Plasma Coating Process for Powder Surface Modification

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Abstract: A plasma reactor is combined with a circulating fluidized bed in order to coat powders. Two reactors, both based on the principle of a Dielectric Barrier Discharge (DBD) have been developed. Initial test results on fluidization, temperature conditioning and coating have been reported.

Keywords: plasma coating, circulating fluidized bed, low temperature

1. Introduction
Coating of powders is of interest for many applications such as improved dispersion and bonding of sub-micron sized particles in polymer composite materials, oxidation prevention of metal particles, processability and synthesis of novel energetic and pharmaceutical materials. Thin layer coating of powders can be used for the development of novel energetic materials with applications in propellants, pyrotechnic materials and munitions. Major applications in this area involve decreased sensitivity, improved ageing properties, improved bonding properties and enhanced burning properties by combination of different materials (e.g. fuel and oxidizer) on the nanoscale. Plasma coating of powders in fluidized bed reactors has been frequently studied [1, 2, 3] but the industrial application requires increased production rates and further development of appropriate design rules for safe process scale-up.

Plasma coating can be seen as an alternative for existing chemical and physical coating processes. Some traditionally used wet chemical coating processes for altering the properties of energetic materials suffer from agglomeration of powders. New physical processes applied for the coating of energetic materials have been reported in literature [4, 5, 6]:
- Atomic layer deposition
- Crystallization
- Plasma techniques

The atomic layer deposition technique has the disadvantage to subject the materials at elevated temperatures. Crystallization as a means to coat particles is limited by reproducibility, coating efficiency and the thickness of the coating layer. The use of non-thermal plasma creates the possibility to treat heat sensitive materials in combination with electrical charging those particles thereby preventing agglomeration before and during the coating process. Further, controlling residence times and coating cycles of powders in a flow through plasma reactor may be used to deposit coatings with variable thickness and even to obtain multilayer coatings.

2. Experimental set-up
A general picture of the developed circulating fluidized bed (CFB) system with an incorporated plasma reactor is shown in Figure 1. Powder is initially brought in the loop-seal (L) where it is fluidized using the bubbling bed regime. A second gas flow is used to disperse particles through the riser column up to the plasma section. Gaseous coating precursors are added to the main (second) gas stream. As standard condition nitrogen gas is used though other gases are applicable.

Fig.1 Experimental set-up for plasma coating in a circulating fluidized bed system. The set-up includes a plasma reactor (P), loop-seal (L), riser (R), cyclone (C) and downcomer (D).

By adjusting the two gas streams the solid hold-up as well as the solid mass flow rate can be controlled. The transport gas is separated from the solid fraction in the cyclone (C), where the powder falls down in the downcomer (D). Very small particles (< 3 µm) will leave the system through the cyclone too. The total length of the fluidized bed (including the plasma section) is 120 cm while the length of the plasma section is 30 cm.
An important operating parameter is the circulating mass flow rate which determines the time it takes for the total powder mass to be circulated. The powder can be treated a defined number of times. How many times the powder needs to be re-circulated through the plasma reactor in order to achieve the desired surface modification depends on the spatial structure of the plasma, the plasma power, the surface area of the particles to be coated and the amount of coating precursor. The circulated mass flow rate can be derived from the fraction of solids which can be determined from the pressure difference in the reactor.

\[ \varepsilon_s = 1 - \varepsilon_g \]  

\[ \frac{\Delta p_{\text{riser}}}{L} = \left(1 - \varepsilon_g\right) \left(\rho_s - \rho_g\right) g \]  

Where \( \Delta p \), \( L \), \( \rho_s \), \( \rho_g \), and \( g \) are the pressure difference across the riser, the length of the riser, solid density, gas density and gravitational force, respectively [2, 7]. It is believed that the plasma process results in unipolar charging of the particles which in turn leads to prevention of agglomeration of the particles [8].

Two types of dielectric barrier discharge plasma reactors with a cross section schematically represented in Figure 2 have been realized. The inner electrode of the Volume Dielectric Barrier Discharge (VDBD) plasma reactor consists of four saw blades with a regular pattern of sharp teeth (5 per cm). The outer electrode, separated from the discharge region by 1 mm borosilicate glass, is formed by a solution of copper sulfate. This liquid electrode is preferred in this setup, because it offers efficient temperature conditioning in combination with a homogeneous electric field distribution. In addition, it allows the observation of the light emitted by the plasma and the possible agglomeration of powder materials on electrodes.

The Surface Dielectric Barrier Discharge (SDBD) reactor uses as dielectric material the same glass tube structure as used in the VDBD reactor (borosilicate of 1 mm thickness and 20 mm inner diameter). In this case the electrode is made of 8 stainless steel (SS 316) strips which are arranged in a circle on the inside surface of the borosilicate tube. The thickness and width of each strip is 0.1 and 2 mm. The distance between the strips is 5.5 mm. In contrast to the VDBD reactor where plasma filaments (microdischarges) are formed in the gas volume between electrode teeth and dielectric barrier, in this case plasma formation occurs only on the dielectric barrier surface at the boundary of the electrode strips. Since the SDBD electrode strips are very thin, the normal fluidization regime is not expected to be influenced by the electrode structure.

