

Review

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Evolution of TSA/TSZ coatings: a review on recent advances on cold gas spraying for steel corrosion protection

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Abstract: For decades, zinc- and aluminum-based coatings have been considered the best material choice for steel corrosion protection since they may act as a protective barrier and show sacrificial behavior. These coatings are often prepared by galvanizing methods. However, their application by thermal spraying techniques (wire arc spraying, WAS and flame spraying, FS) has been proved as a cost-effective solution for the preparation of long-term corrosion-resistant coatings. This review selectively collects the most relevant information about the application and performance of these two techniques on Zn and Al coatings for corrosion protection. The report summarizes separately the Zn and Al data from the effect of the spraying parameters on coating properties on the one hand, and the results shown in long-term studies carried out in relevant and real exposure conditions, on the other. Finally, this review includes a description and comparison of the most recent advances found out with the novel and emerging spray technique, cold gas spray, for the deposition of Zn and Al coatings for corrosion protection purposes. Nevertheless, the use of this technique has not reached the stage of wide industrial application yet and therefore its long-term performance is unknown, which suggests that there is still room for further development.

Keywords: aluminum coatings; cold gas spraying; steel protection; thermal spraying; zinc coatings.

1 Introduction

Coatings have been widely used to prevent or retard the corrosion of steel. The role of coatings for this application is based on two protective strategies. On the one hand, a coating may act as a barrier separating the metal surface from corrosive substances, avoiding them to reach the steel surface, and on the other hand, appropriate coating selection may provide galvanic or cathodic protection to steel. In the first situation (barrier), the porosity and thickness of the coating play a key role in its corrosion resistance and lifetime since this protective layer has to be corroded before metal corrosion starts. Very resistant and inert metallic coatings such as Ni or Co are included in this group, as well as those coatings that lead to the generation of passive layers as corrosion products, which avoid diffusion of aggressive agents to the protected surface, providing additional protection to the substrate as it is the case for Al. In the second situation (galvanic protection), once the corrosion front reaches the steel, the coating is sacrificially corroded whilst the steel remains unaffected. This beneficial effect is possible when the coating material shows lower corrosion potential (E_{corr}) than steel and it is particularly useful when the steel surface is exposed to the corrosive environment because of local defects as cut edges, scratches, or pinholes. In these cases, the protective layer is preferentially corroded instead of the steel. It is widely accepted, that this method for steel protection is feasible for those coating materials showing E_{corr} values lower than -0.8 V approximately (relative to the Ag/AgCl/seawater reference electrode), which is accepted as the E_{corr} criterion for good cathodic protection of steel (Norske Veritas 2010). As shown in Figure 1, coatings based on Zn or Al may be included in this group of materials.

1.1 Zinc and aluminum for corrosion protection

In the steel industry, coatings of pure or alloyed zinc (Zn) and/or aluminum (Al) are largely used for protecting steel

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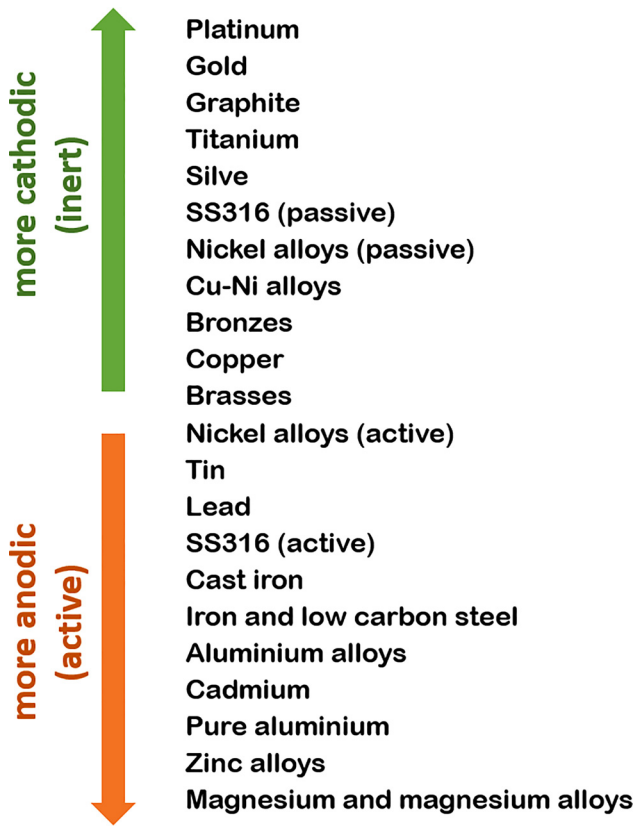


Figure 1: Galvanic series of a number of metals and alloys in seawater.

substrates exposed to corrosive agents such as those present in atmospheric or marine environments (Porter 1994). These two metals, when coupled to steel, may act as sacrificial anodes and are preferentially corroded conferring corrosion protection to steel. The lifetime of a sacrificial anode mainly depends on its mass. Therefore, the lifetime of a coating acting as such is going to be a function of its thickness.

For Al-based coatings, a special situation must be also taken into account. According to the electrochemical series, Al is capable of offering cathodic protection to steel; however, pure Al metal and its alloys are characterized by the generation of a nonporous passive Al_2O_3 layer produced by a passivation process in presence of an oxidant agent. In some environments, this oxide layer is the main responsible for the corrosion resistance shown by Al coatings since it isolates the steel surface from the surrounding atmosphere. Thus, considering that Al may not only act as a barrier layer but also as a sacrificial anode with respect to steel, the long-life corrosion performance of Al alloys (in the form of coatings) is going to be directly related to the coating thickness (or anode mass), to the coating composition (microstructure) and in addition, to

the coating porosity. Comparing the behavior of Al and Zn in aggressive environments, Al is considered to be more resistant in atmospheric conditions because of the formation of this passive protective layer, however, it may be quickly destroyed when the Al coated component is immersed in aqueous chloride solutions. In addition, the Al_2O_3 layer has shown high stability in an aqueous solution in a pH range between 4 and 9, but it is dissolved when the media show high acidity or alkalinity, just the opposite behavior to that shown by Zn coatings (Boukerche et al. 2014). These facts revealed that coating corrosion resistance is highly dependent on its composition and the conditions of the environment that the system is facing.

Nowadays, galvanizing (bath or continuous hot-dip immersion) is the most common method for preparing Zn-based and Al-based coatings on steel substrates. In this method, steel workpieces are immersed in molten baths forming a “chemically” adhered coating that consists of a Fe–Zn or Fe–Al intermetallic interface with a top coat of Zn and Al, respectively. Immersion time, immersion rate, bath temperature, cooling rate, or postannealing treatment are some of the parameters monitored in order to control the quality of the coating. Galvanizing coatings feature high density, low porosity, low oxide content, and good adhesion to the substrate.

Among galvanizing coatings, those based on Zn are the most widely spread because of their high corrosion resistance in many applications, low cost, and good forming properties. However, the corrosion performance of pure Zn coatings is very dependent on the corrosive environment. In order to improve the corrosion performance of Zn coatings for multiple and diverse environments, the use of alloys based on two or more elements has shown significant enhancing capacity. In fact, there is extensive knowledge on the role of Al incorporation to Zn alloys with protective corrosion purposes, and vice versa (Marder 2000). Thus, combining Al and Zn allows for preparing coatings for steel corrosion protection that benefit from the protective properties of both metals.

From a metallurgical point of view, the incorporation of Al to Zn-based coatings mainly avoids the formation of brittle ζ -Fe–Zn interlayer phases in the coating (Figure 2) during galvanizing, which leads to enhancing coating appearance and performance. Since the decade of 1970, 55Al–Zn alloys have been proved as an excellent material for long-life applications, even unpainted. This alloy, with extremely good performance for over 25–35 years, combines the protective properties of both metals (Al and Zn) as it shows a mixed microstructure with a primary Al-based dendritic phase and an interdendritic Zn-based phase. The combination of Zn and Al allows to prepare coatings with

high corrosion resistance in many environments (indoor, outdoor, and/or industry) (Palma et al. 1998).

Despite the fact that galvanized coatings based on Zn and Al is a spread and very known technology for steel corrosion protection; there is still significant interest in developing new coatings with superior corrosion resistance to conventional coatings. In this respect, the inclusion of ternary elements has shown enhanced corrosion resistance of Zn- and Al-based coatings. Among the elements tested, Zn–Al–Mg alloys have featured up to 10 times lower corrosion rate than Zn-based coatings in very harsh environments, like marine coast, industrial installation, and outdoor civil constructions (Schuerz et al. 2009). Magnesium (Mg) inclusion promotes a self-healing protective mechanism on the coating (Prosek et al. 2008a). In Zn–Al–Mg alloys, new Mg–Zn phases are formed in the coating microstructure, which are preferentially and quickly dissolved in corrosive environments. In these conditions, highly resistant corrosion sub-products are generated and stabilized such as simonkolleite $Zn_5(OH)_8Cl_2 \cdot H_2O$, hydrozincite $Zn_5(CO_3)_2(OH)_6$, or zinc hydroxysulfate $(Zn_4SO_4(OH)_6 \cdot nH_2O)$ (Prosek et al. 2008b, 2016). Another ternary element of interest is silicon (Si). It is worth indicating that the commercial alloy 55Al–Zn is not only composed of Al and Zn as it includes a small amount (<2%) of Si. This low concentration of Si into the 55Al–Zn bath has been proved to prevent the generation of brittle intermetallic layers at the coating/steel interface. Despite the fact that Si has no role regarding the corrosion resistance of the 55Al–Zn alloys, the inclusion of a higher concentration of Si (from 5 to 11%), significantly enhances the oxidation resistance of Al alloys at high temperature, since in these conditions the silicon oxide layer shows higher stability than Al_2O_3 . Additionally, Al–Mg alloys are considered the Al-based alloys with the highest corrosion

resistance in marine environments. Nevertheless, Mg content in these alloys has to be carefully controlled as excessive Mg concentrations might have a negative effect on the mechanical properties of the material.

Zn and Al coatings are currently also applied by other methods, such as electroplating, PVD, metallization, or thermal spray (TS) (TSM, “Thermal Sprayed Metallization”) (Fauchais and Vardelle 2012). It is worth mentioning that TSM is a wide-meaning term in the industry and it is used in the literature as a general expression for those metallic coatings obtained by TS although it is mainly related to Zn-based (thermal sprayed Zinc [TSZ]) and Al-based (thermal sprayed Aluminum [TSA]) coatings. Significant differences might be expected in the protective function of Zn and Al coatings applied by other methods, however, this review work wants to focus on the last of these methods, TS, which has been extensively used with protection purposes since the 1900s (Lee et al. 2015).

