Construction and characterization of a sputter deposition system for coating granular materials

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**Abstract**

In many modern ceramic or metal matrix composites the interface between the matrix and the reinforcements (particles or fibres) plays an important role. Either no or only weak mechanical bonding is observed or severe reactions between the matrix and the filler during the manufacturing process take place. A method to promote adhesion or to avoid severe reactions is to use coated reinforcements. A uniform film can act as an adhesion promoter, a compliant layer, a reaction inhibitor or a promoter of thermal transport across the interface.

The aim of this work was to construct a particle coating system based on magnetron sputter deposition which allows to keep the particles or the granular material in motion during the deposition process to guarantee a homogenous coating on every single particle. As particles to be coated diamond granulates and carbon fibres were investigated. For transparent diamond particles the uniformity of a metallic coating could be evaluated by transmission optical methods and was found to be quite high. Carbon fibres, on the other hand, could only partially be coated due to agglomeration and shadowing effects. The system presented here can be considered as suitable for coating spherical or close to spherical granular matter.

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**1. Introduction**

Modern composite materials are used to an ever increasing extent in various areas as different as high strength materials, efficient heat removers or materials with tuneable electrical properties. In many cases the interface between the matrix material and the filler phase is of considerable importance [1–3], especially if the size of the filler particles approaches the low μm or nm range. One example for this material class is copper carbon metal matrix composites (MMC’s) as promising materials for heat sink composites used e.g. in high performance electronic components or in fusion applications. They are characterized by a high thermal conductivity and a coefficient of thermal expansion (CTE) which can be influenced by the carbon content. Carbon may be included into the Cu matrix as continuous fibre, as short, arbitrarily dispersed fibres or as diamond particles.

The complete immiscibility of carbon and copper [4] often leads to the mechanical and thermal failure of the copper/carbon interface. Therefore the embedding of carbon particles in a copper matrix may be a demanding task, which is often impossibly achieved without surface treatment of the carbon reinforcements or the alloying of the matrix.

The deposition of interlayers by Physical Vapor Deposition (PVD) offers a wide variety of possible interface modifications because of the basically unlimited choice of materials which can be deposited [5]. Within the present work the method of magnetron sputtering to deposit interlayers on diamond particles and short carbon fibres has been investigated. The work is not restricted to carbon based materials, but coating either short carbon fibres or diamond particles was the main goal. Previous work [6] has shown that Mo has excellent wetting promoting effects in respect to Cu if it is deposited on glassy carbon or single carbon fibres. Therefore, the focus of this paper is put on the deposition of Mo coatings with thicknesses up to 90 nm on the particulate materials mentioned above. To coat significant amounts of particles and fibres a particle coating system was constructed and assembled which will be described in detail in Section 2 where the main geometrical features and capabilities of the system are given. In Section 3 the coatings deposited will be analysed in respect to their uniformity on the particles as well as to their thickness. A method to determine the thickness of the coatings on transparent particles will briefly be described. Finally, in Section 4 the results will be summarized and an outlook on future improvements to the system will be given.
2. Construction and experimental set-up

An image of the particle coating system is displayed in Fig. 1a, a sketch with the most important geometrical dimensions is shown in Fig. 1b. The system is based on a rotating base plate (1) which is connected to the bottom flange of a vacuum chamber by an axial bearing as illustrated in Fig. 1b. The system is based on a rotating base plate (1) which is connected to the bottom flange of a vacuum chamber by an axial bearing as illustrated in Fig. 1b. Three special cantilever arms (2) are connected to the bottom flange of a vacuum chamber by an axial bearing carrying the cups. Those cup holder systems guarantee the quick removal or changing of the cups. Optional aluminium diverters can be mounted inside the cups to mix the particles and keep them moving during the deposition process as the cups are revolved. The cups are rotated by a friction drive (4). A viton O-ring seal mounted on a driven disc is pressed onto the axes of the cup holder system and guarantees the rotation of the cups at several different angles. The base plate is revolved by a similar mechanism (5) based on a cone friction drive. In this case four different viton O-ring seals are mounted onto an aluminium cone. Both, the driven disc and the cone are variable in height to press the disc against the axes of the cup holder systems and the cone against the beveled edge of the rotating base plate. The actuation of the base plate and the cups is performed by two independent DC-motors outside the vacuum chamber which are connected with the driven disc and the cone friction drive by two ferro-fluidic vacuum rotary feed-throughs. The superposition of both rotations leads to a planetary motion of the cups which guarantees an excellent intermixing of the granular material. The main operational parameters of the system are given in Table 1. If the motor which drives the cups is not employed, the rotational speed of the cups, \( \omega \), is given by the rotational speed of the base plate, \( \Omega \), with a relation of \( \Omega / \omega = 0.2 \).

