Corrosion Protection of Light Metal Using cold Spray Technique

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Abstract: Cold Spray (CS) is a relatively recent spray technology which falls under the larger family of thermal spray processes [1], and there are different approaches known by different names such as: Cold Gas Dynamic Spraying, Kinetic Spraying, High Velocity Particle Consolidation (HVPC), High Velocity Powder Deposition and Supersonic Particle/Powder Deposition (SPD). The basic principle of the cold spray process is very simple: A high velocity (300 to 1200 m/s) gas jet, formed using a deLaval or similar converging/diverging nozzle, is used to accelerate powder particles (1 to 50 μm) and spray them onto a substrate, located approximately 25 mm from the exit of the nozzle where they impact and form a coating. The kinetic energy of the particles rather than high temperature helps these particles to plastically deform on impact and form splats, which bond together to produce coatings and thereby avoids or minimizes many deleterious shortcomings of traditional thermal spray methods such as high-temperature oxidation, evaporation, melting, crystallization, residual stresses, gas release. In this process, powder particles are accelerated by the supersonic gas jet at a temperature that is always lower than the melting point of the material, resulting in coating formation from particles in the solid state and hence no melting and solidification process is experienced by the powders like in traditional thermal spray process [2, 3]. Further this technique is used for corrosion protection of light metals.

Keywords: Cold spray, Thermal spray, Supersonic gas

I. Introduction

Cold Spray (CS) is a relatively recent spray technology which falls under the larger family of thermal spray processes [1], and there are different approaches known by different names such as: Cold Gas Dynamic Spraying, Kinetic Spraying, High Velocity Particle Consolidation (HVPC), High Velocity Powder Deposition and Supersonic Particle/Powder Deposition (SPD). The basic principle of the cold spray process is very simple: A high velocity (300 to 1200 m/s) gas jet, formed using a deLaval or similar converging/diverging nozzle, is used to accelerate powder particles (1 to 50 μm) and spray them onto a substrate, located approximately 25 mm from the exit of the nozzle. Where they impact and form a coating. The kinetic energy of the particles rather than high temperature helps these particles to plastically deform on impact and form splats, which bond together to produce coatings and thereby avoids or minimizes many deleterious shortcomings of traditional thermal spray methods such as high-temperature oxidation, evaporation, melting, crystallization, residual stresses, gas release. In this process, powder particles are accelerated by the supersonic gas jet at a temperature that is always lower than the melting point of the material, resulting in coating formation from particles in the solid state and hence no melting and solidification process is experienced by the powders like in traditional thermal spray process [2, 3]. Moreover, the footprint of the cold spray beam is very narrow typically around 5 mm diameter due to small size of the nozzle (10-15 sq.mm) and spray distance (5-25 mm), yielding a high-density particle beam, results in precise control over the area of deposition over the substrate surface. This process is similar to a micro shot peening and hence the coatings are produced with compressive stresses, rather than tensile stresses, which results in dense and ultra thick (5-50 mm) coatings without adhesion failure. The low temperature formation of coating leads to oxides and other inclusions -free coatings with wrought-like microstructure [2].

II. Types Of Cold Spray Techniques

2.1 Low Pressure Cold Spray (LPCS):

In low-pressure cold spray the accelerating gas, usually air or nitrogen, at relatively low pressure (5-10 bar) and preheated (up to 550°C), within the gas heater to optimize its aerodynamic properties, and then forced through a ‘DeLaval’ nozzle. At the diverging side of the nozzle, the heated gas is accelerated to about in the range of 300 to 600 m/s. Solid powder particles are radially introduced downstream of the throat section of the supersonic nozzle and accelerated toward the substrate as shown in the Fig.1of the LPCS system. The feedstock particles are effectively drawn in from the powder feeder by Venturi effect, i.e. by keeping the static pressure within the nozzle below the atmospheric pressure. This is achieved if the ratio of the cross-sectional area of the supersonic nozzle at the powder entry point, Ai (sq.m) to that of the throat (A*) satisfies following equation: Ai/A*≥1.3Po+0.8 where; Po = gas pressure at the nozzle inlet (MPa) [4]. Due to the elimination of the need of a high pressure delivery system in LPCS, there is improvement in its operational safety, system is more portable,
flexible in automation, and spraying cost also reduced significantly than a HPCS system, but the deposition efficiency with this system typically do not exceed 50%. Also in this system the powder particles does not pass through the throat, hence wear of the nozzle walls occurs only in the supersonic portion of the nozzle and, this ensures a longer service life of the nozzle. Additionally, a LPCS system is more compatible with a number of system modifications.