Thus, in this report, an extensive literature compilation of studies and reports that analyze the performance of TSZ and TSA coatings for steel corrosion protection purposes has been carried out. In this sense, the authors considered it necessary to include a brief introduction to TS techniques and thereafter, to review the most relevant results related to the use of TS methods for coating Zn and Al onto steel substrates. This part of the review will be based on the wire arc spraying (WAS) and flame spraying (FS) techniques which have been preferentially selected, among all TS techniques available, for studying the corrosion resistance of these coatings for decades (Tailor 2016). Following, a fairly new spraying technique such as cold gas spraying (CGS) is presented and described. It is worth indicating that considering the novelty of this methodology, in this section the laboratory-scale studies that have shown the most promising opportunities for preparing Zn and Al coatings by CGS with high corrosion protective performance, have been mainly included and discussed.

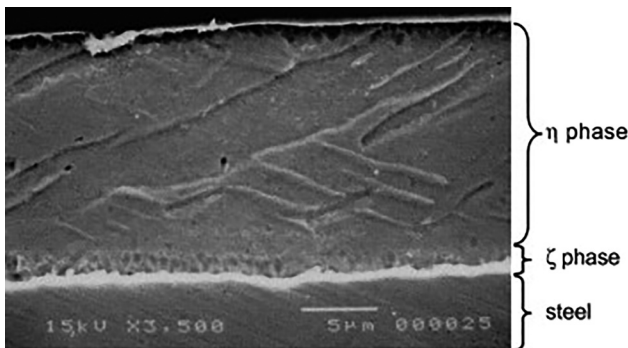


Figure 2: Cross-section of a Zn coating prepared by galvanizing onto steel. The image shows the presence of the ζ -Fe–Zn interlayer phase generated in the coating process. Adapted from Yadav et al. (2007) with permission from Corrosion Science, © 2020 Elsevier Ltd.

2 Zinc and aluminum coatings by thermal spray

2.1 Thermal spray introduction

The TS technology is defined by Hermanek (International Thermal Spray Association 2018) as “a group of coating processes in which fine particles of metallic or nonmetallic materials are deposited in a molten or semi-molten condition to form a coating”. Thus, the coating is formed since

the coating material is heated at high temperature and accelerated to high velocity in form of droplets toward a substrate. The impact of these molten or semi-molten powders onto the substrate leads to the piling up of multiple layered coatings that are mechanically adhered to the substrate.

The properties of these coatings are mainly determined by the precursor material and the spraying parameters used for the deposition. TS coatings microstructure is characterized by a lamellar structure that contains some defects as pores or micro-cracks generated within coating particles. Furthermore, as some spraying processes can be operated in an oxidizing atmosphere, oxidation of coating particles may occur during coating application.

Despite the differences between galvanizing and TS coatings, TS has been used for preparing Zn- and Al-based alloys coatings with corrosion resistance purposes during the last 60 years. Papavinasam et al. (2008) carried out a historical review of the use of TS with protective functions in real applications. In this review, the great importance of the TS technology for protecting steel from rust can be clearly observed and that TS coatings have been preferentially sprayed by two methods, WAS and FS. These TS coatings have shown a lifetime above 25 years; however, in

many cases the application of a sealer topcoat for reaching this long life becomes mandatory.

2.2 Wire arc spraying technology (WAS)

In the WAS technique, an electric arc is generated between two conductive wires (acting as cathode and anode), whose tips are melted. Using a high-pressure gas flow (Air, N₂, or Ar), the molten droplets of the wires are propelled to the substrate (a scheme of a WAS gun configuration is shown in Figure 3). WAS technique's main advantages compared to FS are its high deposition efficiency (DE) (>80%) and spray rate (Table 1).

In the WAS technique, only metals able to be processed in wire shape can be sprayed. Zn and Al show optimal properties as coating materials for WAS since they are low melting points, ductile, and electrically conductive metals. WAS became popular for TSZ and TSA in the decade of 1960 since offered the possibility of deposit these coatings at high rates and with good coating adhesion. However, as in every TS technique, final coating properties will be highly dependent on the wire composition (pure metal, alloy, or core-shell wire), wire configuration (twin or dissimilar wires), and the spraying parameters (Fauchais and Vardelle 2012; Wank 2010). For instance, arc sprayed coatings are characterized for showing over 10% of porosity, medium adhesion and the oxide content will directly depend on the carrier gas used (Davis 2004).

In the following decades, research in WAS was focused on achieving high metallic deposition efficiencies with lower energy consumption. Nowadays, WAS is the most commonly used in literature for testing the corrosion resistance behavior of Zn, Al, and Zn–Al coatings (Zn–15Al, 15 wt% Al, preferentially) (Lee et al. 2015).

2.2.1 Zinc protective coatings by wire arc spraying

Several studies can be found in the literature (Xu et al. 1995) regarding the analysis of the corrosion resistance of TSZ (Table 2). In the study of Kang et al. (2011), the

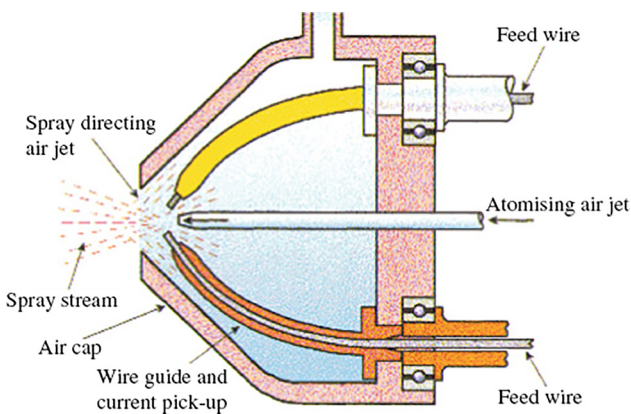


Figure 3: Schematic diagram of the configuration of a WAS gun. Reproduced from Malek et al. (2013a) with permission from Procedia Engineering, © 2020 IOP Publishing Ltd.

Table 1: Comparison of the characteristics of WAS and FS methodologies.

TS method	Heat source	Propellant gas	Spraying temperature (°C)	Particle velocity (m/s)	Feedstock material	Coating materials
Wire arc spraying	Electric arc	Air or N ₂	Up to 6000	Up to 240	Wire	Ductile materials
Flame spraying	Oxyacetylene/oxyhydrogen flame	Air or N ₂	Up to 3000	30–120	Wire or powder	Metallic, ceramic and polymeric materials

Table 2: List of information regarding substrates, surface preparation, thickness, adhesion strength, and electrochemical parameters of thermal sprayed Zn coatings found in the literature.

Coating	Substrate	Surface preparation	TS coating thickness (μm)	Adhesion strength	Sealing	E_{corr} (V)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate	References
Zn	Q235 steel	Sa3, grinding	100	-	Epoxy (30 μm) + fluoropolymer resin (70 μm)	-1.080	-	-	Kang et al. (2011)
Zn-50Al	Q235 steel	Sa3, grinding	100	-	Epoxy (30 μm) + fluoropolymer resin (70 μm)	-1.080	-	-	Kang et al. (2011)
Zn	SS400 steel	Sand blasting	-	-	Epoxy sealing coating	-0.956	22.14	429.02 $\mu\text{m}/\text{year}$	Lee et al. (2015)
Zn-Al	SS400 steel	Sand blasting	-	3.25 \pm 0.3 MPa	Epoxy sealing coating	-1.225	0.49	6.67 $\mu\text{m}/\text{year}$	Lee et al. (2015)
Zn-Sn	SS400 steel	Sand blasting	-	3.57 \pm 0.41 MPa	Epoxy sealing coating	-1.295	3.34	69.81 $\mu\text{m}/\text{year}$	Lee et al. (2015)
Zn	SS401 steel	Grit blasting	200	-	Not sealed	-1.25	4.2	-	Moon et al. (2013)
Zn-15Al	SS401 steel	Grit blasting	200	-	Not sealed	-1.20	1.5	-	Moon et al. (2013)
Zn-5Al	SS401 structural steel	Grit blasting	200	-	Not sealed	-1.18	2.6	-	Moon et al. (2013)
Zn-15Al	S355J2 steel	Sa3, sand blasting	-	10.6 \pm 0.4 MPa	Not sealed	-	-	-	Bobzin et al. (2017)
Zn-15Al	S355J2 steel	Sa3, grit blasting	-	10.8 \pm 0.7 MPa	Not sealed	-	-	-	Bobzin et al. (2017)
Zn-Al	Cold-rolled Q235 steel	-	50	-	Not sealed	-1.09	15.4	-	Liu et al. (2012)
Zn	Ductile cast iron	Degreasing + sand blasting	87	-	Not sealed	-1.07	7.2	-	Bonabi et al. (2018)
Duplex Zn + Al	Ductile cast iron	Degreasing + sand blasting	109	-	Not sealed	-1.25	8.4	-	Bonabi et al. (2018)
Zn-15Al-5Mg	Low carbon steel	Degreasing + sand blasting	300-400	14.2 MPa	Not sealed	-1.284	2.9	-	Zhu et al. (2010)
Zn-15Al-5Mg-0.5RE	Low carbon steel	Degreasing + sand blasting	200-300	14.2 MPa	Not sealed	-1.262	5.3	-	Zhu et al. (2011a,b)
Zn	1.0570 steel	Grit blasting	120-150	-	Not sealed	-0.96	2.8	-	Bobzin et al. (2015)
Zn-15Al	1.0570 steel	Grit blasting	120-150	-	Not sealed	-0.951	2.15	-	Bobzin et al. (2015)
Zn-2Al-2Mg	1.0570 steel	Grit blasting	120-150	-	Not sealed	-0.992	2.08	-	Bobzin et al. (2015)

microstructure of galvanized and arc sprayed Zn coatings are compared. The authors published the Scanning Electron Microscopy (SEM) images of the transversal section of the two coatings shown in Figure 4. The galvanizing coating is characterized by a dense, fine, and highly adhered microstructure whereas the arc sprayed coating feature high porosity and roughness and visually lower adhesion. Despite these differences, the arc sprayed Zn–Al coating shows a lower E_{corr} (>-1.0 V) and corrosion rate than the hot-dip coating. Based on this, it is possible to conclude that an arc sprayed coating could reach a longer lifetime compared to a galvanizing coating. This conclusion was confirmed by Lee et al. (2015), who tested the corrosion resistance of both types of Zn–Al coatings by means of the Copper Accelerated Acetic Acid Salt Spray Testing (CASS test) method (ASTM Standard 2021). From the visual inspection of the results of these tests, it was concluded that after 15 days of exposure to the corrosive environment, less rust is generated in arc sprayed Zn–Al coatings than in galvanized coatings.