The whole set-up can be mounted within a 400 mm diameter vacuum chamber. The magnetron sputter source (Fig. 1b) is mounted on the top flange of the vacuum chamber above the cups.

3. Results and discussion

In the first experiments all free parameters (cup tilting angle \( \alpha \), base plate rotation speed \( \Omega \), cup rotation speed \( \omega \), amount of substrate material filled into the cups, diverter plate geometry) of the particle coating system have been varied within the values given in Table 1 to check their influence on the properties of the deposited coatings. Diamond granulate and carbon fibres were coated by molybdenum. The sputtering parameters for Mo are given in Table 2. The primary purpose of these experiments was to increase the uniformity of the coatings.

The tilting angle \( \alpha \) was varied from 20° to 40° in steps of 5°. Simultaneously, two different amounts of diamond particles were filled into the cups. Experiments with 2.5 cm³, representing a high amount and 1.25 cm³, representing a low amount had been performed. Also \( \Omega \) and consequently \( \omega \) have been varied. With the central motor actuating the cups fixed the rotation of the ground plate with \( \Omega = 0.05 \) rps leads to a rotary speed of the cups of about \( \omega = 0.29 \) and a value of \( \Omega = 0.09 \) rps leads to \( \omega = 0.5 \) rps (see Table 1).

3.1. Diamond particles

The main goal of the present work is to uniformly coat diamond particles with a mean diameter ranging from 100 to 600 μm. For all experiments the deposition parameters given in Table 2 remained unchanged. The main parameters changing the properties of the deposited coatings were identified to be the amount of granular material filled into the cups, the tilting angle of the cantilever arms, \( \alpha \), the arrangement of diverter plates in the cups and the rotation speed.

### Table 1

Parameters of the granulate coating device.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tilting angle ( \alpha )</td>
<td>20°–40° in steps of 5°</td>
</tr>
<tr>
<td>Ground plate rotation ( \Omega )</td>
<td>0.05–0.09 rps</td>
</tr>
<tr>
<td>Cup rotation ( \omega )</td>
<td>0.22–0.5 rps</td>
</tr>
<tr>
<td>Cup volume</td>
<td>100 cm³</td>
</tr>
<tr>
<td>Amount of substrate material per cup</td>
<td>1.25–2.5 cm³</td>
</tr>
</tbody>
</table>

### Table 2

Deposition parameters, which were kept constant in all experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>( 5 \times 10^{-6} ) Pa</td>
</tr>
<tr>
<td>Working gas/pressure</td>
<td>Argon/4.5 \times 10^{-1} Pa</td>
</tr>
<tr>
<td>Sputtered material</td>
<td>Mo</td>
</tr>
<tr>
<td>Sputtering power/voltage/current</td>
<td>200 W/400 V/0.5 A</td>
</tr>
<tr>
<td>Distance target-substrate</td>
<td>( \sim 115 ) mm</td>
</tr>
<tr>
<td>Tilting angle of target relative to ground plate</td>
<td>20°</td>
</tr>
<tr>
<td>Deposition rate on plane substrates</td>
<td>0.14 nm/s</td>
</tr>
<tr>
<td>Deposition rate on granular substrates</td>
<td>0.008 nm/s</td>
</tr>
</tbody>
</table>
It was found that in sputtering times shorter than 30 min not all diamond particles can be coated homogeneously, depending on the amount of particles filled into the cups. This is due to the fact that particles are often buried within the particle ensemble to be coated as the surface to volume ratio decreases with increasing filling volume. On the other hand it has been found that the intermixing behaviour of the diamond particles is better at a high amount of material (2.5 cm³) filled into the cups as opposed to a low filling amount of 1.25 cm³. This is caused by the fact that a higher amount of granular material is crashing against a particle sticking to the wall or the ground of a cup, thus re-introducing formally fixed particles to the mixing process again.

Increasing the tilting angle \( \alpha \) of the cups had the effect that a lower amount of diamond particles sticked to the ground or to the walls of the cups. On the other hand, larger \( \alpha \) increased the amount of particles dropping out of the cups. Although increasing the wall height of the cups to values more than 20 mm (see Fig. 1b), at first glance, would seem a suitable solution for this problem, this would lead to a more prominent shading of the interior of the cup from the vapor stream. To minimize the shading effect tilted sputter targets were used as the thickness of the sputtered coatings is essentially depending on the position of the magnetron sputter target relative to the position of the cups and the sputtering time. In addition, different particle sizes yield different optimal tilting angles. For example it has been found that a tilting angle of 40° leads to very good intermixing and a low drop out ratio of diamond particles with a size 150 \( \mu \)m while, at the same angle, particles with a diameter in the range of 400 \( \mu \)m have a much higher drop out ratio. In Fig. 2, two images of Mo coated diamond particles obtained by optical microscopy (Reichert Polyvar) are displayed. Obviously the tilting angle of the cantilever arm of 30° was too low in the case of Fig. 2a, because one can find several uncoated, poorly or inhomogeneous coated particles. Uncoated particles can be identified by higher brightness but lower reflectivity than the well coated ones in the image and are indicated by white circles. In the case of a higher tilting angle (40°), nearly all particles are coated homogeneously as shown in Fig. 2b, but some particles with partial coatings may be found in every sample because of the statistic nature of the movement of the particles and the deposition procedure [7,8].