![Figure 3.1: Operating principle of low-pressure cold spray [1].](image1)

### 2.2 High Pressure Cold Spray (HPCS):

In high-pressure cold spray, the accelerating gas helium or nitrogen at high pressure (25-30 bar) is preheated (up to 1000°C) to optimise its aerodynamic properties (not to increase particle temperature) and then forced through a converging diverging ‘DeLaval’ nozzle. At the nozzle, the expansion of the gas produces the conversion of enthalpy into kinetic energy, which accelerates the gas flow to supersonic regime (1200 m/s) while reducing its temperature. The solid powder feedstock particles mix with the propellant gas in the pre-chamber zone and are then axially fed into the gas stream, upstream of the converging section of the nozzle at a higher pressure than the accelerating gas to prevent backflow of the carrier gas to the powder feeder as shown in Fig.3.2 The accelerated solid particles (600 to 1200 m/s) impact the substrate with enough kinetic energy to induce mechanical and/or metallurgical bonding. The spray efficiency in this HPSC system is very high, reaching up to 90% as compared to 50 % in LPSC system. Moreover, the temperature of particles remain substantially below the initial gas preheat temperature due to short contact time of spray particles with the hot gas called dwell time and hence the name cold spray coating [4].

![Figure 3.2: Operating principle of high-pressure cold spray [1].](image2)
III. Effect Of Various Parameters

3.1 Effect of particle diameter:
The particle velocity is inversely related to particle diameter as: \( V_p = \frac{k}{d^n} \), where \( V_p \) is the particle velocity, \( k \) and \( n \) are the coefficients related to driving gas conditions for a certain material [1]. The dependence of \( V_p \) on the particle diameter under different spray conditions of temperature, pressure for nitrogen (C1, C2, C3) and helium (C4) gas is shown in Fig.3.1 for copper powder [1]. The converging-diverging de Laval nozzle with throat diameter 2mm, expansion ratio 9 and downstream length 100 mm is used with same carrier and main gas. It is shown that particle velocity decreases for all conditions with increase of particle diameter and decrease is remarkable when particle size is small particularly in the range of 20μm [1].

![Particle velocity vs. Particle diameter for different gas conditions](image)

3.2 Nature of carrier gas:
Regarding carrier gas type, though pre-heated nitrogen gas is used for a wide diversity of materials, but other hard materials cannot be deposited with nitrogen gas because higher velocity is required. Helium provides therefore a solution since it is inert and allows reaching the highest particle velocity. Yoon et al. [1] reported the enhancement of deposition efficiency when process gas changed from nitrogen to helium during cold spraying of NiTiZrSiSn amorphous powder. It is reported by Li et al. that under all conditions the particles accelerated to higher velocity using helium as compared to nitrogen as driving gas. Helium is however 10 times more expensive than nitrogen, making it economically unviable for many applications unless recycled. However, a Helium Recovery System (HRS) installed at Canada, recovers helium from the cold spray chamber with sufficient purity (>99%) allowing for a cost-effective operation by insuring a recovery rate of above 85%. In some applications mixture of helium (He) and nitrogen (N2) is used as carrier gas. Nitrogen being a diatomic gas, and its addition into He increases the enthalpy of the carrier gas for better heat transfer with spray particles, but it also reduces the velocity due to the heavier atomic mass resulting in coatings with reduced density and hardness[1]. However, high corrosion resistance is reported by Balani et al. for cold spray of 1100 Al onto 1100 Al substrate using He–20 vol. %N2 as carrier gas compared to 100 vol.% He processed coating, though both the cold-sprayed coatings were more corrosion resistant compared to the 1100 Al substrate and coating by 100 vol.% of Helium is more hard and dense.

