP). Gas temperatures increased from 150 °C to 350 °C to embed the Cu particles into polymer substrates. The softest material, PU, and the lowest melting temperature, HDPE, gave the maximum penetration depth. Nevertheless, the Cu particles did not deform properly to form a continuous coating due to the substrate softening. Zhou et al. [9] also reported that high temperatures during cold spray deposition of Al powder can soften PEEK450CA30 (thermoplastic) substrates.

The gas flow velocity during metal deposition onto polymer-based substrates is influenced by various parameters, outlined comprehensively in Table 2 [31]. The cold spray process for polymer metallization can be classified into three types based on the gas flow velocity during the spray deposition [37,39,58].

1. Low-pressure cold spraying (LPCS), characterized by a gas pressure range and particle velocities between 300 and 600 m/s [40], introduces the possibility that the comparatively lower kinetic energy of particles might hinder efficient metal deposition. This limitation could arise from the potential inability to reach critical velocities [37,122].
2. High-pressure cold spraying (HPCS) involves particle acceleration within the range of 800 to 1400 m/s using a gas carrier with low molecular weight, such as nitrogen or helium [39], typically operating at upstream gas pressures ranging from 1 to 4 MPa [39,54].
3. Pulsed gas dynamic spraying induces oscillation in the carrier gas stream, generating a sequence of shock waves at a constant frequency [123]. These shock waves result in drastic increases in pressure and temperature within the gas stream, significantly surpassing the conditions experienced in conventional cold spray systems. Consequently, particles impacted by these waves are notably accelerated [39].

A general approach to finding optimal spray parameters for metal coatings on polymer substrates can be facilitated by knowledge of the particle velocity and the substrate temperature distribution during thermal spray deposition. The effect of various process parameters on the mechanical characteristics of cold-sprayed coatings is summarized in Table 3.

Table 3. Process parameters and resulting mechanical properties of cold spraying technology. (Note: Data for metallic substrates are included solely as a comparative baseline to establish thermodynamic boundaries. They are not the primary focus of this review).

Coating Material	Particle Size	Gun Pressure	Gun Temp. (°C)	Carrier Gas	Thickness (μm)	Hardness (Hv)	Porosity	Substrate	Ref.
Ni-20Cr	−45 + 15 μm	20.5 bar	400	N ₂ /He	250	—	1.3%	T22	Kaushal et al. [124]
Ni-20Cr (CA)	74 μm	19 bar	450	Air/He	200 ± 8	590	—	T22	Kumar et al. [125]
Ni-20Cr (BM)	67 nm/60 nm	—	—	—	220 ± 9	601	—	SA516	Wang et al. [126]
Ag/SnO ₂	75 ± 38 μm	16 bar	400	N ₂ /He	250	112 ± 3	—	Copper	Singh et al. [127]
Ni-20Cr	—	20.5 bar	—	—	250	—	1.59%–1.63%	T22	
75Cr ₃ C ₂ –25(Ni-20Cr)	—	38 bar	650	—	293	875.67	<1%	Superni-75	Singh et al. [128]
Ni-20Cr	45 μm	20.5 bar	400	—	248	178.28	1.5%–1.6%	SA516	Bala et al. [129]
Ni-20Cr	−45 + 15 μm	20.5 bar	—	—	164	247	1.5%–1.6%	T22	Bala et al. [130]
Ni-50Cr	—	—	—	—	254	221	—	SA516	
Ni-20Cr (80% Ni)	14 μm	19 bar	450	Air	400	456–601	—	SA516	Kumar et al. [131]
Ni-20Cr (72% Ni)	13 μm	—	—	—	—	—	—	—	
Ni-20Cr	14 μm	20.5 bar	400	He	250	279	—	SA516	Bala et al. [132]
Ni-20Cr-TiC	13 μm	—	—	—	—	234	—	—	
Ni-20Cr-TiC-Re	11 μm	—	—	—	—	243–336	—	—	

5.2. Effect of Process Parameter on Flame Spraying

A well-chosen process parameter is essential for selecting a coating material that imparts a range of characteristics, including heat resistance, wear, erosion, corrosion, and oxidation, as well as restoring mis-machined or worn components back to their original size. A number of process parameters affect flame spraying performance, including the type of coating wire used, spraying distance (mm), wire feeding rate (mm/s), the flow rate of oxygen or hydrogen (lpm), and the pressure of oxygen or hydrogen (bars) [133].