The corrosion of arc sprayed Zn and Al coatings has been also studied in simulated splash and tidal zone in marine environments, and not only in lab-scale experiments. In these studies, it has been observed that both, TSZ and TSA coatings show very low corrosion rates when applied in the three regions under evaluation (splash, tidal, and immersed zones) during very long-term experiments. Nevertheless, a significant reduction of the corrosion lifetime was observed when it was applied only in the tidal zone of a steel immersed structure in order to simulate that Zn and Al are acting as a sacrificial anode that protects the exposed steel surface that is immersed (Hou et al. 2003).

The effect of other alloying elements on Zn arc sprayed coatings performance has been deeply analyzed in the

literature. In this respect, the higher corrosion resistance of arc-sprayed Zn–Al coatings is confirmed and the results obtained point out that corrosion protection of steel by Zn–Al coatings follow the trend Zn–15Al $>$ Al $>$ Zn (Moon et al. 2013).

The strong impact of the arc spraying parameters on the properties of the obtained coatings is widely acknowledged. Thus, Gulec et al. (2011) showed that coating thickness can be adjusted and that this parameter is directly proportional to the current intensity applied during spraying. As expected, salt spray tests carried out with these samples demonstrated that Zn–Al alloys provide higher corrosion protection than Zn or Al coatings, but mainly, that the corrosion rate of the coating is directly related to its thickness, that is, a higher thickness involves longer lifetime. Djerourou et al. (2013) demonstrated that not only a physical property such as microhardness but also corrosion resistance of arc sprayed Zn–Al coating is significantly influenced by the spraying distance. Thus, the author concluded that the best Zn–Al protective behavior was observed setting this parameter to 100 mm. Thorough surface preparation is paramount to achieve an arc sprayed coating with high adhesion. In fact, demanding surface preparation levels Sa₂/2 and Sa3 are highly recommended for arc sprayed Zn coating in order to ensure a continuous interface contact between coating and substrate (Bobzin et al. 2017). Finally, the use of high temperature and air atmosphere in the WAS technique may lead to the oxidation of Zn metal during deposition. As it was observed by Huang and coworkers (Chen et al. 2016), the oxide content increases the wear rate of the coating and as a result, the corrosion protection of the arc sprayed coating decreases because of the generation of local defects and unprotected zones.

The use of dissimilar wire metals has been evaluated as a new strategy for improving the corrosion resistance

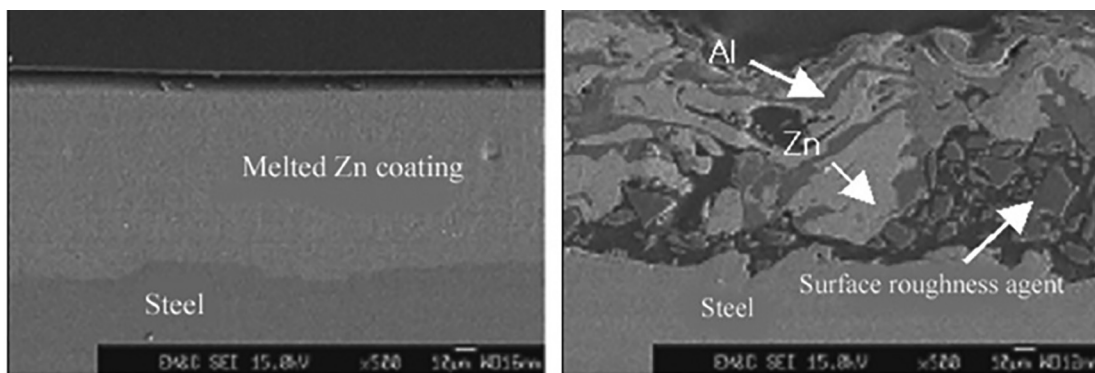


Figure 4: Comparison of the microstructure of galvanized and arc sprayed TSZ coatings. SEM images of the cross-section of a hot dipping (left) and arc sprayed coating (right). Adapted from Lee et al. (2015) with permission from Corrosion Reviews, © 2020 De Gruyter.

of the most common Zn–Al compositions. By this method, Zn–Al pseudo alloyed coatings were prepared by Liu et al. (2012) It is worth describing that compared to a Zn–Al alloyed coating, the microstructure of a Zn–Al pseudo alloy is characterized by discrete particles of Zn and Al plus the alloyed phases of both metals. The coating showed less noble E_{corr} than the Zn–Al alloys after 400 h of salt spray test, which has been interpreted as a better corrosion resistance performance. Nevertheless, the behavior of these protective layers in long-term experiments would have to be tested to confirm this conclusion. Following this idea, corrosion studies conducted on double-layered Zn–Al coatings can be found in the literature. In some of these studies, the double-layered Zn–Al coating has shown lower E_{corr} and better performance in salt spray test after 750 h than Zn, Al, and Zn–Al coatings (Bonabi et al. 2018).

The addition of Mg to a Zn–Al greatly enhances the corrosion protection of steel. In Yu's research group a deep study was carried out focused on the opportunities of arc sprayed Zn–Al–Mg coatings for steel protection (Zhu et al. 2010). It is worth mentioning that arc spray shows some methodological limitations for preparing coatings containing Mg, and the most important is the complexity of manufacturing Mg wires for arc spray equipment. In a first attempt (Zhu et al. 2011b), these authors studied the microstructure of arc sprayed Zn–Al–Mg coatings with Zn–14.9Al–5.9Mg–3.00 (wt%) composition, in which they identified a wide variety of phases (Zn, $\text{Mg}_2\text{Zn}_{11}$, $\text{Al}_{12}\text{Mg}_{17}$, and some oxides, MgAl_2O_4 , Al_2O_3 , and ZnO). The analysis of the microstructure and properties of the Zn–Al–Mg coating revealed a layer with low porosity but low adhesion to the substrate. In addition, the presence of Mg into the coating composition leads to an increase in its E_{corr} and corrosion current, which can be inferred as a decrease in the corrosion protection ability. The adhesion of the coating may be improved by incorporating a small amount of rare earth to the Zn–Al–Mg alloy, however, these new elements had a detrimental effect on the coating performance since it was corroded even faster than the Zn–Al–Mg coating (Liu et al. 2008; Lu et al. 2013; Zhu et al. 2011a).

Zn–Mg cored wires were used by Bobzin et al. (2015) for coating steel with Zn–Al–Mg coatings containing 1–2 wt% of Mg and Al. From the comparison of the results in salt spray tests with Zn–Al–Mg coating, Zn and Zn–15Al alloys, the authors concluded that Zn–Al–Mg clearly presents higher corrosion resistance because corrosion products generated during the corrosion process (Simonkolleite and double-layer hydroxide) provided a dense barrier against the electrolyte.

2.2.2 Aluminum protective coatings by wire arc spraying

Same as Zn coatings, Al has optimal properties to be used in arc spraying (Table 3). However, certain limitations can be found for Al arc spraying regarding the use of not inert propellant gases. Thus, high aluminum oxidation may occur when air is used as an atomization gas instead of nitrogen (Lee et al. 2015). This is a relevant point, as the use of inert propellant gases will directly involve an increase in the costs of arc sprayed Al coatings.

In the report of Abedi Esfahani et al. (2012), a typical SEM transversal section of an arc sprayed Al coating can be observed. As expected, the comparison of TSA and TSZ coating microstructure clearly revealed that these coatings are pretty similar, featuring high porosity and roughness compared to a hot-dip galvanizing coating. In contrast, Al arc-sprayed coatings are characterized by the presence of darker regions in the microstructure corresponding to oxide phases (Malek et al. 2013a,b), as it has been confirmed by Energy Dispersive X-ray Spectroscopy analysis (EDS) (Chaliampalias et al. 2008a,b).

Several studies can be found in the literature (Choe et al. 2015; Lee et al. 2015; Malek et al. 2013a,b) comparing E_{corr} of arc sprayed Zn and Al coatings. In general, Al coatings show a less noble corrosion potential than Zn coatings, but their corrosion rate can be higher than Zn depending on the exposure conditions. These differences can be explained by the different corrosion mechanisms of Zn and Al materials. In harsh environments, Al coatings are quickly oxidized forming a barrier that avoids corrosive substances reaching the steel substrate. This passive oxide layer acts as an insulator which explains the lower E_{corr} but lower corrosion rate of Al coatings with respect to Zn.

The porosity shown by arc sprayed Al coatings is considered the main disadvantage of this technology. In addition, this porosity is sometimes interconnected and pitting cannot be totally avoided. For instance, Abedi Esfahani and co-workers (2012) initially observed that after 44 days of immersion in a 3.5% NaCl solution, a dark Al_2O_3 layer is generated on the top side of Al coatings that theoretically perfectly protect steel. Afterward, the SEM cross-section of the arc sprayed Al coating revealed that more oxide phases were generated inside the Al coating due to the introduction of the electrolyte through the coating porosity, highlighting a feasible future failure of the coating corrosion resistance. However, electrochemical experiments in simulated marine environments (3.5% NaCl (aq)) (Egtvedt et al. 2012; Hou et al. 2003; Wang and Sun 2011; Zhao et al. 2010), have indicated that the porosity shown by arc sprayed Al coatings may not be a relevant

Table 3: List of information regarding substrates, surface preparation, thickness, adhesion strength, and electrochemical parameters of thermal sprayed Al coatings found in the literature.

