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To cite this version:
Vincent Bortolussi, François Borit, Anthony Chesnaud, Michel Jeandin, Matthieu Faessel, et al.. Cold spray of metal-polymer composite coatings onto carbon fiber-reinforced polymer (CFRP). International Thermal Spray Conference 2016 (ITSC 2016), DVS, May 2016, Shanghai, China. 7 p. hal-01337696

HAL Id: hal-01337696
https://hal-mines-paristech.archives-ouvertes.fr/hal-01337696
Submitted on 27 Jun 2016

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Cold spray of metal-polymer composite coatings onto Carbon Fiber-Reinforced Polymer (CFRP)

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The growing use of Polymer-Matrix Composite (PMC) materials within transport industry raises new security concerns, especially those due to lightning. To protect these electrically insulating materials, conductive coatings can be applied. Due to the high level of required properties, cold spray is believed to be an effective way to achieve these coatings. Recent studies showed that obstacles remained to be overcome when cold spraying metallic particles onto Carbon Fiber-Reinforced Polymer (CFRP). These are rather due to a poor adhesion of metallic particles onto carbon fibers, which prevents coating build-up. This study therefore developed the use of PEEK addition to metallic powder. The goal is to promote the coating-substrate bond strength provided that the coating could be conductive. The work focusses on composite coatings made of PEEK thermoplastic polymer powder and copper powder. The influence of spraying parameters, powder shape, size and distribution were investigated for various polymer ratios. Depending on these parameters, various microstructures could be achieved, which resulted in different electrical and bonding properties. Coating cross-sections were studied using morphological operations coupled with quantitative image analysis. Relevant parameters to feed a model for simulation of the sprayed microstructure were thus determined. This model as an effective optimization tool allowed to carefully select powders and mixture composition to produce adherent and electrically conductive coatings. Electrical properties were assessed using the Van der Pauw method with dedicated device and samples. The latter were specifically designed to lead to significant and accurate resistance measurements. These measurements showed the feasibility of PEEK-copper composite coating of CFRP. Incidentally, beyond electrical applications, this type of cold-sprayed composites can be claimed to be suitable for a large range of applications.

1 Introduction

The manufacturing of most recent commercial aircrafts involves lighter materials such as Carbon Fiber-Reinforced Polymer (CFRP). These materials often combine stacks of carbon fibers embedded in a matrix made of a thermoplastic polymer such as PEEK (PolyEther-Ether-Ketone). Unlike aluminum alloys, CFRP shows a high electrical resistivity due to the polymer matrix which is not suitable for protection against lightning impact. To promote this protection, aircraft manufacturers use lightning screens, which involve complex manufacturing processes. Amongst thermal spray processes, cold spray is believed to be an elegant solution to coat CFRP with electrically-conductive materials. The past 2 years showed an increasing number of articles dealing with metallic cold spray coating onto polymers and composite materials. In 2006, Sturgeon et al. [1] investigated for the first time cold spray coating of carbon fiber/PEEK with aluminum. They achieved adherent and dense coating using helium as a spraying gas and observed the behavior of the coating under thermal cycling. However, it must be mentioned that the PEEK matrix was reinforced with short carbon fibers, which means a microstructure significantly different from that with continuous fibers. Short fibers globally and locally reinforced PEEK on which the coating was sprayed. A similar study was presented by Zhou et al. [2] in 2011, still using short carbon fibers/PEEK composite on which they could spray aluminum and copper. However, to be deposited successfully, copper had to be sprayed onto an aluminum bond coat. A more recent study focused on epoxy matrix composite which exhibited a different thermomechanical behavior in the cold spray process. Affi et al. [3] stated the difficulty to grow an aluminum coating onto epoxy. They used a plasma-sprayed aluminum underlayer on which the cold spray coating could grow. They also investigated the effect of the granulometry of the aluminum powder. In 2014, Che and Yue [4] used the cold spray to coat a continuous carbon fiber/epoxy composite with aluminum, copper and tin. Only scarce particles of tin were reported to be adherent to the substrate, whereas they could not obtain a coating with copper and aluminum. These papers showed the difficulty to achieve dense and adherent coatings onto both carbon fibers and epoxy [5]. It appears that thermoset polymers are hardly suitable for cold spray while metallic coating can be obtained onto thermoplastic polymers. Hence some authors only focused on non-reinforced polymer substrates, with good results [5-7].