The microstructural characteristics of Al₂O₃–13%TiO₂ coatings were examined by Grove et al. [134]. At different parameters, different coatings were deposited on the 7075Al alloy substrate. The study then examined the effects of the acetylene-to-oxygen ratio, the stand-off distance, and surface roughness and porosity on the crystalline phase, surface roughness, and porosity. Volumetric oxyfuel ratios significantly influenced the porosity, roughness, and crystallinity of the coatings. In contrast, the stand-off distance affected coating thickness but not the Al₂TiO₅ phase or coating roughness. Moreover, a 1:2.5 C₂H₂:O₂ volumetric ratio will result in a denser coating, lower porosity, and lower surface roughness. As shown in Table 4, the mechanical characteristics of coatings produced by powder and wire flame spraying are influenced by various process parameters.

Table 4. Process parameters and resulting mechanical properties of wire flame spray and powder flame spray. (Note: Data for metallic substrates are included solely as a comparative baseline to establish thermodynamic boundaries. They are not the primary focus of this review).

Coating Material	Process	Particle Size	O ₂ Pressure	Air Pressure	C ₂ H ₂ Pressure	Spray Distance (mm)	Thickness (μm)	Hardness (HV)	Porosity	Substrate	Ref.
FeCr	Powder Flame	100 μm	3 bar	0.4 bar	0.7 bar	150	865	800 HV	4.42%	Plain carbon steel	Uyulgan et al. [135]
NiCrAlTi	Powder Flame	—	1.9 bar	0.4 bar	2.1 bar	150	540–560	301–395 HV	5%	AISI 304 SS	Hidalgo et al. [136]
Ni-20Cr	Flame Spray	50 μm	2.2 bar	—	1.2 bar	205	—	244 ± 19 HV	10.97 ± 0.2%	Mild Steel	Dejang et al. [137]
Al (1000)	Powder Flame	131.64 μm	4 bar	4 bar	0.7 bar	~250	125–292	32 HV	—	S235JR steel	Muszytyfaga-Staszuk et al. [138]
Sn (1000)	—	16.79 μm	—	—	—	~250	1.43	12 HV	—	—	
PA12 (polymer)	—	166.14 μm	4 bar	—	—	—	—	9 HV	—	—	

Table 4. Cont.

Coating Material	Process	Particle Size	O ₂ Pressure	Air Pressure	C ₂ H ₂ Pressure	Spray Distance (mm)	Thickness (μm)	Hardness (HV)	Porosity	Substrate	Ref.
ProXon P21	Power Flame	−105 + 44 μm	400 bar	350 bar	0.7 bar	150	800	192 ± 23 HV	<8%	35CrMo4	Amokrane et al. [139]
ProXon P31	Power Flame	36 nm	3.0 bar	—	1.2 bar	—	900–1000	317 ± 71 HV	6.2%	Carbon steel	Sharma et al. [140]
NiCrBSi	Power Flame	36 nm	3.0 bar	—	1.2 bar	—	900–1000	210 HV	6.2%	Carbon steel	
NiCrBSi + 0.4% CeO ₂	Power Flame	36 nm	3.0 bar	—	1.2 bar	—	900–1000	215 HV	6.5%	Carbon steel	
NiCrBSi + 1.2% CeO ₂	Power Flame	36 nm	3.0 bar	—	1.2 bar	—	900–1000	238 ± 12 HV	6.8%	Carbon steel	
NiCrBSi + 2% CeO ₂	Power Flame	36 nm	3.0 bar	—	1.2 bar	—	900–1000	226 ± 8 HV	7.3%	Carbon steel	
NiCrBSi + 1.6% CeO ₂	Power Flame	36 nm	3.0 bar	—	1.2 bar	—	900–1000	221 ± 9 HV	7.9%	Carbon steel	
Ni-Cr	Wire Flame	—	2.35 bar	4 bar	2.35 bar	100–150	—	50–55 HV	—	AlMg ₃ alloy	Kucukrendeci et al. [141]
Al ₂ O ₃	Wire Flame	—	2.35 bar	4 bar	2.35 bar	100–150	100–300	812 HV	—	AlMg ₃ alloy	
Cr ₂ O ₃	Wire Flame	—	2.35 bar	4 bar	2.35 bar	100–150	100–300	1215 HV	—	AlMg ₃ alloy	
Ni-WC (EWAC 1002)	Flame Spray	—	2.9 bar	0.4 bar	1.2 bar	20	—	3528–6130 HV	2.2%	Mild steel	Kahraman et al. [142]
Ni-C-Si-Br (EWAC 1004)	Flame Spray	—	2.9 bar	0.4 bar	1.2 bar	20	—	280–640 HV	—	Mild steel	
Metco 41C	Powder Flame	−106 + 45 μm	1.9 bar	—	2.1 bar	150	—	176–195 HV / 345–392 HV	11%	Steel rods	