Coating	Substrate	Surface preparation	TS coating thickness (μm)	Adhesion strength (MPa)	Sealing	E_{corr} (V)	J_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate	References
Al	Q235	Sa3, grinding	100	–	Epoxy (30 μm) + fluoropolymer resin (70 μm)	–0.860	9.69	0.66 $\mu\text{m}/\text{year}$	Kang et al. (2011)
Al	SS400 steel	Sand blasting	–	–	Epoxy sealing coating	–1.021	0.16	2.26 $\mu\text{m}/\text{year}$	Lee et al. (2015)
Al–Mg	SS400 steel	Sand blasting	–	4.69 \pm 0.50	Epoxy sealing coating	–0.905	0.02	0.29 $\mu\text{m}/\text{year}$	Lee et al. (2015)
Al	SS401 steel	Grit blasting	200	–	Not sealed	–1.00	1.4	–	Moon et al. (2013)
Al	Ductile cast iron	Degreasing + sand blasting	94	–	Not sealed	–1.20	1.3	–	Bonabi et al. (2018)
Al	Mild steel	Sa3, sand blasting	150	27 \pm 3	Not sealed	–1.012	5.0	–	(Abedi Esfahani et al. 2012)
Al	(Fe–0.05C–0.25Mn wt%)	Sa2.5, degreasing + sand blasting	220–400	9–12	Not sealed	–	–	–	Malek (2013)
Al	(Fe–0.05C–0.5Mn wt%)	Sa2.5, degreasing + sand blasting	220–240	–	Not sealed	–	22.72	–	Zhao et al. (2010)
Al/Zn	S235	Acetone + sand blasting	220–240	–	Not sealed	–	2.54	–	Zhao et al. (2010)
Al	HSS (X80 steel)	Acetone + sand blasting	150–200	–	Epoxy resin	–0.980	15.23	0.161 $\text{g}/\text{m}^2 \text{ h}$	Wang and Sun (2011)
Al–Zn	HSS (X80 steel)	Grit blasting	150–200	–	Epoxy resin	–0.628	12.50	0.089 $\text{g}/\text{m}^2 \text{ h}$	Wang and Sun (2011)
Al	Mild steel	Acid de-scaling + sand blasting	100	4.86 \pm 0.05	Not sealed	–0.896	4.86	–	Lee et al. (2016)
Al	(Fe–0.25C–0.95Mn wt%)	Sand blasting	–	–	Not sealed	–0.811	0.7	–	Kim et al. (2007)
Al	SS304	–	120	–	Not sealed	–0.85	–	–	Han et al. (2009)
Al	Mild steel (1020)	Sa3, sand blasting	390	17.9 \pm 2.0	Not sealed	–	–	–	Paredes et al. (2006)
Al	S235JR steel	Degreasing + sand blasting	90–185	–	Not sealed	–0.724; –0.765	52–3.3	0.56–0.04 $\mu\text{m}/\text{year}$	Pardo et al. (2009)

issue in long exposure periods. In these reports, it is demonstrated that during the test new corrosion products such as aluminum hydroxides and chlorides are generated. These products show a pore filling effect and enhances the corrosion resistance of the oxide passive layer generated and hence, their presence reduces the corrosion rate of the coating (Lee et al. 2016). Thus, these studies underline that the incorporation of a porosity sealing in the coating configuration is an important point to consider in order to use arc sprayed Al coatings for protective purposes (Figure 5). In this respect, the use of organic or inorganic sealers is highly recommended for long-service TSA applications. In the literature, many types of sealers have been applied on the coating surface, including polyurethane, phenolic, epoxy, vinyl, and/or wash primers (Lee et al. 2017; Papavinasam et al. 2008). As an example, Choe et al. (2014) demonstrated that the application of an epoxy sealer on different metallic arc sprayed coatings (Zn, Zn–Al, Al, and Al–Mg) drastically decreases the corrosion rate of these protective layers. A different strategy was followed by Liu with the aim of improving the sealing properties of arc sprayed Al coatings (Liu et al. 2010). This author studied the opportunities of traditional hydrothermal sealing treatment and concluded that after this treatment a continuous film of aluminum hydroxides is generated onto the Al coating surface. This film covers most of the pores in the surface and reduces the current density (j_{corr}) of the coating with respect to the untreated one even after 90 days of immersion in 3.5% NaCl solution.

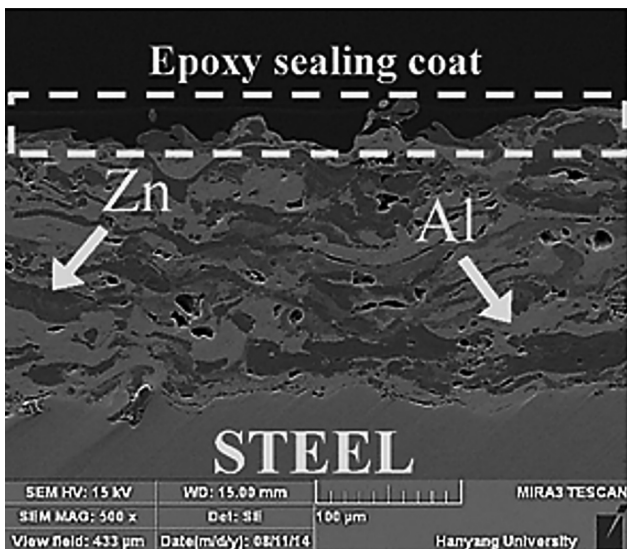


Figure 5: SEM cross-section of Zn-23Al protective system composed of a Zn–Al pseudo alloy coating sealed with an epoxy resin. Reproduced from Choe et al. (2014) with permission from Materials, © 2020 MDPI AG Ltd.

As for arc sprayed Zn coatings, several studies can be found in the literature regarding the study of arc sprayed parameters on final Al coating properties (Ellor et al. 2004; Horner et al. 2015; Kim et al. 2007). Thus, Gulec et al. (2011) found out that despite the high porosity observed in Al arc sprayed coatings, coating thickness can be increased from 200 to 400 μm by increasing current intensity from 100 to 300 A. As expected, the visual inspection of these coatings after salt spray tests demonstrated that thicker Al coatings provided higher corrosion protection than thinner coatings. The effect of thickness on corrosion behavior of arc sprayed Al coatings was also studied in deep by the Kim group (Han et al. 2009), concluding that corrosion resistance is slightly enhanced when coating thickness increases from 60 to 120 μm . However, the deposition of thick coatings might have some limitations associated with the generation of coatings with high porosity, which might bring a negative and undesirable effect on the actual protective performance of the coating.

The role of the surface preparation, or roughness, on the coating adhesion of arc sprayed Al coatings has been studied by Paredes et al. (2006). These authors have observed that substrate and coating roughness are directly linked, and, those substrates prepared with the highest roughness showed the highest coating roughness after deposition. In this respect, they also observed that low surface preparation leads to a slight loss of adhesion strength of the arc sprayed Al coatings deposited onto steel substrates.

Finally, it is worth indicating that WAS offers the opportunity of depositing pseudo alloyed coatings by means of using dissimilar wires instead of twin wires (Calla and Modi 2000). For corrosion purposes, this methodology allows obtaining Zn–Al coatings with higher Al content (up to 27%) than those obtained using Zn–Al alloyed wires, as the highest Al content incorporated for wires manufacturing is close to 15%. These pseudo alloys show promising corrosion resistance compared to Zn–Al alloy.

2.3 Flame spraying technology (FS)

In general, in the FS process, an oxy-fuel flame is used as a source of heat for melting the metallic precursor material (Figure 6). This material can be feed into the flame chamber (temperature up to 3000 $^{\circ}\text{C}$) in wire or powder form and therefore, it proceeds to a molten or semi-molten state. The material particles are propelled onto the substrate surface using air or an inert gas (N_2 or Ar) as a propellant (Wank 2010). Many feedstock materials are commercially available for this technique due to the opportunity of using

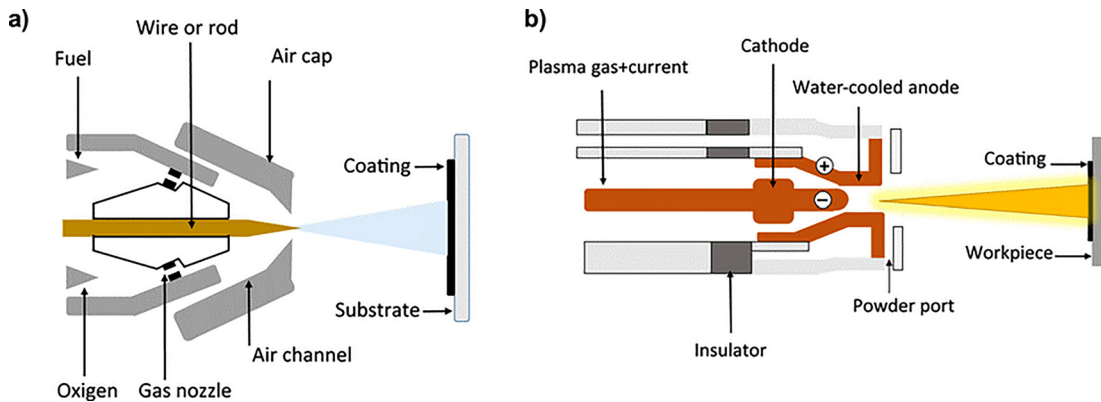


Figure 6: Schematic diagram of the configuration of an FS gun: (a) Powder feed and (b) wire feed. Reproduced from Lan et al. (2020) with permission from Encyclopedia of Renewable and Sustainable Materials, © 2020 Elsevier Publishing Ltd.

materials in powder form, which is a significant advantage compared to the arc wired technique. On the contrary, one of the disadvantages more frequently marked for FS coatings is that they are prone to show higher oxide content, and lower adhesion, to the substrate than the arc sprayed coatings (Table 1) (Davis 2004) due to the higher temperature reached into the flame chamber.

Initially, this FS technique was the most used for TSZ and TSA coatings as it was portable and the coating thickness was easily controlled because of the low deposition rate compared to WAS technique. Nowadays, this technique has been displaced by WAS and is primarily used for depositing metallic coatings for protection purposes (wear and corrosion) in small and/or intricate parts (Papavinasam et al. 2008).

2.3.1 Zinc protective coatings by flame spraying

Compared to WAS, fewer amount of studies are found in the literature regarding the use of FS for Zn coating. As expected for TS coatings, the cross-section of the FS Zn coating showed higher porosity and roughness than the galvanizing coatings and no interlayer Fe–Zn can be identified (Vourlias et al. 2007a,b). Vourlias et al. tested the corrosion resistance of both layers (FS and galvanized Zn) in two different atmospheres, oxidizing (2007a) and marine simulated atmosphere (2007b), and observed a higher resistance of the FS Zn coating to cracks generations during corrosion, in spite of showing less homogeneity of its microstructure. These results pointed out that not only both coatings provide high corrosion protection to steel under these conditions but also highlighted the high protective performance of Zn FS coatings (Chaliampalias et al. 2008a,b).

Further developments on the FS technique have shown that outstanding quality coatings can be obtained by this

technique (Gorlach 2009). Using Zn–15Al alloy wires instead of powder as feedstock material, Zn–15Al coatings showing 150–200 μm thickness, lower porosity, and oxide content, and higher adhesion than arc sprayed were prepared onto steel substrates. In addition, these coatings did not show clear signs of corrosion after lab-scale salt spray tests, even without a sealer topcoat, indicating their high protective behavior. Recently, Chaliampalias (2016) has demonstrated that the oxide scale generated on FS coatings is prone to delaminate at prolonged exposure time, suggesting that thicker FS coatings are mandatory in order to achieve hot-dip Zn coatings performance for corrosion resistance.

2.3.2 Aluminum protective coatings by flame spraying

Same as Zn, the amount of reports regarding the use of FS for Al deposition is also considerably lower compared to those focused on WAS technique (Moon et al. 2013).