Another important issue is the implementation and arrangement of diverter plates within the cups which is schematically depicted in Fig. 3a, b. Two different set-ups were tested, an arrangement of three 25 mm long diverter plates (Fig. 3a) and an arrangement of 6 short diverter plates (Fig. 3b). The height of the plates was approx. 10 mm. Coating experiments showed that the six short plates lead to a much better intermixing behaviour than the three long diverter plates. From visual inspection it was obvious that in the case of the long plates particles tended to preferably stick within the crevice between the plate and the bottom of the cup. This effect was much less pronounced for the short plates.

The rotary speed of the ground plate and the cups, finally, is the parameter which has the least influence on the coating properties. The only effect definitely observed was that at low angle \( \alpha \) and high rotation speed \( \omega \) the particles stuck to the wall of the cups due to
the centrifugal forces. All other sets of rotation speed may influence the duration of the deposition time to achieve a homogenous coating of all particles because the time of the maximum exposure of the particle ensemble to the vapor beam is changed. Other than that, no conclusive influence on the intermixing behaviour was observed.

3.2. Short carbon fibres

The coating of carbon fibres is an even more intricate process. In this case the agglomeration and the adhesion of the fibres on the cups are a severe problem. Also the fibres tend to clog amongst themselves. Consequently the mixing of the fibres by the aluminium diverters is not done in a satisfying way. Not all fibres are coated and often fibres are only partially coated as it is displayed in Fig. 4. This image was achieved by optical microscopy as well. Due to this problem some mechanisms to vibrate the cups have been tested, but have not been proved satisfactory yet. Due to the poor uniformity of the films no thickness measurements have been performed in the case of the fibres.

3.3. Thickness measurement

A first approach in thickness measurement was to mount a plane substrate in one of the cups and to determine the thickness by profilometry and photometric measurements. In the range of rotation speeds $\Omega$ and $\omega$ given in Table 1 the deposition rate derived from the thickness measurement did not vary significantly and amounted to 0.14 nm/s. On the other hand, the statistic nature of the movement of a collective of particles has the effect that a significant amount of particles will not be on the surface of the particle aggregate within the cup and will therefore not be exposed to the vapor beam. This will result in significantly lower deposition rates on the particles. A realistic approach to determine the thickness of coatings on transparent granular materials is based on the detection of the transmission intensity of light rays passing through the sample and is described in detail in Ref. [9].

Basically, a commercial slide scanner model Reflecta CrystalScan 7200 with a maximum resolution of 7200 dpi was used to measure the transmission through the coated diamond particles. A slide frame served as the sample holder, where a small amount of granular material was placed, scanned, and then the image was color-split. Only the green channel was used for analysis. The film thickness was calculated by using the 1-byte-brightness value (0–255; 0...black, 255...white) measured in Digital Micrograph and the extinction coefficient $\kappa$ for Mo [9].

The diamonds contain several pairs of coplanar faces of different sizes. Most probably the particle will come to rest on one of these faces. A ray passing the diamond through this central area will not be scattered, as the area is normal to the beam direction, whereas light at the borders of the diamond will be scattered in several different angles. As a result the scanned image of a diamond has a dark circumference and a local transmission maximum in the center. Only the central part can therefore be treated like a parallel plate substrate and is consequently used for further analysis. Fig. 5a illustrates an image of scanned diamonds. The brightness profile along the dashed line through one of the diamonds is given in Fig. 5b.

For the transmission measurement the brightness values of 20 diamonds were averaged, and corrected by the background brightness. As the light beam passes the coating twice, the coating thickness is 50% of the measured thickness.

To check the results obtained from those photometric measurements the coating thickness was determined on single particles by Focused Ion Beam (FIB) cross-sections performed in the chamber of a Scanning Electron Microscope (SEM). Table 3 gives a summary of the experimental parameters for the samples investigated by the methods described above. The cantilever tilt angle $\alpha$ was always 40° and the mean diameter of the granulate approx. 150 µm. The thickness value for sample 50 (Table 3) is an average for particles placed in all 3 cups with different diverter arrangements. In the case of sample 57-S3 the rotation of the ground plate was stopped and only the cup was rotated while being directly placed beneath the sputter source to allow for a significantly increased coating thickness on this sample.