3.3 Effect of temperature:
The velocity of the gas at the throat (Vt) of the Laval nozzle is also a function of its temperature as: \( V_t = (\gamma R T_t)^{0.5} \), where \( \gamma \) is the ratio of gas specific heats, \( R \) is the specific gas constant, \( T_t \) is the gas temperature at the throat, respectively. Hence the particle velocity increases with an increase in gas temperature. Though, gas pre-heating provides higher particle velocity but it also raises the risk of oxidation and/or nitridation which in turn can be detrimental for the design functionality of applied coatings. However, it is also reported that at higher temperatures the gas density and viscosity will decrease and hence the drag force of the gas, which is the force responsible for particle acceleration should decrease at higher gas temperatures and hence this area needs to be further explored [1]. It is also reported that critical velocity (Vc) decrease with the increase in the particle temperature by about 14m/s with a temperature increment of 100oC, due to the thermal softening effect, shown in Fig.3.2, [1].
3.4 Effect of oxidation condition:

Li et al. has reported the dependence of critical velocity on the particle oxidation conditions. It is reported that the large discrepancy among the critical velocities for copper particle can be attributed to the difference in oxygen content of the copper powder. The results as shown in Fig. 3.3 showed that with copper powder the critical velocity ($V_c$) changed from about 310 m/s at an oxygen content of 0.02 wt.% to 610 m/s at an oxygen content of 0.38 wt.% and with nickel based Monel alloy, the critical velocity was increased from 583 to 632 m/s as the oxygen content was changed from 0.016 to 0.108 wt.%. The study revealed that at high oxygen content, sprayed particles need to break and extrude the oxide scale on impact, therefore the critical velocity is dominated by oxide on the powder and is independent of the material properties as compared to low oxygen content materials.

3.5 Effect of Nozzle Design:

However, improvements in nozzle design using gas dynamic models have lead to higher deposition velocities and the ability to deposit larger particles, which results in denser coatings and higher deposition efficiency. So the particle velocity is also influenced by the nozzle design like its nozzle inlet diameter, throat diameter, exit diameter or expansion ratio (i.e., the ratio of the area of the exit to the throat), the entrance convergent section length (upstream length) and the divergent exit length (downstream length). It is found that increasing the length of the nozzle has a significant effect on particle velocity. It is examined that the calculated velocity of a 12 μm copper particle can be increased from 553 m/s to 742 m/s, with a 33% increase in particle velocity by increasing the length of the nozzle from 83 mm to 211 mm, with nitrogen as the carrier gas. This increased velocity leads to an increase in the deposition efficiency from less than 10% to close to 80%.
However, there are fabrication and material constraints that limit the practical length of the nozzles. So new materials need to be tried to improve powder flow through the nozzle and optimization in design is required to minimize the gas flow through the nozzle. Karthikeyan used specially designed tungsten carbide nozzle for coating on a special alloy GRCop-84 and Champagne et al. successfully used thermoplastic nozzle to mitigate the effect of clogging of steel nozzle by Al particles. Fig. 5.4 shows the optimum value of 5 mm of nozzle exit diameter for maximum acceleration of particles with different diameters using nitrogen gas at a pressure of 2MPa and temperature of 300°C. Li et al., designed a short cold spray gun nozzle for applications in limited internal diameters and calculated the optimal design of expansion ratio of 6.25 with nozzle divergent section length of 40mm for nitrogen or helium gas at the standoff distance of 30mm and found that dense coating can be deposited by the designed short spray gun.

### 3.6 Effect on Microstructure:

The particle velocity (Vp) also affects the microstructure of the cold sprayed coating. The first layer of the particles on the surface is tamped or ram down hard by the high velocity particles for successive layer and the top layer remain porous as compared to inner region having dense microstructure. The thickness of this top porous layer is influenced by the spray conditions, material properties and the morphology of the particles. Since this particle velocity greatly increased with helium as accelerating gas as compared to nitrogen gas under the same operating conditions, so a better tamping effect is reported by Li et al. with helium gas, resulted in a thinner top layer than using nitrogen. It is also reported the larger top porous layer of titanium coating by cold spray using nitrogen as accelerating gas; even though the deposition efficiency is larger than 80%.

### IV. Corrosion Protection By Cold Spray

While there are numerous applications for cold spray [15], metallic coatings for localized corrosion protection comes up as the most attractive application for this technology, given the economical, technical and environmental challenges posed by traditional coating methods. Because of its passivation behavior, Aluminum has superior general corrosion resistance compared to other metals. Cold spray represents a cost-effective technique to deposit thick metallic aluminum coatings on magnesium alloy surfaces with minimum surface preparation and without mechanically or thermally compromising the substrate properties (see Figure 4.1). The presence of aluminum on the surface of magnesium has been shown to reduce the general and galvanic corrosion tendency of magnesium components (see Figure 6.2a). In galvanic corrosion, only small areas surrounding the dissimilar interface require protection, for which cold spray represents an innovative alternative to the use of washers and insulating bushings (see Figure 6.2b).