From a materials point of view, a comparison of the arc and FS Al coatings can be found in Pombo Rodriguez et al. (2007) research. These authors carried out a detailed analysis of the differences in the oxide content generated into Al coatings produced by WAS and FS using air as propellant gas. The XPS results showed that the oxide content on the surface of both Al coatings was quite similar. However, the composition of the internal layers revealed that, unexpectedly, the arc sprayed Al coating showed higher oxygen content than the FS deposit. According to these authors, this could be explained by the fact that during the electric arc spraying procedure free oxygen concentration and temperature are higher than during FS. Corrosion behavior of the arc sprayed and FS Al coatings was tested according to ASTM B 117/90 standard. After 4000 h of exposure to a saline environment, on the

surface of both coatings, no rust signs were observed in the surface samples, so it could be concluded that the steel substrate was perfectly protected by both Al coatings. X-Ray Diffraction (XRD) and metallographic characterization of the Al corroded coatings revealed that, on the one hand, the corrosion products generated in arc sprayed coatings were different than in FS Al coatings and on the other hand, the arc sprayed coating showed a clear loss of thickness after 4000 h of exposure. From these results, the authors concluded that in the arc sprayed Al coatings the oxidized aluminum products do not remain adhered to the Al coating and are removed from the surface faster than the corrosion products generated in a FS Al coating. This fast removal of the protective layer will reduce the corrosion protection of the arc sprayed Al coating, if it is compared with the resistance of the FS Al coatings. Shrestha and Sturgeon further tested the corrosion resistance of these two Al coatings (deposited by WAS and FS) (Shrestha and Sturgeon 2005). For the tests, Al coating was prepared with a $\varnothing 8$ mm defect (hole) in the coating center, exposing the S355J2 steel to the environment (Figure 7). Electrochemical parameters of these systems were determined and demonstrated that Al FS coatings showed lower E_{corr} and corrosion rate than arc sprayed coatings, that is, higher cathodic protection, after 21 days of immersion in 3.5%

NaCl solution. In addition, it is relevant to mention that no rust signs were observed on the steel surface exposed to the saline solution which means that Al coating provided successfully a physical barrier and sufficient cathodic protection to the steel.

Chaliampalias has compared both oxidation and corrosion performance of FS Al coatings (Chaliampalias et al. 2008a,b). The use of Al protective layers allows increasing the oxidation temperature resistance of steel compared to a Zn coating. In this situation, FS Al coating acts as a diffusion barrier of oxygen and it is homogeneously consumed at long exposure times due to the diffusion of oxygen through the Al layer. Nevertheless, this FS Al coating was prone to delaminate at very high temperatures (>1000 °C) which may make it mandatory to prepared very thick Al layers in order to achieve the desired corrosion resistance. The FS Al coating was also tested in salt spray conditions under exposure to Cl^- and O_2 corrosive agents. In these experiments, it was observed that corrosion leads to local agglomerations of corrosion products consisting of Al-oxides, chlorides, and hydrates, in the coating surface and microstructure. In this case, the corrosion products showed certain positive effects on coating corrosion resistance as they sealed or covered the coating porosity and did not allow the diffusion of the corrosive agents to the steel surface.

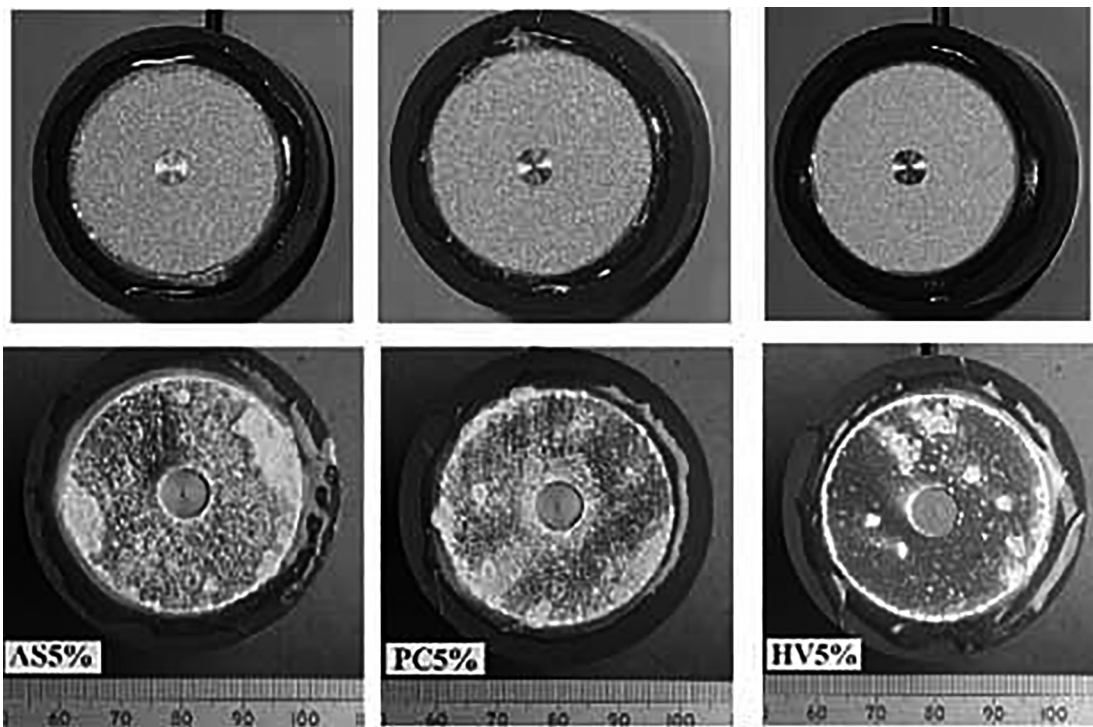


Figure 7: Images of the evolution of FS and WAS Al coatings deposited onto S355J2 plates with a $\varnothing 8$ mm defect. As-sprayed (top) and after 31 days of immersion in aerated 3.5 wt% NaCl solution (bottom). Reproduced from Shrestha and Sturgeon (2005) with courtesy of TWI Ltd.

Considering the high oxidation resistance shown by these Al coatings, the Rizzo group studied the opportunities of using TSA in a fluid catalytic cracking regenerator (very high oxidant atmosphere, $O_2 = 2\%$ and $SO_2 = 3\%$) (Caminha et al. 2004). Under these conditions, FS Al coating was not totally able to protect steel from oxidation at long exposure times, since some O_2 and SO_2 diffusion through the coating could not be avoided because of the high porosity showed by the Al coating. All these results highlighted the relevance of the final coating properties on its corrosion protective performance. In FS, same as other TS techniques, the proper selection of the spraying parameters setup is mandatory in order to perfectly manage the characteristics of the Al coating (oxide content, adhesion, thickness, porosity...). In this respect, Glogovic reported that among the parameters analyzed in his study (powder supply, step, and spraying distance), powder feeding rate is the most relevant parameter to take into account for corrosion purposes since there is a direct relationship between powder feeding rate and final coating thickness (Glogović et al. 2011).

As mentioned, in FS Al coatings the corrosion products generated can show a pore-blocking effect. However, the sealing effect of the corrosion products is not enough for solving the issue generated by the high porosity present in FS Al coatings. This point is highlighted in Pardo et al. research work (2009). In this study, aluminum was coated onto different Mg alloy substrates by FS technique and a post-treatment was carried out at a pressure of 32 MPa at room temperature in order to reduce the level of porosity of the Al coating. From the comparison of the cross-section of the Al coating with and without the cold-pressing post-treatment, it could be concluded that the application of this treatment leads to a significant reduction of the porosity level on the coating, and in addition, it improved the bond strength of the coating to the steel surface.

FS and WAS are classified as low-velocity processes among the TS techniques since the carrier gas has a low velocity and as a result, the particles impinge to the substrate surface with low kinetic energy. It is accepted that, in consequence, these coatings own low coating density and low adhesion strength. In order to improve the bond strength of coatings, attempts to use high-velocity processes for TSZ or TSA can be found in the literature. High-Velocity Oxy-Fuel (HVOF) process is based on the combustion of fuel with oxygen or air in a combustion chamber at pressures between 0.24 and 0.82 MPa. The expansion of gases in a de Laval nozzle leads to a supersonic gas flow (very high gas velocities, up to 2000 m/s), which is used to accelerate particles toward the substrate surface (Wielage et al. 2006). This technique has been tested for the

deposition of metallic anticorrosive coatings (Ti- and Al-based coatings). In the case of HVOF Al-coatings, it has been determined that high quality aluminum coatings with a wide range of thickness, high-cohesive strength (above 20.0 MPa), and low porosity (<1%) can be deposited onto steel surfaces (Chow et al. 2000). In addition, these coatings have shown good corrosion resistance, which is assigned to their dense and homogeneous layer morphology (Gorlach 2008; Shrestha and Sturgeon 2005). Despite these results, it is worth indicating that although HVOF can be used for spraying metallic anticorrosion coatings, there are still some drawbacks for on-site application where anticorrosion coatings are typically required.

2.4 Long-term tests in real situation

Despite differences described between galvanizing and arc and FS coatings; TS technology has been tested and used for preparing Zn- and Al-based coatings with corrosion resistance purposes in real situations for the last 90 years. In the literature, several reports and studies which analyze the applications of TS coatings for the industry can be found. In Table 4 the most relevant long-term studies and their results regarding steel corrosion protection application are summarized.

In this context, Fauchais highlights in its review article (Fauchais and Vardelle 2012) the remarkable performance of the Zn coated sluice gates and canal lock gates of the St. Denis Canal in France in the early 1930s, which remain in perfect conditions nowadays. Until the 1950s the use of TSA coatings was not as extended as Zn for corrosion protection purposes. At that time, the American Welding Society (AWS) Committee on Thermal Spraying started an extensive study of the corrosion protection afforded by metallic coatings to steel. At the end of this researching program, it was concluded that Al coatings (sealed and/or unsealed) perform better than other materials in seawater, as well as in severe marine and industrial environments (AWS 1974; Papavinasam et al. 2008).

The use of TSA coatings was then widely spread and nowadays, many examples of the performance of Al coatings in big structures such as steel bridges, tanks, oil and gas pipelines, oil and gas platforms, ship hulls, sluice gates, and canal lock gates, etc are documented (Cavassi and Cornago 1999; Ce and Paul 2017; Control 1983; Fukumoto 2008; Koch et al. 2002; Rezakhani 2007; Szymański et al. 2015; Wijewardane 2015). In some of them, TSA coatings provided corrosion protection for more than 50 years (Fauchais and Vardelle 2012; Mandeno 2013). As an example, Kuroda and Kawakita reviewed the general

Table 4: List of long-term studies and their conditions based on thermal spray coatings.