This paper focuses on the coating of continuous carbon fibers/PEEK composites with copper using cold spray. Previous studies showed that copper particles rebound on carbon fibers and break them at the impact. In this work to limit fiber failure and obtain an adherent coating, a method was proposed i.e. spraying a mixture of PEEK powder with copper powder. This method can be claimed to be original. One must refer only to a somewhat similar experiment focused on spraying various ratios of polymer powder with copper and aluminum in order to obtain frictionless but electrically conductive coatings [8]. In the present paper, the influence of cold spray parameters was investigated as well as powder granulometry and particle shape. The concept of critical velocity was not valid in this specific case. Then the coating microstructure was observed and analyzed. A
morphological model of the coating was then developed from quantitative image analysis of the same microstructure. Morphological models are very useful to determine numerically physical and mechanical properties of multiphased materials exhibiting periodic or random structures. They allow to perform numerous numerical simulations on representative volumes. Varying the spatial distribution and size parameters of the phases can thus be easily done to investigate their influence on materials properties, primarily those of coatings [9-13]. In this study, the model would be used to numerically perform a morphological optimization of the microstructure, allowing to select the best powder to lead to optimized properties.

2 Materials and Processing

Two copper powders were sprayed: the first powder was a high-purity (≥99.95 wt%) spherical copper powder. Particles size ranged from 10.6 µm (d10) to 33.1 µm (d50) with a d50 of 19.6 µm as obtained by laser granulometry. The second powder was an irregular and coarser copper powder, the particle size of which ranged from 11.4 µm (d10) to 114 µm (d90) with a d50 of 57.6 µm. Copper powders were mixed with Vicote 702 PEEK powder, the particle size of which ranged from 26.5 µm (d10) to 88.5 µm (d90) with a d50 of 52.8 µm. The mixture of PEEK and copper was observed with a SEM. Spherical copper particles appeared in bright grey whereas irregular PEEK particles appeared darker, Fig. 1.

![SEM view of the powder mixture](image)

This paper focuses on only one mixture of powder i.e. 80 vol.% of copper and 20 vol.% of PEEK, termed as 80/20, Fig. 1. However, tests were performed using various ratios. The substrates were small samples of 25x25x2 mm³ made of aeronautical grade continuous carbon fibers plies embedded in a PEEK matrix. Plain Victrex PEEK 450G samples of the same dimensions were also coated. PEEK in the composite, Victrex 450G and powdered PEEK, were all three different. However, a common glass transition of 140 °C and a melting temperature of 330 °C were considered. The CFRP surface presented an original rugosity with small bump of PEEK and valley with carbon fibers at the bottom.

Spraying experiments were carried out using a KINETICS 3000M cold spray system by CGT-Gmbh with a "MOC" nozzle perpendicular to the substrate. Spraying pressure and temperature were optimized as well as the powder flow rate, passing speed and passing step. Stand-off distance was kept at 80 mm from the substrate and all samples were sprayed in one pass only.

Coatings were cross-sectioned, polished, and metallized using a Cressington sputter coater to be observed with a Leica optical microscope. Metallization greatly enhanced the contrast between the various phases in the microstructure, which improved image analysis. Analyses were performed using ImageJ and mostly SMIL [14] in python scripts.

The electrical resistance of the coatings was checked with a simple digital ohmmeter. Coating samples for electrical conduction measurements were sprayed onto thinner (<1 mm) substrates of PEEK for their electrical behavior being investigated using the Van der Pauw method [15]. Contrary to CFRP, PEEK is insulating, which thus allowed to measure the conductivity of the coating only. These coatings were sprayed through a mask to obtain a cloverleaf shape with a diameter of 20 mm. This shape is optimal for the Van der Pauw method because it concentrates current lines in the middle of the samples, thus reducing measurement errors. The resistance of the coating were therefore measured in the various current ranges of 1 mA, 10 mA, 100 mA, 500 mA and 1 A in a HFS600E-PB4 Linkam system chamber with a Keithley 2450 Sourcemeter.