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**Figure 3.4:** Effect of nozzle exit diameter on velocity of particles of different sizes using nitrogen at a pressure of 2MPa and temperature of 330°C [1]

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**Figure 4.1:** Scanning electron micrograph illustrating a high-density aluminum cold spray deposit on Magnesium alloy AZ31.
Titanium (Ti) based coatings on carbon steel plates are being investigated in the study in terms of heat transfer performance. The coatings were fabricated from powders using a cold gas dynamic spray system (CGDS). Heat transfer experiments were performed on a simple single plate heat exchanger set-up. Test results showed that the use of Ti-based coatings on carbon steel plates instead of using pure Ti plates for heat exchangers in seawater applications is quite promising. Not only that the Ti-based coatings have potential in terms of corrosion protection, they also have the potential of having better heat transfer performance than plain Ti or stainless steel plates. The materials of plate heat exchangers (PHEs) for seawater applications have to be corrosion resistant. Due to this, titanium (Ti) has been extensively used as the main heat transfer material. Although Ti has really good resistance to corrosion [1-3], it has lower thermal conductivity than carbon steel. Also, Ti PHEs are more expensive than stainless steel (SS) or carbon steel (CS) PHEs. For seawater applications, the plates in the PHE may not necessarily be made completely from Ti. It is possible to coat carbon steel plates with thin layers of Ti. With this, corrosion protection of the carbon steel plates is not only the possible benefit but also the development of corrosion resistant plates that are more thermally conductive than plain Ti plates. In this study, the authors propose the use of the cold gas dynamic spray (CGDS) method to fabricate Ti coatings on steel plates. It is also proposed that by adding carbon nanotubes (CNT) into the Ti coating, the thermal conductivity of the coating can be augmented. However, before applying the method on actual scale PHEs, sample coatings have to be evaluated for their heat transfer performance in a small scale set-up. The integrity of the coatings in terms of strength and corrosion resistance has to be examined as well.

Cold gas dynamic spray process is emerging as a boon in the thermal spray category for producing coatings so as to avoid the material degradation in the field of surface engineering. Cold gas-dynamic spray (or simply cold spray) is a process of applying coatings by exposing a metallic or dielectric substrate to a high velocity (300–1200 m/s) jet of small (1–50 μm) particles accelerated by a supersonic jet of compressed gas. This process is based on the selection of the combination of particle temperature, velocity, and size that allows spraying at the lowest temperature possible. In the cold spray process, powder particles are accelerated by the supersonic gas jet at a temperature that is always lower than the melting point of the material, resulting in coating formation from particles in the solid state. As a consequence, the deleterious effects of high-temperature oxidation, evaporation, melting, crystallization, residual stresses, debonding, gas release, and other common problems for traditional thermal spray methods are minimised or eliminated (Ghelichi et al., 2009). Eliminating the deleterious effects of high temperature on coatings and substrates offers significant advantages and new possibilities and makes cold spray promising for many industrial applications. In this research, attempt has been made to develop copper coatings by low-pressure cold spray process on ASTM B 435 (Ni alloy) which finds widespread applications in industrial components due to its corrosion resistance. Coatings have been produced by cold spray process by varying input parameters. The design parameters selected for producing the coatings are selected to be stagnation pressure, stagnation temperature of the carrier gas, type of powder feeding arrangement, and stand-off distance. The coatings so developed have been characterized to measure coating thickness, micro hardness and surface roughness. The combined techniques of X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive analysis (SEM/EDAX) and electron probe microanalysis (EPMA) have been used to analyze the microstructure of developed coatings.
V. Results And Conclusions

- A number of materials have already proven to be suitable for deposition by cold spray from decorative articles to biomedical, automotive, power plants and space industries.
- Cold spray was successfully employed to create a corrosion resistant barrier coating of aluminum on a ZE41A-T5 Mg substrate and CS was demonstrated as a method of material restoration for Mg panels. Coatings of CP Al, HP Al, 5356 Al and 4047 Al were produced.
- Corrosion protection by cold spray is a revolutionary method whereby protective metals can be directly and locally applied to magnesium alloys to reduce or eliminate general or galvanic corrosion in specific areas.
- Cold spray represents a viable alternative to traditional methods for localized galvanic corrosion protection of magnesium and its alloys. The use of Al alloy powder as the coating materials means a good galvanic compatibility between the coating and the underlying substrate.
- The relatively soft nature of Al powder also leads to a high degree of deformation in the powder particle during the deposition process producing a dense coating layer with low permeability to corrosion agents such as salts.

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