Coating material	TS technique	Exposition conditions	Exposure time (years)	References
Zn, Al, and Zn-13Al	WAS/FS	Atmospheric, splash, tidal, and immersion in natural seawater	18	Kuroda et al. (2003, 2006)
Zn, Al, and Zn-13Al	WAS/FS	Atmospheric exposure in coastal area	33	Katayama and Kuroda (2013)
Zn-15Al and Al	FS	Coastal-marine atmospheric exposure	2	de Rincón et al. (2009)
Zn-15Al and Al	FS	Atmospheric exposure	3.5	Panossian et al. (2005)
Duplex Zn/Al	FS	Coastal-marine atmospheric exposure	6	Salas et al. (2012)
Zn, Al	Wire FS	Atmospheric and seawater immersion	19	AWS (1974)
Zn, Al	Wire FS	Atmospheric, splash, tidal, and immersion in natural seawater	10	Kumar and Bukowski (1982)
Zn, Al, and Zn-35Al	Powder/wire FS	Atmospheric and seawater immersion	10	Watkins (1974)

use of TS coatings for corrosion protection in the marine environment in Japan since the 1960s (Kuroda et al. 2003, 2006). These authors also conducted a 33-year long study, which compared the performance of Zn, Al, and Zn-15Al TS coatings and concluded that Al coatings sealed with a polyurethane paint showed the best corrosion resistance among the coatings tested. At the end of this 33-year long study, Katayama and Kuroda (2013) concluded that the high lifetime showed by the arc and FS Al and Zn coatings seemed to be directly related to the initial thickness. Furthermore, the authors established that the high corrosion resistance of Al coatings under atmospheric exposure is directly related to the generation of a passive oxide film on the coating, whereas, in Zn and Zn-Al coatings, corrosion is inhibited due to the formation of a barrier of Zn corrosion products onto the Zn layer.

Zn-15Al alloy is the most studied Zn-based composition among the TS coatings. An interesting long-term comparative evaluation of the corrosion resistance of the Zn-15Al alloy with other Zn- and Al-based coatings exposed to the atmosphere was carried out by de Rincón et al. (2009) and Panossian et al. (2005). In these studies, FS and WAS coatings were exposed to atmospheric conditions in different places over the world. After visual inspection, it was concluded that the corrosion resistance of the coatings followed the sequence: FS Zn-15Al > FS Al > continuous hot dipping Al-13Si > continuous hot dipping 55Al-Zn. These results demonstrated the high performance of FS and WAS Al and Zn coatings compared to galvanized coatings. Nevertheless, it is worth keeping into consideration that for achieving these results, the FS Zn-15Al protective layers had to be significantly thicker than the hot-dip ones and the use of a top sealer was necessary for all the TS coatings.

TSA has been widely applied in the offshore oil and gas industry, mainly in oil platforms in the North Sea, to

provide corrosion protection. Conoco's Hutton platform, built in 1984, is one of the most mentioned examples of the use of TSA in offshore environments (Thomason 1985). In this tension leg platform, the tethers and risers were TSA coated and then sealed with vinyl sealer and silicone sealer, respectively. After three years, both tethers and risers were inspected and it was observed that the TSA coating was in excellent condition with no significant reduction of coating thickness or evidence of corrosion in the steel. Nevertheless, some blistering signs were identified in tethers but not in the risers (Fischer et al. 1995). Recently, special attention is focused on TSA coatings as a long-term corrosion control method for structures subjected to temperatures exceeding 120 °C, such as the risers and pipelines used for transportation of oil from the sub-sea. In these studies, it has been concluded that Al coatings show interesting potential to protect S355J2 steel at high temperatures, even when the coating is damaged. However, additional experience is still necessary for this application regarding the calcareous deposits formed in these conditions and also their influence on the corrosion protection offered by the coating (Ce and Paul 2016, 2017).

In the petrochemical industry, piping and equipment are insulated for energy conservation, process control, and thermal protection. Corrosion under insulation (CUI) is a problem that involves very high maintenance costs, loss of production time, and equipment outages in this sector. For this reason, TSA coatings have been also proposed as an interesting alternative for preventing CUI (Bock 2015). Thus, TSA coatings have shown high corrosion and chemical resistance in harsh environments and at high temperatures (Fuad et al. 2017). Additionally, TS technology offers the opportunity of obtaining coatings on site with higher deposition rates that provide long-term protection, which involves significant life cycle cost savings.

3 Cold gas spray coatings for steel corrosion protection

3.1 Cold gas spraying technology method

Commercially available since less than 30 years (Irissou et al. 2008), the CGS technique has emerged as an alternative to conventional TS techniques for some applications, such as deposition of protective coatings, repairing, or even additive manufacturing (Assadi et al. 2016; Champagne and Helfritsch 2015; Frazier 2014; Gärtner et al. 2006; Kashirin et al. 2004; Mastrini et al. 2013; McCane et al. 2003; Wilhelm and Klesen 2018). CGS is considered a high-velocity process since in this technique, metallic or nonmetallic powders are heated at relatively low temperature, below the melting point of the metal, and accelerated at high pressure through a DeLaval nozzle up to supersonic velocities, ranging from 300 to 1200 m/s (Figure 8).

Thus, compared to WAS and FS techniques, CGS uses high kinetic energy but low thermal energy for the coating deposition. Under these conditions, the particles adhere to the substrate by plastic deformation when impinging onto the substrate surface. As the particles are not molten because of the low gas temperature, CGS may be considered as a solid-state deposition technique (Hassani-Gangaraj et al. 2015). There is still controversy on the actual adhesion mechanism in CGS, however, it is widely accepted that coating deposition only occurs when the sprayed particles exceed a critical impact velocity which depends on powder and substrate properties (Assadi et al. 2011; Schmidt et al. 2009).

CGS coatings are characterized by low porosity, high adhesion, and a dense “splattered” microstructure. In addition, temperature and gases (mainly N_2 or He,

although in some cases Air) used during the spraying procedure prevent the oxidation and degradation of the original powder material (Silva et al. 2017). For all these reasons, this technique has been presented as optimal for those applications that require dense and well-consolidated coatings and for those materials extremely sensitive to temperature. Nevertheless, there are still some drawbacks that must be overpassed by this technique for becoming economically competitive with WAS and/or FS such as, its high gas consumption and for hence high costs, the high residual stress measured in the coatings, and the low DE obtained with some materials.

3.2 Zinc coatings by cold gas spraying

In Hassani-Gangaraj et al. (2015) and da Silva et al. articles are listed a wide selection of materials sprayed in order to study the corrosion behavior of CGS coatings. These reviews reveal that there is a great interest in protecting steel also using CGS technology. For this application, less noble metals than steel, for instance, Zn, Al or Mg, (galvanic protectors) can be sprayed by CGS on the one hand; and more noble materials such as Cu, Ni, or Ti, can be deposited onto steel (barrier coatings), on the other. Thus, CGS provides the possibility of study a wide variety of materials with corrosion protection purposes.

In agreement with other TS techniques, CGS coatings properties (porosity, adhesion, oxide content, residual stresses, microstructure, etc.) can be managed depending on feedstock material properties, spraying parameters, gas used, or nozzle design. Among these, feedstock material properties show significant relevance. Even though a general rule for the suitability of materials for CGS is not established, it might be considered that according to the bonding mechanism suggested for CGS coatings, plasticity or deformability of metal particles is an important parameter for optimal deposition by CGS (Papyrin et al. 2007). In this respect, Zn is one of the ideal materials proposed for CGS applications since this is a soft and low melting point metal (≈ 419 °C). Hence, high-quality Zn coatings can be obtained using either an inert gas or air and low temperature which makes this technique an economical alternative to conventional coating methods.

Maledi et al. (2017) carried out recently a comprehensive study of the effect of CGS spraying parameters on Zn coating quality. They analyzed the effect of spraying temperature, pressure, and distance on the microstructure and mechanical properties of these Zn coatings deposited on mild steel substrates. From their results, it can be concluded that high-quality coatings are obtained at a

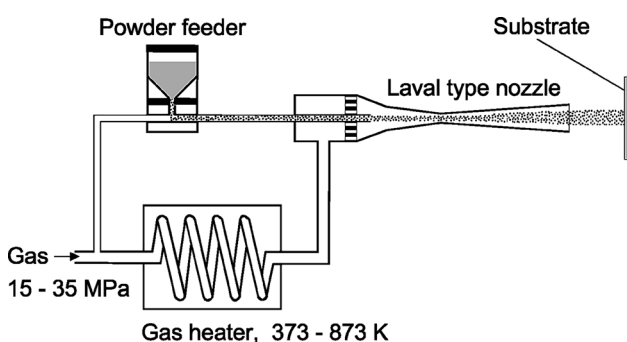


Figure 8: Schematic diagram of the configuration of a CGS equipment. Reproduced from Gärtner et al. (2006) with permission from Journal of Thermal Spray Technology, © 2020 Springer Nature Ltd.

pressure of 7 and 8 MPa and with temperatures ranging from 450 to 550 °C. However, it is worth mentioning that partial oxidation of Zn particles and diffusion of Zn into the steel surface was observed at the highest spraying temperature.

According to Legoux et al. (2007) current models for predicting critical velocities and deposition efficiencies, which lead to optimal spraying conditions, take only into account the temperature of the sprayed particles but not the surface temperature. These authors demonstrated that this parameter has great relevance in the spraying procedure. To demonstrate this, they sprayed Zn, Al, and Sn onto carbon-steel substrates and observed that by increasing substrate surface temperature the DE of Zn decreases, even at high spraying temperature (high impact velocity).

Li et al. study (2005) reported a typical picture of the lamellar structure of a CGS Zn coating. In this image, it can be observed that Zn coatings present a dense microstructure composed of deformed and well-packed metal particles. Zn coatings with this microstructure were deposited by spraying Zn particles at very low pressure (2 MPa) and using N₂ as carrier gas at different temperatures. However, the most important point of this study was the identification of nanograins in the interfaces of the bonded particles indicating that some recrystallization or melting process took place during the impact of the particles. Li et al. (2010) verified these results, as they also observed these nanograins by transmission electron microscopy in Zn coatings obtained using similar conditions and both He and N₂ as carrier gas. According to the adhesion test carried out by these authors, the induced melting process during the particles' impact clearly improves the cohesion between deposited particles, which is considered one of the main disadvantages of the CGS coatings (Hassani-Gangaraj et al. 2015).

The microstructure and adhesion of Zn–Al alloys deposited onto different substrates by CGS have been also tested. Zn–5Al alloy was sprayed onto AZ91 and AA7022, Mg-based and Al-based alloys, respectively, in order to study the microstructure of these coatings (Wank et al. 2006). In agreement with previous results, induced melting of metal particles in impact regions is observed at particle–particle interface. In addition, the generation of interlayer phases due to the reaction of the coating particles with the surface suggests that a strong coating–surface bonding exists. However, the presence of interlayer phases cannot be considered as an ideal situation. Liang et al. (2016) observed some iron diffusion from the substrate to the coating when a surface mechanically treated IF steel was coated with Zn–Al alloy by CGS (Figure 9). The as-sprayed

coating showed high hardness and adhesion, however, an annealing step induced the generation of brittle intermetallic compounds (IMCs) in the interface and the presence of these compounds involved the decrease of the stripping resistance of the coating.

