Investigation of low-pressure cold-gas dynamic spraying of polyamide-12 (PA12) on steel surfaces

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Abstract. Due to their good tribological properties and corrosive resistance, thermoplastic coatings are becoming increasingly important in industrial applications. Thermal spray technologies in general and flame spraying in particular belong to the most common application methods. However, the high thermal energy inevitably leads to the risk of thermal decomposition, especially in the case of materials such as polyamide-12, which have a small discrepancy between the melting and degradation temperatures. Furthermore, flame-sprayed coatings often are highly porous, reducing its effectiveness as a corrosive barrier. As an alternative approach, polyamide-12 coatings were applied to steel substrates using a conventional low-pressure cold-gas dynamic spray system. Various mixtures including ceramic powders (Al₂O₃) as well as different injection concepts were investigated and evaluated. The focus was put on the resulting coating morphology. Furthermore, the cold-gas spraying system was modified with a continuous temperature control for the gas temperature to enable a more precise adjustment based on the melting temperature of the material in order to reduce the risk of thermal degradation.

1. Introduction
The cold-gas dynamic spraying process, also simply known as cold spraying, is a relatively new spraying process developed in the 1980s by Alkhimov et al. [1] at the Institute of Theoretical and Applied mechanics of the Russian Academy of Science in Novosibirsk. Alkhimov et al. observed that under certain conditions in a supersonic wind tunnel experiment, tracer particles start depositing on surfaces rather than rebounding or eroding the surfaces. While not being the first to notice this effect, they used this observation to develop a new coating process with high deposition rates. With the cold spray process, it is possible to deposit various polymers, metal and metal alloy coatings, including metals such as copper or titanium, which at higher temperatures are, due to their high reactivity, very difficult to spray with conventional thermal spraying processes [2].

Although not entirely confirmed, it is generally assumed that the bonding of the particles in cold spraying is the result of the plastic deformation of the particles and the underlying layers/substrate, enabling a conformal contact, which combined with a high pressure, promotes a bonding of the particles [3]. The so-called critical velocity, which is necessary for this plastic deformation to occur, has been the topic of many studies in recent years [4–8].

Originally developed as a process that requires high pressures exceeding 20 bar, which are needed to obtain the high critical velocities of most metals, low-pressure cold-gas spraying (LPCGS) systems have been developed for the application of softer metals, which require lower critical velocities for a successful deposition [9]. In low-pressure cold-spraying, ceramic particles are often mixed with powders. These hard particles serve multiple purposes: They keep the nozzle clean by removing softer...
particles that might stick to the inner walls of the nozzle. Furthermore, they clean the substrate surface of impurities and oxides, activate the surface similar to grit blasting process, often rendering the conventional surface preparation unnecessary. They also have a densification effect by shot peening the already applied layers. Finally, hard particles often remain embedded in the coating, and hence reinforcing the coating [10, 11].

Mostly used for spraying metals, cold spray processes have been the subject of several studies for their ability to apply polymer coatings in the past few years because of their solid state deposition of particles, which reduces the risk of thermal degradation of the polymers. Alhulaifi et al. [12] simulated the cold spray process of polymers and concluded that unlike in usual cold spray applications, reaching a critical velocity is not always desirable, as the high sheer forces associated with higher impact velocities tend to remove previous layers. These simulations are backed with experiments from Xu et al. [13], who successfully deposited polyolefin particles with particle velocities as low as 100 m/s. Ravi et al. [14, 15] used a commercial cold spray system to successfully deposit ultra high molecular weight polyethylene (UHMW-PE) coatings on polymer as well as aluminum substrates. However, they noticed that a mixture of polymer and fine alumina particles was not only necessary for the aforementioned cleaning of the nozzle and the shot peening effect beneficial for the coating density and adhesion, but also played an important role for the cohesion of the coating because of intermolecular forces.

In this study, the viability of spraying polyamide-12 powder on steel substrates utilizing a commercial low-pressure cold-gas dynamic spraying system is investigated. Both pure powder and multiple mixtures with fine alumina particles were tested. Furthermore, the influence of the gas temperature and gas pressure was investigated. The results were analyzed in terms of both the coating topography and morphology.

2. Experimental and materials

The material used in this study was a pure polyamide-12 (PA-12) powder (Kern GmbH, Großmaischeid, Germany). The particle size distribution was measured via laser diffraction spectroscopy (S3500, Microtrac GmbH, Krefeld, Germany), resulting in the following values: D10 23 μm, D50 43.7 μm and D90 64.2 μm. Alumina particles were mixed with the thermoplastic powder to keep the nozzle clean during operation and to enable a shot peening effect (densification) of the polyamide particles. For this purpose, a commercial thermal spray powder Amperit 740 (H.C. Starck GmbH, Goslar, Germany) with a particle size distribution of -22+5 μm was used. The flowability of both powders and the respective mixtures was measured with a Revolution Powder Analyzer system (PS Prozesstechnik GmbH, Basel, Switzerland).