5.3. Effect of Process Parameter on Electric Wire-Arc Spraying

Process parameters in wire arc spray include particle temperature (max. 5000 °C), velocity (100–300 m/s), stand-off distance (up to 25 mm), max. spray rate, powder input, pressure (4–6 bar), etc. [20,77,143]. Lin et al. [144] studied the electrochemical characteristics of FeNiCrBSiNbW-coated AISI 1045 steel produced by twin wire arc spraying and found that crystallization influenced them relative to those of uncoated AISI 1045 steel. To achieve the distinct crystallization pattern, the coatings at 450 °C, 550 °C, and 650 °C were annealed separately for 1 h at their respective temperatures. Amorphous phases of iron and chromium, Fe₃B and Fe₂₃B₆, become crystalline at 650 °C. Increasing the annealing temperature decreased corrosion potentials and increased current densities. The corrosion resistance of the high-temperature annealing process was lower than that of the as-sprayed process. The high amorphous phase content of the coating is due to the absence of borides (Fe₃B and Fe₂₃B₆). Younes et al. [145] investigated how the chemical composition, mechanical properties, and magnetic performance of FeCo/Al₂O₃-coated steel are affected by mechanical alloying and thermal spraying. After mechanical alloying for 20 h, the powder crystalline size reduced (from 18 to 7 nm), and lattice strain increased (from 0.36% to 0.56%). Thermal spraying led to the formation of distinct phases (Al₂FeO₄, CoFe, CoFe₂O₄, and CoAl₂O₄) in the coating. Chemical composition also affected magnetic performance. As a result of the change in chemical composition achieved through thermal spraying and mechanical alloying of the coating, the mechanical properties (Young's modulus, micro-hardness) of the coating were also increased [146].

Liu et al. [35] concluded that arc spraying cannot be used to evaporate metal coatings on graphite fiber-reinforced polyimide substrates because the feeding wire tip must be heated past its melting point. During arc spraying, overheating of Al droplets can cause thermal damage to the substrate. Due to this limitation, arc-sprayed particles cannot be controlled, unlike in other thermal spraying processes, such as flame spraying, which allows independent control of the spray plume to avoid overheating impinging metal particles. According to Table 5, several process parameters influence the mechanical properties of wire arc spray coatings, whereas the chemical characteristics are largely unaffected.

Table 5. Process parameters and mechanical properties of electric wire-arc spraying. (Note: Data for metallic substrates are included solely as a comparative baseline to establish thermodynamic boundaries. They are not the primary focus of this review).