In this regard, a short number of research articles are found in the literature focused on the study of CGS Zn coatings for protective purposes. Chavan et al. (2013) tested the corrosion protection of CGS Zn coatings on mild steel. In this study, they prepared very thick coatings ($750 \pm 50 \mu\text{m}$) using low pressure (2 MPa), low temperature (350 °C), and air as carrier gas. SEM micrographs of the coating cross-section revealed that the Zn layer obtained using air as carrier gas show higher porosity than using an inert gas (compared to literature data). It is accepted that a high porosity is detrimental for high corrosion resistance, for this reason, Zn coating was heat-treated (150 °C, 1 h) in order to increase its density. The corrosion resistance of both samples was tested by electrochemical corrosion tests carried out in 3.5% NaCl solution and the heat-treated coating, with low porosity, showed slightly more noble E_{corr} and one order magnitude lower corrosion current density (Figure 10), that is, a significant lower corrosion rate. This indicates that the heat treatment improved the corrosion resistance of the CGS Zn coatings. Despite the fact that this coating provided efficient protection to the mild steel substrate, the authors pointed out that long-term natural exposure tests need to be carried out to evaluate the long-term benefit of heat treatment of the coating.

The sacrificial performance of Zn and Zn–Al coatings deposited by CGS was evaluated in a study carried out by Huang et al. (2017). In this report, the authors prepared Zn and Zn–Al coatings onto S235 steel plates with a broken

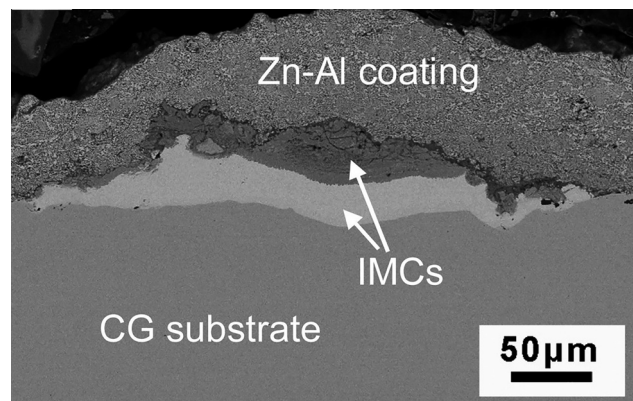


Figure 9: Cross-section of a surface mechanically treated IF steel coating with Zn–Al by CGS. The image shows the formation of different Fe–Zn–Al phases (IMC) in the substrate–coating interface after 120 min of annealing. Reproduced from Liang et al. (2016) with permission from Applied Surface Science, © 2020 Elsevier Ltd.

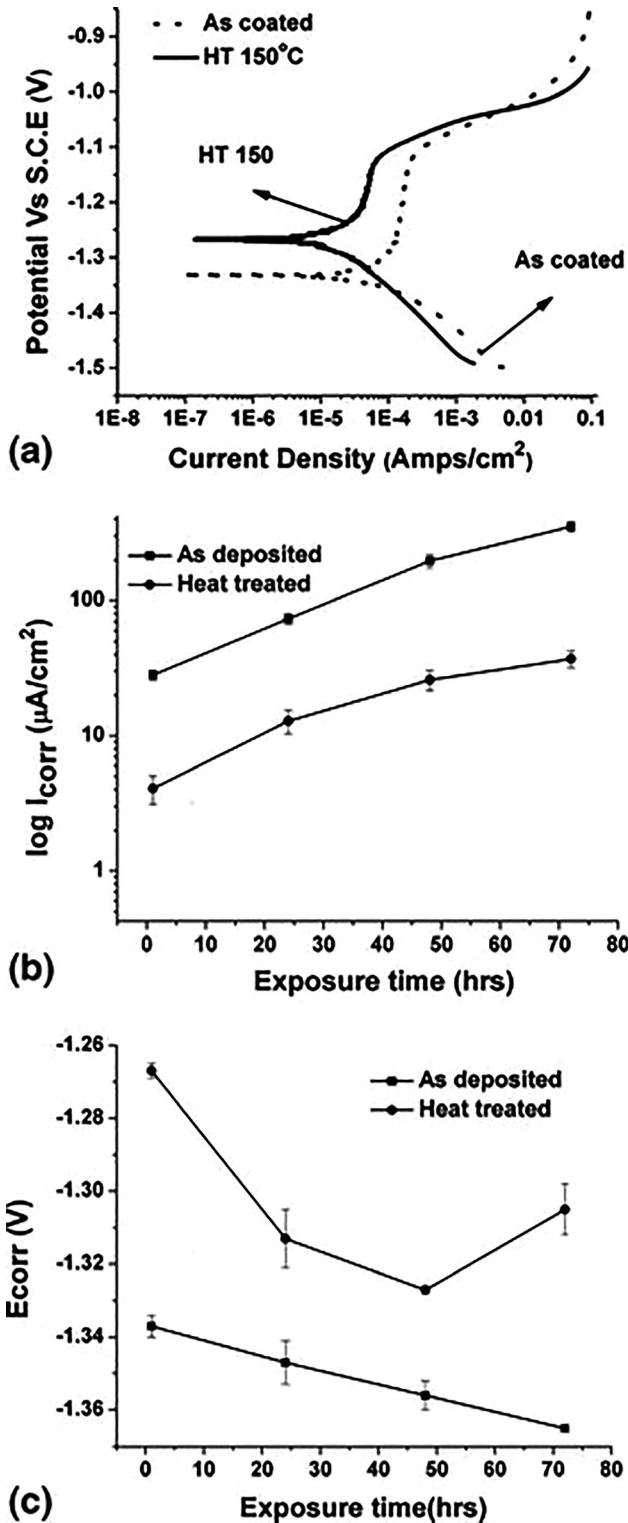


Figure 10: (a) Polarization plot of the zinc coatings in as-coated, heat-treated conditions for a test duration of 1 h and variation of (b) corrosion current density (I_{corr}) and (c) corrosion potential (E_{corr}) with exposure time for as-coated and heat-treated coatings. Reproduced from Chavan et al. (2013) with permission from Journal of Thermal Spray Technology, © 2020 Springer Nature Ltd.

area of 1 and 10 mm simulating a damaged zone on the surface. The authors calculated the corrosion potential and corrosion rate on the entire coating surface (including the naked region) via numerical simulation. These simulations showed that only in the samples with the 10 mm scratch, the coating was not able to sacrificially protect the steel surface since the corrosion potential in this area was higher than -0.7 V (Ag/AgCl/seawater reference electrode) and the corrosion rate on the center of the plat was excessive.

Recently, Wang et al. (2019) have demonstrated that it is feasible to prepare a CGS coating with the promising alloy composition Zn–Al–Mg. For the application of this coating, the authors used a mechanical mixture of Zn, Al, and Mg powders with a 13:3:1 ratio. After inspection of the cross-section of the coatings, it was observed that these showed a microstructure composed of clearly differentiated regions of Zn, Al, and Mg which had not been neither partially blended during the spraying process. The corrosion tests carried out with these coating allow concluding that Al and Mg improved the corrosion resistance of the material due to the formation of a passivation film that covered the coating surface, protecting it and reducing the corrosion rate. Additionally, these authors included TiO_2 in the coatings composition in order to increase the wear resistance and self-cleaning activity of the surface although the results obtained did not allow drawing a clear conclusion regarding the effect of the presence of this additive.

An interesting comparison of the Zn and Zn–Al CGS and wire FS coatings properties was carried out by Blose et al. (2005). They observed that CGS coatings showed lower porosity and adhesion than wire flame ones but higher corrosion resistance in accelerated salt spray tests (conducted over 1000 h). However, Zn and Zn–Al CGS coatings showed very low DE, which can be considered as a great disadvantage for this TS technique. The authors studied the direct cost of both techniques (wire flame and CGS). And concluded that, CGS spray might be considered as an alternative to conventional spraying techniques in very long-term corrosion applications since these coatings do not require short-term removal or recoating, which compensates for the high investment of the application of the CGS coatings.

3.3 Aluminum coatings by cold gas spraying

Al shows optimal properties for CGS deposition since, same as Zn, it is a soft and low melting point metal (≈ 660 °C).

Therefore, plastic deformation of metal particles when impacting onto the substrate may be achieved easily. Thus, high-quality Al coatings can be obtained using low pressures (low-pressure cold gas spray, LPCGS) of either an inert gas or air and low temperatures which leads to significant cost savings in the CGS deposition process (Rokni et al. 2015, 2017).

Cavaliere and Silvello reported a broad study of the effect of a wide number of parameters (particles size and material, gas pressure and temperature, particles velocity and substrate hardness) on mechanical properties and microstructure of titanium, copper, and aluminum coatings obtained by CGS (Cavaliere and Silvello 2014). These authors created a database containing more than 370 experimental conditions that was useful for developing a model capable of simulating the properties of the coating depending on the parameters set during spraying. Recently, Huang et al. (2018) studied the effect of some of these parameters on the DE of high purity Al onto S235 steel by LP-CGS. These authors concluded that the highest DE is reached when feeding rate and spraying distance are set between 25 and 30 g/min and 20–25 mm, respectively. In addition, they observed that DE increases proportionally to spraying temperature and decreases when gun transverse speed is increased.

Nevertheless, in Huang's study, it can be observed that the DE of Al by CGS is not very high. Ogawa et al. (2008) demonstrated that there is a certain delay in the deposition of metal particles in this method, that is, the number of particles deposited directly onto the substrate surface (which is achieved in a first traverse pass of the CGS gun onto the surface) is low and it increases exponentially by increasing the number of passes. This is explained since during the first traverse pass of the spraying gun, the not molten particles instead of being deposited are used for preparing and softening the substrate surface. Ogawa results not only underline the importance of good surface preparation for reaching particles deposition but also that spraying parameters must be carefully controlled in order to avoid this kind of effect and for achieving high DE.

It is accepted that the temperature window for spraying Al by CGS is between 150 and 450 °C, which is far away from the melting point of Al. A report from Sirvent et al. (2018) investigated the effect on the coating microstructure of using higher temperatures for Al CGS. From the comparison of the microstructure of two coatings sprayed at 350 and 500 °C, it was concluded that both showed similar microstructure (low porosity and same Al phases as in the raw powder); however, the coating obtained at 500 °C showed lower thickness and their particles were more deformed during deposition. These changes were

explained by the higher softening of the Al particles during the spraying procedure due to the high temperature used. As a result, a decrease in the microhardness of the Al CGS coating sprayed at 500 °C was observed.