3 Results

Coatings were first optimized based on visual inspection of surface coating homogeneity and their surface mass. The first goal was to identify spraying parameters for the best coating build-up onto the substrate. Investigations were made on process gas parameters i.e. pressure and temperature. The particle surface flow rate seen by the substrate which depends on the passing speed, the passing step and the powder flow rate was also investigated.

3.1 Pressure and temperature influence

The influence of temperature and pressure of the carrier gas on coating build-up was investigated. All sprayings were performed with the same particle surface flow rate (i.e. using given passing step, speed and powder flow rate). Pressure and temperature ranged from 300 to 500 °C and 1.0 to 2.0 MPa, respectively. Coatings made of spherical copper particles tended to grow easily compared to those made of irregular particles. In the case of spherical copper particles, the optimized parameters seemed to be 1.5 MPa and 400 °C. In the case of irregular particle, thickest coatings were obtained at 1.5 MPa and 500 °C. However, these graphs do not show the coating homogeneity, Fig. 2. Under certain conditions, the coatings exhibited a high surface mass with many large...
defects at the surface such as craters or uncoated zones.

Fig. 2. Influence of the gas parameters on the surface mass of the coatings

3.2 Influence of particle surface flow rate

The influence of the particle surface flow rate was investigated with gas parameters kept at 1.5 MPa and 400 °C. The passing speed and step ranged from 100 to 300 mm.s⁻¹ and from 1 to 3 mm respectively. First, homogeneous coatings could be sprayed with a lower speed and a smaller step with non-optimal gas parameters, as shown on sample (a), Fig. 3.

Second, when using spherical copper particles, increasing the passing speed by 100 mm.s⁻¹ or the passing step by 1 mm had exactly the same influence on the deposited mass. However, coating topography changed. Third, still with spherical particles, the particle surface flow rate and the gas parameters had an equal influence on coating build-up. It was possible to achieve thick and homogeneous coating by optimizing the temperature and pressure or the passing speed, step or flow rate. For irregular copper particles, the spraying window was narrower. Particle surface flow rate should be high enough to avoid surface defects but it led to thick coatings, i.e. with a high surface mass.

3.3 Coating microstructure

The microstructure of the coating showed two different phases. The PEEK powder was highly deformed, to result in a grey matrix which was surrounded by bright yellow copper particles. A third “phase” made of black holes was due to debonded copper particles. Spherical copper particles exhibited plastic deformation solely when impacting each other. They therefore mostly remained spherical, except on their impacted side.

Fig. 3. Top views of coatings at different spraying parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coating</th>
<th>Passing speed</th>
<th>Passing step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 MPa, 300 °C</td>
<td>Spherical copper particles</td>
<td>100 mm.s⁻¹</td>
<td>1 mm</td>
</tr>
<tr>
<td>1.5 MPa, 400 °C</td>
<td>Spherical copper particles</td>
<td>300 mm.s⁻¹</td>
<td>1 mm</td>
</tr>
<tr>
<td>1.5 MPa, 400 °C</td>
<td>Irregular copper particles</td>
<td>100 mm.s⁻¹</td>
<td>2 mm</td>
</tr>
</tbody>
</table>

Fig. 4. Microstructure with (a) irregular particles, (b) spherical particles, (c) copper volume ratios in the coatings, (d) magnified view of (b)