Coating Material	Spray Distance (mm)	Power Input	Particle Temp. (°C)	Wire Dia. (mm)	Thickness (μm)	Roughness (μm)	Hardness (HV)	Porosity	Substrate	Ref.
NiCrTi	150–250	6–80 kW	≤5000	1.6–3.2	250–300	9.858	355	5.11%	T22	Sharma et al. [147]
Ni-5Al						10.774	327	4.91%	T22	
Ni-5Al						10.992	367	4.90%	T91	
NiCrTi						8.694	428	4.92%	T91	
Ni-5Al	150–250	6–80 kW	≤5000	1.6–3.2	250–300	3.17	240	<2%	T-11	Kant et al. [143]
Ni-5Al						2.93	250	—	GrA1	
Ni-20Cr	150–250	—	—	2	—	3.04	273.5	1.53%	T22	Kumar et al. [148]
Ni-20Cr						2.79	379.8	1.54%	SA516	
Ni-5Al						3.23	203.8	1.55%	T22	
NiCrB	200	29–31 V / 190–210 A	—	1.6–3.2	400–600	—	—	<4.5%	SA213-T2	Wang et al. [149]
FeCrSiB	200	30 V / 190–200 A	≤5000	2	250–300	—	650	4.08%	SA213-T2	Li et al. [150]
NiCrTi						—	380	2.49%		
Fe-Cr						—	480	5.02%		
Ni-5Al	150–250	6–80 kW	—	2	250–300	2.986	275	1.85%	T11	Kumar et al. [151]
Ni-20Cr						2.803	460	1.00%	T11	
Ni-20Cr						2.823	278	1.30%	GrA1	
Ni-5Al						2.930	245	1.51%	GrA1	

5.4. Effect of Process Parameter on Plasma Spraying

In terms of deposition phenomena, the main operating parameters are the carrier gas, the plasma gun power in the plasma chamber, the operating pressure, the angle of powder injection into the plasma chamber, and the primary gas. Several factors influence this processing method, including the power input to the torch, powder characteristics, powder feed rate, and gas flow rate [152]. An analysis of the mechanical properties and deformation behavior of plasma-sprayed thermal barrier coatings was conducted by Zhang et al. [153]. Increasing passage thickness or deposition temperature resulted in denser micro-structures with higher elastic modulus. As a result of increased cohesion among the splats, the surface coating modulus was higher. According to Abbasi et al. [154], atmospheric plasma-sprayed CuAl₂ intermetallic coatings are micro-hard, micro-structured, fracture-tough, and corrosion-resistant. Compared with base steel in NaCl solution, the sprayed coating had 7% porosity, 575 HV microhardness, and a lower corrosion rate. Using plasma-sprayed NiCrAl/Al₂O₃ wt.% TiO₂ with and without sealing treatment, Zhang et al. [155] assessed corrosion performance. As a result of the sealing treatment, the coatings were significantly more resistant to corrosion than those sprayed as-is. Additionally, the sealing treatment significantly affects the electrochemical properties of the coatings.

Guanhong et al. [85] evaluated the effect of plasma spray current on metallized polymer. Thermal damage occurred to carbon fiber-reinforced unsaturated polyester substrates at high currents and prolonged spraying times during plasma spraying of Al₂O₃, even with pre-deposition of Al as a bond coat. Higher plasma jet velocity and energy resulted in greater absorption of incident energy and particle impact at high temperatures. Further processes can be controlled by adjusting parameters such as air cooling, the stand-off distance between the heat source and the substrate, and the temperature of the heat spray. The deposition of metal coatings on polymer substrates is significantly influenced by the stand-off distance [17,75]. Metal particles have a lower oxide content and higher impact velocity over shorter distances. However, too-short standoff distances can cause excessive thermal loading on heat-sensitive polymer materials. There is no doubt that shorter stand-off distances can improve coating morphology; however, excessively low stand-off distances for thermal spray deposition on polymer-based materials are not recommended.

During thermal spraying, compressed air is injected into the substrate to cool it effectively and prevent thermal damage. Floristan et al. [120] showed that air cooling could significantly reduce cracking risk and improve stand-off distances for plasma spraying TiO₂ coatings on glass substrates, resulting in shorter stand-off distances and reducing cracking risks. Studies by Ashrafizadeh et al. [74] and Voyer et al. [17,75] show that this technique also works on polymer substrates. In addition to reducing coating porosity and improving coating morphology, compressed air also improved the electrical conductivity of the coated substrate without causing thermal damage. Fiber-reinforced polymer substrates need further research to evaluate their efficacy.