The lamellar structure of Al CGS coatings can be found in Astarita (2013) and Morgan's papers (2004). In these images, Al CGS coatings show the dense microstructure composed of well-deformed and well-packed metal particles typical of CGS deposits. Moreover, Astarita et al. observed that in these Al coatings, the grain structure of the substrate appears unaffected after spraying. In CGS the deposition is carried out at a low temperature, conversely to conventional TS techniques (i.e. WAS and FS), in which the high temperatures used can modify the substrate microstructure.

It is worth remembering that Al is able to protect another material either by galvanic protection (sacrificial anode) or by generating a protective passive layer that keeps the substrate isolated from the aggressive environment. This fact is quite relevant since Al has been successfully sprayed by CGS onto different materials for corrosion protection purposes. However, the coating properties, spraying parameters, and protection mechanism must be adapted to the material that wants to be protected.

Thus, Zhang et al. (2018) coated Al onto S355 steel by CGS and sealed the Al coating using an organic commercial sealer. This coating showed a dense microstructure with nonappreciable oxide content and good adhesion with the substrate. After salt spray tests using a 3.5% NaCl solution, these authors observed that only those surface regions where the sealer failed (by blistering) had been corroded, but no signs of steel corrosion were identified. EDS analysis revealed a high concentration of oxygen and chloride in the corroded areas which are related to the presence of corrosion products with a pore-blocking effect. Mario Rosso's research group (Peter et al. 2016) observed that Al coating finishing had a great relevance on the corrosion performance of this CGS coating. They sprayed Al onto AISI 1045 steel substrate by using N₂ and He as carrier gas and noticed that Al coatings prepared using He showed higher quality finishing and adhesion than those obtained using N₂. When the corrosion resistance of these coatings was tested in a salt spray test, surface defects such as cracks and pin-holes or failure adhesion points acted as preferential sites for starting coating corrosion, which allowed concluding that defects and bad coating adhesion are detrimental for corrosion resistance.

The use of Al as protective material of light alloys (mainly Mg alloys) has been widely studied in the literature. DeForce et al. (2007, 2011) evaluated the corrosion

protection offered by different Al and Al alloys coatings for protecting Mg in marine environments. For this analysis, these authors coated ZE41A-T5 Mg alloy panels with commercially pure (CP) Al (99.5%), high purity (HP) Al (99.95%), 5356 Al (5 wt% Mg), 4047 Al (12 wt% Si), and custom-made Al-5%Mg powders by CGS (Figure 11). The characterization of the coatings indicated that all of them showed low porosity and high adhesion. The corrosion tests carried out with these coatings revealed that there is a minimum Al coating thickness necessary in order to achieve corrosion protection. In this case, this fact is explained since Mg is a less noble metal than Al, then Al cannot act as a sacrificial anode with respect to Mg. Therefore, Al coatings will be a barrier layer, and high coating thickness is necessary to avoid the diffusion of corrosive agents to the Mg alloy surface. In addition, it was observed that the best corrosion performance was achieved by the HP Al coating. This coating had the lowest concentration of impurities and this, according to the authors, showed a beneficial effect on its corrosion behavior. The presence of impurities leads to the generation of anode-cathode couples into the

coating that accelerates the corrosion rate of the coatings based on Al alloys. A similar result was observed by Diab et al. (2017) and also, Tao et al. (2010) who compared the corrosion performance of an HP Al CGS coating and bulk Al pure component.

An interesting comparison of the Zn and Al CGS coatings was carried out by Dzhurinskiy et al. (2012). They observed that in Al CGS coatings the E_{corr} of the coating was shifted to lower values whilst the corrosion rate was moved to higher values when increasing the amount of Zn added to the coating composition. This data highlights that the presence of Zn in the coating modifies the protective mechanism of the CGS coating. The Al coating acts as a barrier preventing corrosive substances to reach the steel surface but when Zn is included in the coating, it provides cathodic protection to the steel surface, since with Zn into the coating composition, the coating can be sacrificially corroded.

Al CGS coating is also tested for corrosion protection in other applications, for instance, in CUI (Bai et al. 2017; Tao et al. 2010). After simulated CUI conditions, Al CGS

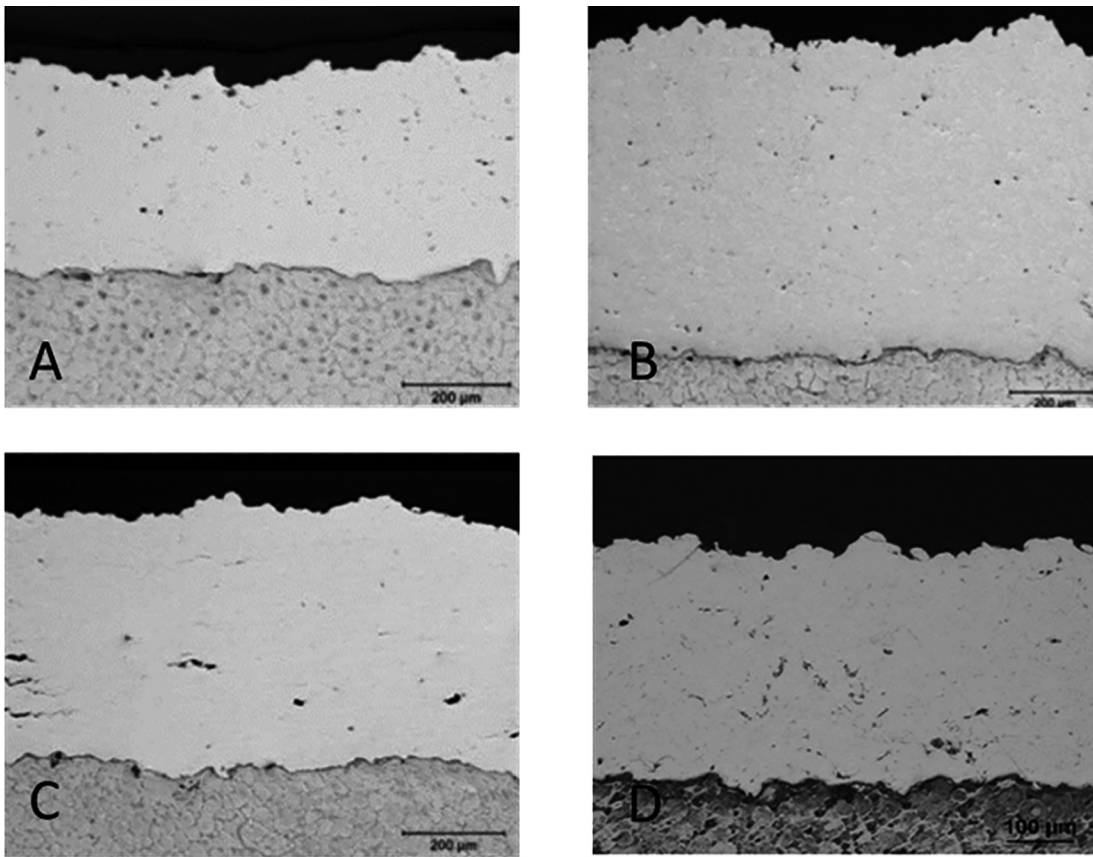


Figure 11: Cross-section of (a) CP-Al (99.5%), (b) 4047 Al (12 wt% Si), (c) 5356 Al (5 wt% Mg) and (d) custom-made Al-5%Mg on ZE41A-T5 Mg substrates. Adapted from DeForce et al. (2007, 2011) with permission of Journal of Thermal Spray Technology, © 2020 Springer Nature Ltd.

coatings showed good performance in protecting carbon steel pipes, even though, they were degraded in forms of general thinning, pores, and cracks. In addition, it was found out that their performance is better in thermal cycling conditions than in isothermal conditions. Finally, CGS for repairing components is one of the main applications of this technology. In this respect, some articles can be found in literature focused on the study the opportunities of Al CGS coatings for protecting repaired or welded workpieces (Li et al. 2015; Zhang et al. 2018).

4 Conclusions

As it has been demonstrated, TSZ and TSA coatings have been widely used for steel corrosion protection satisfactorily, showing even better performance than conventional hot dipping coatings in some specific situations. Among the different TS techniques, two TS methods WAS and FS have stood out for this target within the last decades because of its low cost and high DE and rate. Additionally, these methods are suitable to coat very large surfaces and/or workpieces.

Despite the significant differences shown between immersion and TS Zn and Al coatings microstructure, it is well-known that the properties of the coating, hence its protective behavior, can be perfectly managed by setting optimal spraying parameters. In this respect, the high corrosion protection ability as well as the protective mechanism of these coatings have been widely demonstrated and studied at laboratory scale using medium and long-term experiments in simulated and relevant environments, as it has been described. In these studies, it has been shown that, as a difference against immersion coatings, the preparation of the surface before the spraying and the finishing process has a key role in final Zn and Al coating performance. Furthermore, thickness coating and sealer application are considered as the most important parameters in TS coatings for corrosion protection. Thus, Zn and Al coatings lifetime prepared by WAS or FS will directly depend, on the one hand, on the coating thickness, that is the coating weight, since it works as a sacrificial material, and on the other hand, on the sealer application that acts as an extra barrier layer. A perfect combination of both brings the opportunity of prepared Zn and Al coatings which can reach a lifetime longer than 40 years.

Results shown by CGS highlight that Zn and Al coatings obtained by this methodology may show better properties for corrosion protection application than conventional WAS and FS coatings, that is, higher thickness, lower porosity, lower oxide content, and higher adhesion.

CGS coatings properties are still more dependent on spraying parameters than conventional TS methods. Currently, fundamental research on the CGS technique is still necessary in order to get a detailed knowledge of the opportunities of this technique. In addition, it is mandatory to make great efforts for increasing deposition efficiencies and reducing costs of CGS, only this way, this spraying method might become economically competitive with conventional coating methods for corrosion protective purposes (galvanizing but also, TS).

Despite its novelty and present cost, in this review, it has been demonstrated that CGS can be considered as an innovative and promising alternative to conventional methods for preparing sealing and protective coatings. Additionally, Zn and Al, the main metals proposed for corrosion protection applications, have been shown as ideal materials for CGS.

In this respect, the discussed results show that CGS opens the window to the application of coatings with a wide range of compositions for obtaining high anticorrosion performance since CGS is not limited to feedstock materials in wire shape and with high oxidation resistance. Nevertheless, many efforts are still necessary to understand better the relationship between CGS properties and their behavior in corrosive environments. Until date, many of the studies found in the literature for predicting the performance of CGS coatings were carried out at a laboratory scale, and there is still a lack of long-term experiments in simulated or relevant atmospheres in order to know the actual lifetime resistance of CGS coatings.

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