Cross-section images were used for quantitative phase analysis. The surface fraction and density of copper along the vertical axis were investigated. In microstructures which involved spherical copper, the volume ratio of copper could be approximated by the surface ratio when averaged over a large number of images. The averages were computed with an automatic image segmentation method from 13 images of 2560x1920 pixels² with a resolution of 0.242 µm per pixel. The coatings made of irregular particles showed 73 vol.% of copper (a), and those made of spherical copper particles 67 vol. %, Fig. 4 (b). Powder shape could be responsible for the difference in copper ratio between the spherical and irregular particles. These measurements also showed that approximately 10 vol.% of copper were missing in the
coating. These particles might have rebounded due to a lower velocity when impacting other copper particles. At a higher magnification, one could see that copper particles were well packed but often separated by a thin gray gap. It was believed that this gap was made of highly-deformed PEEK which surrounded the particles i.e. PEEK filled gap. This led to a microstructure which was slightly different from purely metallic coatings obtained by cold spray. PEEK prevented direct contact, diffusion and chemical bonding. Moreover, many deformed particles were still separated by PEEK even on the impacted side. The number of contacts between irregular particles was higher than that when using spherical particles.

3.4 Morphological model

The presence of PEEK filled gaps and the morphology of the microstructures could be assumed to govern the electrical conductivity of the coating. To simulate the current paths, a 3D morphological model was developed. The goal was to be able to investigate into the electrical behavior, from optimization of the metal phase morphology, and later from the selection of the best powder shape and size. The development of such model involved 3 steps:

- Segmentation of cross-sectional images to separate phases and remove visual artifacts or defects.
- Image analysis to extract image quantitative information according to 3 morphological criteria, termed correlation functions.
- Multi-scale morphological model development and optimization based on the 3 previously-mentioned morphological criteria extracted from experimental images.

The segmentation process resulted in two images: a binary image with copper particles in white and PEEK matrix in black. Fig. 5. (d). Debonded particles were added numerically to fill the holes. The second image showed labeled particles which allowed us to assess the efficiency of the process to segment neighboring particles. Fig. 5. (c). The main drawback in the segmentation process was that it could not segment every PEEK filled gap which separated close particles. The resolution and the color gradient were not good enough, so when the particles were too close, the process filled the gap with copper.

In the binary images three morphological criteria were considered to characterize the microstructure. The first criterion was the covariance, the probability that for a given point in the copper phase, if it was translated from a vector, it was still in the copper phase. This criterion corresponded to the spatial distribution of the copper numerically. The second criterion was the cumulative granulometry obtained by opening. This criterion described the size of copper phase. The third criterion related to the distribution of PEEK filled gap size. This criterion was approximate as the algorithm could not segment all the PEEK filled gap. This distribution appeared to follow a modified exponential distribution of parameters $k$.

Microstructures modeling involved two scales. The first scale was that of the copper particles. These were described by a Boolean model of spheres. The diameter of each sphere followed a gamma distribution of parameters $a$ and $\lambda$. Boolean spheres were distributed spatially according to $\theta$, the intensity of the Poisson’s point process. Hence, the first scale involved three parameters which were calculated from the granulometry and the covariance through experimental images. Boolean spheres were distributed using an initial set of parameters in a $512 \times 512 \times 4$ voxels space. The covariance and the granulometry were computed on a slice of this simulated microstructure. $\theta$, $a$ and $\lambda$ were optimized using a “Nelder-Mead” algorithm to fit the experimental covariance and granulometry. The “Nelder-Mead” algorithm involved a simplex method, robust and useful in this case as there was no direct mathematical link between covariance, granulometry and these parameters. Moreover, to simplify the optimization process, a constitutive equation was derived from stereological formula linking $\theta$, $a$, $\lambda$ and the experimental surface ratio of copper.

![Fig. 5. (a) Original microstructure, (b) simulated microstructure, (c), (d) segmented microstructure](image)

The second scale was that of the PEEK filled gap between neighboring particles. In the first scale, aggregates of particles were modeled by intersecting spheres, so most of them needed to be separated as in the real microstructure. In every aggregate of particles (connex spheres), germs were implanted in the center of the particles. On each germ a cell grew following a “Johnson-Mehl” tessellation. The cell nucleation and growth were time dependent. Cell boundaries were considered as PEEK filled gaps and were colored in black. They could therefore separate the particles from each other. The thickness of the boundaries was randomly computed following the exponential
distribution which fitted the PEEK filled gap size distribution. Hence a simulated microstructure could be computed according to the three morphological criteria, which met the experimental microstructure, Fig. 5 (b).