Another study by Yang et al. [156] investigated the effect of flame remelting of NiCrBSi-30%Mo coatings plasma-sprayed on AISI 1045 substrate on wear performance and microstructure. The research demonstrates that flame remelting a coating as it is applied significantly reduces micro-defects and roughness and increases hardness, elasticity, and wear resistance. Laser remelting improves the microstructure of plasma-sprayed coatings, according to Wang et al. [157]. Corrosion resistance must be enhanced by optimizing process parameters [158]. Li et al. [159] deposited a NiCrAlY/Al₂O₃-20%TiO₂ gradient coating on a Cu-Be alloy and studied its thermal shock performance using atmospheric plasma spraying. The thermal shock behavior of a gradient coating was investigated using XRD, SEM, and EDS techniques. This was done to determine the influence of phase composition and microstructure on the coating's thermal shock response. Gradient coatings are characterized by lamellar structures (uniform thickness and good interfaces) on the surface. Gradient coatings have been shown to have a higher hardness (875 HV) than substrates (199 HV). However, during cycles 37 and 467, at temperatures of 600 °C and 400 °C, respectively, the gradient coatings failed due to thermal shock. The reason may be a temperature gradient, a mismatch in thermal expansion, or oxidation. According to Table 6, several process parameters influence the mechanical properties of plasma-sprayed coatings.

Table 6. Process parameters and mechanical properties of plasma spraying. (Note: Data for metallic substrates are included solely as a comparative baseline to establish thermodynamic boundaries. They are not the primary focus of this review).

Coating Material	Particle Size	Current (A)	Voltage (V)	Stand-off Distance (mm)	Arc Gas Pressure	Carrier Gas Pressure	Thickness (μm)	Hardness (HV)	Porosity	Substrate	Ref.
NiCrAlY	−45 ± 10 μm	500	60–65	100	4.1 bar	2.8 bar	~228	—	2.88%–4.42%	Superni 75, 600; T11, T22	Singh et al. [160]
NiCrAlY	−45 ± 10 μm	700	35	90–110	4.1 bar	2.8 bar	Bond: 150; Top: 200	—	2.88%–4.42%	SF 800H	Singh et al. [161]
Ni ₃ Al	Ni: 74 μm; Al: fine						—	—	2.37%–4.01%		
Stellite-6	−180 ± 53 μm						—	—	2.07%–3.74%		
NiCoCrAlY	22–45 μm	500	60–65	100	—	1 bar	—	335 ± 57	2.1%	T91	Sundaresan et al. [162]
NiCrAlY	−45 ± 10 μm	700	35	90–110	—	—	384	—	2%–4%	GrA1	Sidhu et al. [163]
Ni-20Cr	−45 ± 5 μm						Bond: 152; Top: 213	—	2.5%–4%		
Stellite-6	−180 ± 53 μm						Bond: 172; Top: 214	—	2%–3.5%		
Ni ₃ Al	Ni: 74 μm; Al: fine						Bond: 178; Top: 198	—	2%–4.5%		

6. Future Research Direction

Polymer-based materials are expected to have excellent mechanical and physical properties, including a high strength-to-weight ratio, enhanced corrosion and wear resistance, and high chemical resistance. There are, however, several limitations to polymer-based materials, including their low thermal and electrical conductivities, which limit their use in electrical charge conduction and in environments with elevated temperatures. As a way of enhancing the thermal and electrical conductivity of polymer-based materials, it is

possible to metallize them by deposition of metals onto the surface. Furthermore, the new metallic–polymeric system can provide expanded functionality by leveraging the deposited metal coatings to enable high-performance applications, such as resistive (Joule) heating.

Metallization of polymer-based materials via thermal spraying is the focus of this study, which explores the associated challenges and solutions. Polymers' low thermal conductivity and heat capacity pose challenges in controlling substrate temperature during deposition, leading to potential degradation or changes in the properties at high temperatures. Thermal spraying processes for polymer metallization, including cold spraying, flame spraying, electric arc wire spraying, and plasma spraying, are investigated. There is no doubt that these processes involve varying levels of heat loading on polymer substrates, depending on spraying parameters and feedstock materials. However, it is still possible to deposit metal on polymers successfully.