The coatings were applied utilizing a modified Dymet 413 spraying system (Dycomet Europe, Akkrum, Netherlands) operated with compressed air with a maximum pressure of 9 bar and a temperature of up to 650 °C. Usually, with this spraying system, the gas temperature can only be set using five separate settings. Because preliminary experiments showed no coating buildup without a preheating of the compressed air and severe thermal degradation of the thermoplastic powder occurred at the second temperature setting (gas temperatures around 350 °C), a more nuanced temperature control was needed. For this purpose, a potentiometer with a resistance range of 0 - 44 kΩ was installed into the circuit of the highest temperature setting. This allows stepless temperature control of the compressed air between 200 and 650 °C.

Because of instable feed rates and clogging problems when using the internal powder feeder unit of the Dymet 413 with light powders such as polymers, an external, conventional feed disk type powder feeder was utilized (Single-10C, Plasma-Technik AG, Wohlen, Switzerland). The carrier gas flow was minimized so that the powder injection was not forced, but still controlled by the Venturi effect-based suction of the nozzle.

The tests were carried out on samples with a 40 mm diameter and a thickness of 6 mm, made of carbon steel C45 (EN 1.0503). Prior to the spraying, the samples were grit blasted with corundum EKF-60 with a pressure of 4 bar at a distance of 100 mm and an with angle of 45°. Afterwards the
samples were cleaned in an ultrasonic bath. The compressed air temperature, the process pressure and the volumetric mixing ratio of the powders were varied. These spray parameters are summarized in table 1. All coatings were applied with a gun movement velocity of 6000 mm/min and a y-step of 2 mm in a single pass with a spraying distance of 20 mm. The powder feeder was set to 20% feeder disk velocity. During all coating tests in this study, the samples were heated with a backside mounted heat gun GHG 600 CE (Bosch GmbH, Stuttgart, Germany) up to a front surface temperature of approximately 120 °C, which was measured with an optical pyrometer.

**Table 1. Spraying parameters.**

| Parameter       | Unit | A   | B   | C   | D   | E   | F^a |
|-----------------|------|-----|-----|-----|-----|-----|-----|
| Temperature     | °C   | 200 | 200 | 200 | 240 | 200 | 350 |
| Pressure        | bar  | 4   | 4   | 4   | 4   | 6   | 8   |
| Mixing ratio    |      | 2:1 | 3:1 | 4:1 | 2:1 | 2:1 | 2:1 |
| (PA-12 : Al₂O₃) |      |    |    |    |    |    |     |

^a modified powder injection

In addition to the typical radial injection of the powder before the nozzle, experiments were conducted with a radial powder injection behind the nozzle. The setup is shown in figure 1. This setup allowed the injection of pure polyamide-12 powder, which would otherwise quickly clog the nozzle in a conventional injection setup. In this setup, however, a higher temperature setting (setting 2, ca. 350 °C) and a high pressure (8 bar) were chosen to accommodate for the shorter time to heat up the particles and to transfer the kinetic energy.

![Figure 1. Radial injection of powder behind (type I) and in front of the nozzle (type II).](image)

Some of the coatings were subsequently remolten at 180 °C for 2 hours to remove porosity. All coatings were metallographically prepared by creating cross-sections and examined by either light microscopy (BX51M, Olympus K.K., Shinjuku, Japan) or scanning electron microscopy (SEM) (JSM 7001F, Jeol Ltd., Akishima, Japan) with a BSD detector. The topology, including the roughness and waviness, of the coatings was measured with an optical profilometer InfiniteFocus (Alicona Imaging GmbH, Raaba, Austria).
3. Results and discussion

3.1. Effects of the powder mixture ratio

The powder mixture ratio has a significant effect on the flowability of the mixtures, which is shown in figure 4 represented by the specific break energy, which is the energy needed for a powder to break apart and start an avalanche in the Revolution Powder Analyzer test [16, 17]. While pure alumina, which was supplied as a fused and crushed powder (figure 3), has a relatively high break energy because of the tendency of fine powders to agglomerate, the 2:1 mixture has an improved flowability compared to both pure powders. This improvement decreases with higher mixture ratios, showing no recognizable difference to the pure polyamide powder (figure 2) with the 4:1 ratio.

These differences in the flowability are visible in the resulting coatings exemplary displayed in the top views and topographical reconstructions (figure 5) and cross-sections (figure 6). Sample A, which was applied with a 2:1 mixture ratio, shows a macroscopically uniform coating. Sample B shows about the same coating thickness, although the coating is less uniform, with several uncoated spots visible. Sample C, with a volumetric powder mixture ratio of 4:1, shows a much thinner and very uneven coating. The coating thickness, roughness and waviness of the three samples are summarized in table 2.

| Sample | Thickness [µm] | Roughness Ra [µm] | Roughness Rz [µm] | Waviness Wa [µm] |
|--------|----------------|-------------------|-------------------|------------------|
| A      | 438 ± 41.7     | 21.2 ± 4.1        | 107.2 ± 18.8      | 42.2 ± 26        |
| B      | 388 ± 112.6    | 21 ± 3.4          | 95.1 ± 12.7       | 30.2 ± 9.9       |
| C      | 265 ± 78.4     | 28.7 ± 3.8        | 126.5 ± 11.3      | 28.5 ± 9.4       |
Figure 4. Specific break energy (in kJ/kg) for both pure powders and the respective mixtures.