3.5 Electrical behavior of the coating

Resistance measurements showed that coatings made of spherical copper hardly conducted electricity. In contrast, when using the irregular shaped copper, one could measure a resistance which fell down to below 1 Ω, using a mere portable ohmmeter. However, the conductivity of these coatings needed to be investigated thoroughly using an insulating substrate. Coatings sprayed onto PEEK substrate were first cross-sectioned to check whether the microstructure and the copper ratio were identical to those sprayed onto CFRP. Copper ratios were measured using the previously-described segmentation method. The difference was small enough to ascertain the microstructures were similar, Fig. 6.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Final average surface ratio of irregular copper</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFRP</td>
<td>73%</td>
<td>3%</td>
</tr>
<tr>
<td>PEEK</td>
<td>68%</td>
<td>4%</td>
</tr>
</tbody>
</table>

Fig. 6. Copper ratio in coatings onto two substrates

Two thicknesses for the 80/20 coating were sprayed. Increasing the passing speed from 100 to 200 mm.s\(^{-1}\) decreased the mean thickness from 781 µm to 358 µm. Decreasing thickness also increased the number of surface defects, which consequently reduced the conductivity. The conductivity was determined from four measurements, along each side of the cloverleaf-like sample. Some slight anisotropy was showed from vertical and horizontal measurements, which might be due to defects, incorrect probe positioning or sample dissymmetry. When increasing the current intensity, a slight resistance drop was observed. Finally, regardless of thickness, under a 1 A current there was a quick damage of the coating which could burn and corrode. This left current line marks at the surface. Intensity was high enough to burn PEEK and heat up the whole sample.

Conductivity appeared to depend on coating thickness with a drop of 1500 S.m\(^{-1}\) when passing from 781 µm to 358 µm. This behavior was questionable but one can assume that the thicker the coating was, the more complex it was. This involved the paths between copper particles from one side to the other, which led to an electrical loss. At 1 A, the coating quickly burnt, which decreased the measured resistance. The presented value was not therefore obtained in an equilibrium state.

Conductivities could be compared with that obtained on similar samples of pure cold spray copper onto PEEK. The conductivity of the composite coatings was shown to be three decades below the conductivity of pure copper coatings, which, incidentally could reach the bulk copper conductivity i.e. 6.e7 S.m\(^{-1}\), Fig. 7.

![Fig. 7. Coatings conductivity](image)

4 Discussion

4.1 Coating build-up

First, while investigating the influence of cold spray parameters, the goal was also to control the thickness and the homogeneity of the coating to obtain low-thickness, homogeneous and conductive coatings. The influence of gas pressure and temperature was studied. The optimum spraying window was shown to involve a low pressure with a rather high temperature. Moreover, the particle surface flow rate was seen to have a similar or higher influence on coating build-up when compared to that of gas parameters. A typical spraying pressure for pure copper is 2.0 MPa. One may therefore assume that the critical velocity of copper does not govern the build-up and homogeneity of the coating. These are mainly due to the presence of PEEK. This leaves bonding between deformed copper particles as a second order mechanism. This is also confirmed by the fact that the lower the pressure and the higher the temperature were, the thicker the coating was.

Second, coating build-up highly depends on the particles surface flow which is a combination of the passing speed, passing step width and powder flow rate. For example, when spraying irregular powder changing the passing step by 1mm or the passing speed by 100 mm.s\(^{-1}\) led to a similar surface mass evolution. On the other hand, this result was not valid for the spherical powder. A thorough study was carried out to compare the behavior of the two copper powders, leading to a qualitative model of the composite coating build-up. The build-up exhibits a similar non-linear behavior between the two copper powders. This behavior was particularly exhibited when reducing the particle surface flow rate with the two powders to result in a low-thickness (as low as possible but homogeneous) coating. With the spherical powder, a 100 µm thick and homogeneous coating could be achieved, which however remained insulating. Cross-section observations showed that the coatings contained in fact only scarce copper particles. With the irregular copper, reducing the particle surface flow rate
led to some large heterogeneity with many surface defects. This could be explained by the size of the particles. Coating build-up is believed to be a two-stage process, which depends on the type of particle (fine spherical or coarse irregular), Fig. 8.