According to the available literature on wire arc spray, it performed very well. Still, it also has some limitations and challenges, such as adhesion strength, substrate damage, and coating quality, which must be addressed. Significant advancements are required to mitigate the limitations of wire arc spray in terms of its effectiveness. The wire arc spray method can be considered an alternative to other methods when its advantages outweigh its limitations and when the choice of materials and surface preparation is carefully considered. Further research is needed on wire arc spraying to demonstrate that it is a practical, feasible technique among thermal spraying methods.

In the context of polymer metallization, all four methods discussed (cold spray, flame spray, wire arc spray, and plasma spray) are technically feasible, though each carries distinct thermal and operational risks that dictate its specific applications. Based on our review, the following recommendations are suggested for each technique:

Due to its extremely high operating temperatures (up to 14,000 °C), plasma spraying poses the highest risk of thermal degradation of polymers. Therefore, its application should be strictly limited to high-melting-point, thermally stable thermoset composites, and only when refractory metals or ceramics are used, with secondary cooling methods (e.g., cryogenic cooling) actively employed.

While more affordable, flame spray relies on direct combustion, which can easily warp or burn sensitive thermoplastics. It is primarily recommended for depositing low-melting-point metals (such as zinc or aluminum) onto robust, heavily grit-blasted polymer matrices where thick, porous coatings are acceptable and strict dimensional tolerances are not required.

Wire arc spray represents an excellent middle ground, offering high deposition rates with a relatively lower heat input to the substrate compared to plasma and flame spray. It is highly recommended for large-scale, cost-sensitive industrial applications, such as applying anti-corrosion zinc or aluminum layers to civil and marine polymer-composite structures. Pre-heating or applying a bond coat is suggested to maximize adhesion. Among the thermal spray methods currently investigated, cold spraying is overwhelmingly recommended as the most suitable for polymeric substrates. Because deposition occurs in the solid state via kinetic energy rather than thermal energy, it effectively eliminates the risk of oxidation and thermal degradation. It is highly recommended for thermally sensitive thermoplastics and fiber-reinforced composites that require dense, highly conductive, and defect-free coatings, such as those used in aerospace lightning-strike protection and biomedical implants.

To advance the commercial viability and technical reliability of thermal spray metallization on polymeric substrates, future research must be explicitly structured around overcoming six major technical barriers:

- **Substrate Thermal Degradation:** Polymers possess inherently low heat capacities. Future work must prioritize research on the temperature distribution in substrates (e.g.,

fiber-reinforced polymers) that exhibit anisotropic thermal properties during the thermal spray process. Developing advanced analytical and numerical models to account for this anisotropy is critical to prevent polymer warping and thermal degradation.

- **Poor Adhesion:** The transition from mechanical interlocking to strong adhesion remains challenging for polymer-metal interfaces. There is evidence that substrate topography strongly influences the deposition process [164]. Moving beyond simple qualitative SEM assessments or basic roughness parameters (e.g., Ra and Rz), researchers must generate quantitative surface topography data to correlate precise surface profiles with long-term adhesion strength.
- **Erosion During Deposition:** Hard metallic particles often erode rather than deposit on thermosets. Proper characterization of the deposition powder is essential. To control the kinetic energy of the impact, particle size must be measured accurately, preferably by count rather than volume, to determine the exact kinetic thresholds that separate the erosion regime from the deposition regime. Particle shape also plays a crucial role in influencing the drag force during acceleration. Various particle size distributions and shape analyses can be carried out using particle analyzers or by analyzing SEM images via ImageJ (National Institutes of Health, Bethesda, MD, USA) [165,166].
- **Coating Porosity:** While methods like flame and arc spraying are highly cost-effective, they frequently yield higher coating porosity. Future research should focus on optimizing process parameters or employing in situ densification techniques to achieve dense, impermeable metallic layers suitable for demanding environments without relying on extreme heat.
- **Limited Parameter Windows:** The thermal sensitivity of polymers creates extremely narrow operational windows. Establishing generalized parameter windows requires precise calculation of particle velocity based on the nozzle geometry. Since few facilities possess particle image velocimetry (PIV), future hypotheses must rely on analytical or computational fluid dynamics (CFD) models to theoretically calculate impact energy and optimize stand-off distances without inducing thermal damage [167,168].
- **Lack of Standardized Characterization Methods:** Currently, evaluating the bond strength and microhardness of thin metallic coatings on soft polymers is fraught with inconsistencies. Future research must establish standardized testing protocols tailored specifically for polymer-based substrates to ensure reproducibility and accurate comparative analysis across the industry.