![Image](image.png)

**Fig. 5.** Thickness determination of Mo coatings on diamond granulate by photometry using a high resolution optical scanner: (a) scanned diamonds; (b) brightness profile (green channel) along the dashes line in part (a). Image taken from Ref. [9].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time</th>
<th>Filling amount/cup</th>
<th>Actuation mode</th>
<th>$\Omega$</th>
<th>$\omega$</th>
<th>Diverter plate configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>30 min</td>
<td>1.25 cm$^3$</td>
<td>All 3 cups actuated</td>
<td>0.05 rps</td>
<td>0.29 rps</td>
<td>Average of different set-ups</td>
</tr>
<tr>
<td>51-S1</td>
<td>60 min</td>
<td>1.25 cm$^3$</td>
<td>All 3 cups actuated</td>
<td>0.05 rps</td>
<td>0.29 rps</td>
<td>3 plates, 25 mm each, tilt 10°</td>
</tr>
<tr>
<td>51-S3</td>
<td>60 min</td>
<td>1.25 cm$^3$</td>
<td>All 3 cups actuated</td>
<td>0.05 rps</td>
<td>0.29 rps</td>
<td>6 plates, 20 mm each, tilt 10°</td>
</tr>
<tr>
<td>57-S3</td>
<td>120 min</td>
<td>2.5 cm$^3$</td>
<td>One cup placed directly under target</td>
<td>0 rps</td>
<td>0.29 rps</td>
<td>6 plates, 20 mm each, tilt 10°</td>
</tr>
</tbody>
</table>
from the photometric measurement.

Thus leading to the significantly lower thickness value determined
low that the digitalization threshold of the scanner was reached,
thickness was so high that the intensity of transmitted light was so
from FIB cross-sections, except for sample 57-S3 where the film
methods using the scanner correlate well with the ones resulting
showed that indeed the deposition rate on the granulate
cubes, so, at an average particle side length of 150
calculating the number of particles at the surface of the aggregate
significantly lower than for the plane substrate,

The determination of the film thickness on the granulate
showed that indeed the deposition rate on the granulate \( R_G \) was
significantly lower than for the plane substrate, \( R_S \) with a ratio \( R_G / R_S = 0.057 \), i.e. \( R_G \) is about 6% of \( R_S \). This ratio can be estimated by
calculating the number of particles at the surface of the aggregate
within the bowl: for simplicities sake all particles are considered as
cubes, so, at an average particle side length of 150 \( \mu m \), \( 3.7 \times 10^5 
particles fit into a cube with a volume of 1.25 cm\(^3\) (see Table 3). On
the total surface of the cube, which is approx. 7 cm\(^2\), \( 3.09 \times 10^4 
particles can be located. This yields a surface to volume ratio of
approx. 8.3%. This is in reasonable agreement with the value of \( R_G/R_S \)
of about 6%. Of course this is just a crude estimate which neglects
the motion of particles completely, but shows that the exposure of
particles to the vapor beam during intermixing plays an essential
role for the determination of the deposition rate on the granulate.

4. Conclusion and outlook

The main advantage of the particle coating system presented in
this paper when compared to e.g. electrochemical coating tech-
niques is that not only metallic elements but also carbides, nitrides,
etc. can be deposited by employing reactive sputtering techniques.
Another convenience of this system is the possibility to deposit
multi-layers or graded coatings by exploiting the possibility to
operate different sputter sources and to choose arbitrary profiles of
motion for the base plate. In addition to that not only spherical or
close to spherical particles but also powders and fibres may be
covered with this system if adequate systems to shake or stir the
particles can be implemented.

It was also shown in previous investigations that the pre-treatment of the substrate using
different plasmas increases the interfacial bonding [10,11]. The pre-
treatment of the fibres or particles with a plasma can also be
implemented in the existing system.

At first glance the PVD process might seem disadvantageous
with respect to the deposition rate which was shown to be signif-
ically lower on the granulate when compared to substrates which
are permanently exposed to the vapor beam. Nonetheless, for the
intended application sputter coated fillers in composite materials
an interfacial layer with a thickness in the range of 10–200 nm
(depending on the selected material) will be sufficient to improve
the adhesion or the thermal transfer between the matrix and the
inclusion. For the present system this results in deposition times in
the range of 15–60 min, but there is still considerable room to
increase the rate by simply increasing the sputtering power or by
decreasing the distance of the sputter source to the cups. It is also
a fact that continuous coatings prepared by electrochemical
methods are not easy to achieve for a layer thickness of less than
200 nm.

Therefore future work will focus on optimising the present
particle coating system in terms of coating uniformity, thickness
control and deposition rate. The described method can then readily
be used for the deposition of functional layers on various high
thermally conductive fillers such as SiC, AlN or diamond particles.

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