- Fine copper particles impact the substrate surface and rebound due to the absence of PEEK, coarse PEEK particles impact the surface at the same time as for copper particles. They adhere to the fibers, while copper particles are embedded in larger PEEK particles.
- Copper particles impact the previously-sprayed layer, deformed on copper or are embedded into PEEK.
- Coarse particles impact the substrate surface and rebound. They cannot be embedded into PEEK because of their size.
- Once a few amount of PEEK adheres to the surface with embedded smaller copper particles, larger particles finally impact, stacks or rebound. Their irregular shape can limit rebound and promotes anchoring in the already-deposited layers.

![Schematic illustration of the two-stage build-up process for two types of copper shape](image)

**Fig. 8.** Schematic illustration of the two-stage build-up process for two types of copper shape

This build-up process would explain why it was possible to obtain low-thickness coatings with spherical particles. At a lower particle surface flow rate only the first layer i.e. a sort of bond coat was sprayed. This corresponds to the first stage of the process. This layer does not contain enough copper particles to be conductive. With coarser particles sprayed at a low particle surface flow rate this type of layer cannot be obtained, since it produces a rough surface with defects. This highlights the role of the particle surface flow rate, which therefore controls PEEK deposition at the surface, allowing the coating to build-up.

The key phenomenon leading to this type of microstructure remains unknown. More precisely, the question is to know when does copper is embedded into PEEK. Is it during its flight through the nozzle or at the impact?

### 4.2 Electrical behavior and microstructure

The study of the microstructure led to conclude first that a significant amount of copper is lost during spraying, one may assume due to rebounds. Second, even at a high copper ratio, the metallic phase formed by the spherical particles does not percolate. The particles remain separated by thin layer of PEEK. This phenomenon seems to be unavoidable. Image analysis showed that most spherical particles were non connex, while many irregular ones were. An original morphological model was therefore developed to investigate various particle morphologies as the PEEK filled gap size distribution was approximately the same for the two types of microstructures. A higher number of contacts between irregular copper particles was assumed to govern the coating conductivity.

### 5 Conclusion

An original method was developed to coat Carbon Fiber-Reinforced Polymer by cold spray using polymer mixed with copper powders to result in a conductive layer. The resulting composite coatings were optimized through the study of the deposited surface mass depending on process parameters, copper particles shape and size. Interpretations of the phenomenon leading to the build-up were proposed. A morphological analysis method was developed to investigate into coating microstructures. The extraction of relevant data on the copper phase fed a morphological model of the coating microstructure. Finally, the Van der Pauw method was applied on geometrically optimized samples to assess the conductivity of the coatings. It was shown that coatings made of irregular copper particles could reach 1e3 S.m⁻¹ whereas those containing spherical particles remained insulating. These phenomena were mostly explained using the developed simulation tools coupled with investigation of microstructures and coating build-up.

### 6 Outlook

This work highlighted the interest in composite cold-sprayed coatings to achieve multi-property materials. A further goal would be to achieve gradient composite coatings in cold spray e.g. using multiple powder feeders. In this study, the polymer was shown to be an efficient coating binder. Moreover, its combination with rigid materials allowed to achieve dense coatings. Its mechanical behavior in cold spray should require to be further studies, with mechanical simulation and/or in-situ characterization during spraying.

Last but not least, morphological models can be expected to be developed as powerful tools to optimize coatings properties which depend on particle morphology. Laborious and systematic spraying campaign could thus be avoided.

### 7 Acknowledgments

This work was carried out within the “C.O.MET” FUI program. The authors would like to thank all the
members of the program consortium and BPI France, Pôle Astech, Pôle de la céramique, Pôle des microtechniques and DGAC for financial support. The authors gratefully acknowledge financial support from the Air Force Office of Scientific Research (grant FA9550-15-10461).

8 References