By systematically addressing these six barriers, the field can establish and investigate the possibilities of novel applications. These include using metal coatings as resistive heating elements or heat sources on coated FRPC pipes to reduce fluid viscosity at low ambient temperatures and monitoring the structural health of polymer-based structures by controlling the impedance of embedded or surface-deposited metal coatings.

7. Conclusions

Thermal spray metallization has proven to be a highly effective strategy for overcoming the thermal and electrical limitations of polymer-based materials, enabling advanced functionalities such as lightning strike protection and resistive heating. Through a critical comparison of performance metrics, this review determines that no single thermal spray technique is universally optimal; rather, selection must be dictated by polymer class and application constraints. Cold spraying stands out as the most suitable method for thermosensitive thermoplastics requiring dense, low-porosity coatings without thermal degradation. Conversely, for large-scale industrial scalability, electric arc-wire spraying provides the most cost-effective solution, provided that interfacial adhesion is enhanced through adequate surface conditioning. While plasma spraying offers superior shear ad-

hesion, its severe thermal load restricts its feasibility to only the most thermally resilient composites. Several types of polymers can be metalized, including thermosets, thermoplastics, and fiber-reinforced composites, with thermosets being significantly less susceptible to oxidation or thermal degradation during the deposition process. Although research suggests thermal spraying has potential as a valuable powder metallization technique, rising equipment costs and uncertainty about which process parameters are necessary for a successful, substrate-safe deposition prevent widespread adoption. For thick PM, a well-developed mechanical interface is essential. In most PM methods, more efficient, eco-friendly, cost-effective, and scalable polymer-surface preparations are needed to achieve optimal results.

There is no doubt that thick powder metallization will become an integral part of a variety of emerging technologies, such as high-speed transportation, zero-emission vehicles, hydrogen infrastructure, and other emerging technologies in the near future. Materials sciences, manufacturing industries, and global sustainability stand to benefit significantly from advances in PM methods. For the metallization of thick polymer-based structures, further exploration and development of thermal spray methods, especially cold spraying, are required. For future research, the goal is to identify the optimal deposition parameters for dense metallic powders on a wide range of polymeric substrates while preserving surface integrity, thermal stability, and coating adhesion strength. Addressing these challenges can make thermal spray metallization a crucial tool for enhancing the performance of polymer-based structures and their applications across various industries.

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Abbreviations

The following abbreviations are used in this manuscript:

ABS	Acrylonitrile Butadiene Styrene
APS	Air Plasma Spraying
ASTM	American Society for Testing and Materials
CFRP	Carbon Fiber-Reinforced Polymer
CVD	Chemical Vapor Deposition
DC	Direct Current

DE	Deposition Efficiency
EDS	Energy-Dispersive Spectroscopy
EDX	Energy-Dispersive X-ray Spectroscopy
FRPC	Fiber-Reinforced Polymer Composites
FS	Flame Spraying
GFRP	Glass-Fiber-Reinforced Plastic
HDPE	High-Density Polyethylene
HPCS	High-Pressure Cold Spraying
HV	Vickers Hardness
LPCS	Low-Pressure Cold Spraying
Lpm	Liters per minute
PA12	Polyamide 12
PA66	Polyamide 66
PC	Polycarbonate
PEEK	Polyetheretherketone
PIV	Particle Image Velocimetry
PLA	Polylactic Acid
PM	Powder Metallization
PMC	Polymer Matrix Composites
PP	Polypropylene
PS	Plasma Spraying
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVD	Physical Vapor Deposition
RF	Radio Frequency
Rb	Rockwell Hardness B-Scale
Rc	Rockwell Hardness C-Scale
SEM	Scanning Electron Microscopy
SOD	Stand-off Distance
SS	Stainless Steel
TS	Thermal Spray
UV	Ultraviolet
XRD	X-ray Diffraction
YSZ	Yttria-Stabilized Zirconia

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