Figure 5. Top view and topographical reconstructions (5x5 mm) of coatings produced with different powder mixtures; A: 2:1 ratio PA-12:Al₂O₃, B: 3:1, C: 4:1.

Figure 6. Cross-sections of coatings produced with different powder mixtures; A: 2:1 ratio PA-12:Al₂O₃, B: 3:1, C: 4:1.

A close up of the cross-sections of samples A and C reveal that the alumina particles remain embedded in the coating (Figure 7). Generally, the coatings are still highly porous, indicating that the fraction of alumina has no effect on the porosity of the resulting coatings and that the shot peening effect (hammering) known from other low-pressure cold-gas coatings is not as prominent in this coating.
3.2. Effects of the gas temperature

Although a larger degree of partial melting of the thermoplastic powder and thus a better fusion between individual particles was assumed, the microstructures of the resulting coatings show almost no discernable differences with clear boundaries between the particles still being visible in both cross-sections. Figure 8 shows the cross-sections of the two samples A and D. They were both sprayed with almost identical spray parameters, the only exception being the process temperature at 200 °C for sample A and 240 °C for sample D respectively. At high powder mixture ratios, high temperatures lead to a clogging of the nozzle, as the polyamide particles already partially melt in the powder injector and start sticking to the wall of the nozzle.

3.3. Effects of the gas pressure

Figure 9 shows the cross section of a coating (sample E) sprayed with a low temperature setting with high pressure (6 bar). Compared to sample A, which was sprayed with the same temperature setting but employing a lower pressure (4 bar), several bonded particles are visible, indicating that because of the higher kinetic energy of the particles, the pressure has a significant influence on the cohesion and porosity of the coating, thus leading to an increased plastic deformation and compression heating. The downside of a higher pressure can be seen in the top view of the coating: due to the highly abrasive properties of the alumina particles, coupled with the gas temperature, which is still above the melting
point of the thermoplastic, lower layers of the coating easily are blasted off the substrate. This effect can be reduced with lower alumina content.

![Cross-section and top view of a coating produced at 6 bar pressure.](image)

**Figure 9.** Cross-section (left) and top view (right) of a coating produced at pressure of 6 bar.

### 3.4. Remelting of coatings

To create pore free coatings, existing coatings sprayed with parameter A (mixture 2:1, low pressure, low temperature) as well as a rectangular sample coated with pure polyamide-12 (Sample F) by means of upstream radial injection (type II in figure 1, coatings shown in figure 10 before and after remelting) were heat treated at 180 °C for 2 h. Prior to remelting, the coating is very rough and highly porous. After remelting, the coating is smooth (roughness Ra 0.4 ± 0.1 µm, Rz 1.4 ± 0.7 µm) and transparent, indicating a very dense structure. Cross-section images (figures 11 and 12) of both remolten coatings show microstructures with no visible pores and with a good adhesion to the substrate. Since the defects in the microstructure of the coating generated with parameter A correspond in shape and size to the aluminum oxide particles, it can be assumed that these defects are not pores, but holes created in the cross sectioning process.

![Sample F: Pure polyamide-12 coating before (left) and after (right) remelting.](image)

**Figure 10.** Sample F: Pure polyamide-12 coating before (left) and after (right) remelting.
Conclusions

Polyamide-12 coatings were successfully applied by means of low-pressure cold-gas dynamic spraying. A variety of factors have been investigated and evaluated with regard to their effects on the microstructure of the coating. The investigation suggested that higher process pressures might help in reducing the coating porosity. However, because of the still comparatively high gas temperatures (above the melting point of the material), higher pressures also lead to a great erosion of the applied coating, hence necessitating further temperature control modifications in future studies.

By means of an upstream radial (type II) injection, pure polyamide-12 powder was applied to steel substrates without risking a clogging of the nozzle as it is the case with a conventional downstream (type I) injection. Subsequently, heat treating the coating at 180 °C lead to the production of a pore free polyamide coating that could be used both as a good corrosion barrier and a tribological coating.

Although currently being a two-step process with a need for more spraying parameter optimizations, the low-pressure cold-gas dynamic spraying process shows great potential to apply both dense reinforced and pure polyamide-12 coatings. Since the process only relies on pressurized air and electricity, which both can be generated carbon neutral, it is also preferable to conventional thermal spray processes with respect to the ever-increasing environmental requirements.

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