The AC high voltage is applied by means of a power supply (designed and manufactured at TNO) which is capable of producing short (~1 µs) pulses with alternating polarity and controlled repetition rate in the 1-100 kHz range. The voltage is adjustable from 1-20 kV, the power dissipated in the discharge can be varied from 10 – 300 Watt (by means of controlled repetition rate and voltage).
• Initial tests of powder coating using the VDBD reactor with CuO particles (20-30 micron) and HMDSO coating precursor

**Fluidized bed and plasma formation**

Setting the conditions of the fluidized bed comprises the study of the complicated balance between the gas flow in the loop-seal and the one in the riser. When the gas flow in the riser is too low, particle build up takes place on the electrodes. Particle build-up must be prevented because it will result in inhomogeneous treatment, prevention of plasma formation or possible hot spots of the plasma which may result in an unsafe operating condition. On the other hand, when the flow is too high, obstructions will occur in the cyclone and the downcomer. For each type of powder material (specific and volume mass densities, morphology, surface energy) there is a need for thoroughly testing of fluidized bed conditions.

Figure 4 shows two pictures of the VDBD plasma reactor obtained at different gas flow rates. An increase of the gas flow rate to approximately 43 liter per minute appeared necessary to avoid the build up of particles on the electrode (the space between electrode blades). The plasma is homogeneously distributed over the length of saw teeth electrodes and is stable for an extended period of ~4 hours.

![Figure 3](image1.png)
Fig. 3 (left) Picture of the VDBD plasma with fluidized bed at low circulation gas flow (27 lpm), (right) at 43 lpm.

**Power dissipation and temperature rise**

The experimental set-up has been constructed for coating of temperature sensitive materials and before the investigation of the process has been started, tests have been done in order to measure how power dissipation influences the gas temperature downstream of the plasma reactor. The measured temperature, monitored 150mm downstream from the plasma by means of a thermocouple, may be slightly lower than the real temperature due to cooling.

In Figure 4 the measured temperature of the gas as a function of power input in the plasma for both VDBD and SDBD reactors is given.

![Figure 5](image2.png)
Fig. 5 Temperature versus power in plasma. At the same power input, the gas temperature in the SDBD reactor is ~15 degrees less than in the VDBD reactor.

The experiments are not performed in combination with the fluidized bed, however the gas flow rate of 40 lpm is sufficient for CFB experiments. It is clearly observed from the graphs in Figure 5 that in the SDBD reactor heat is more efficiently transported to the surrounding cooling fluid which is held at 20 degrees Celsius with an external thermostatic cooler. This can be explained by the fact that the SDBD plasma is only formed at the dielectric surface where the most efficient cooling takes place. A further difference between the VDBD and SDBD is the controllability of electrical power input by frequency and voltage settings. In case of the VDBD reactor power measurements, the frequency has been increased from 13 to 26 kHz resulting in a linear increase of power. During variation of the pulse repetition frequency at constant voltage amplitude, the energy per pulse increased explaining the more than doubled increase of power input. In case of the SDBD, the voltage appeared to have more influence on power dissipation when compared to the VDBD reactor. This is explained by the fact that the SDBD plasma reactor can be operated at a very low voltage threshold (3.6 kV) compared to the VDBD plasma reactor (6 kV). Increasing the SDBD reactor voltage from 3.6 to 5 kV increased the energy per pulse period (one positive and one negative pulse) from 1.7 mJ to 8.5 mJ.

**Pressure differences**

Differential pressure measurements have been performed with copper oxide as a powder in the CFB. The particle mass flow rate during these tests has been determined at approximately 2–7 gram per second. With a flow of the carrier gas (nitrogen) of 43.5 liters per minute (lpm), each particle has a residence time of 0.1 seconds per circulation. In order to obtain a residence time of the particles in the plasma reactor of 10 seconds the total amount of powder has to circulate 100 times.

Prior to the coating experiments extensive test have been performed in order to compare the calculated pressure drops according to Eq. (2) with measured values. During
the experiments it has been observed that the turning on of the plasma causes an additional pressure drop over the plasma section. This effect is apparent from measured pressure drops shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>No plasma, no CFB</th>
<th>Plasma, no CFB</th>
<th>Plasma with CFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta p_{2,3}$ [Pa]</td>
<td>44</td>
<td>44</td>
<td>56</td>
</tr>
<tr>
<td>$\Delta p_{2,3}$ [Pa]</td>
<td>52</td>
<td>68</td>
<td>127</td>
</tr>
</tbody>
</table>

Table 1: Pressure drop in the circulating fluidized bed.

In the situation without CFB, when the plasma is turned on the pressure difference over the plasma section $\Delta p_{2,3}$ [Pa] increases with 16 Pa. When the CFB is turned on as well, this pressure increases even further to the value of 75 Pa. At this moment we do not have determined the main cause of this sharp increase of the pressure drop over the plasma section. Possible mechanisms may be related to the flow-resistive effect of plasma gas filaments (bound together due to their ion space charge), the electric wind or gas heating.

Coating of particles

Preliminary experiments in which copper oxide particles (20-30 micron mean size) are treated the VDBD plasma reactor with HMDSO coating precursor have been performed. It is known that when HMDSO is added to a plasma with no oxygen present in the nitrogen carrier gas, the layer formed on the particles will be polymeric with a structure close to $[(\text{CH}_3)_2\text{SiO}]_n$. However, with increasing oxygen content, a gradual change is observed from organic polydimethylsiloxane-like coatings to inorganic quartz-like deposits [9]. In this experiment 20 gram per hour of HMDSO was added to 44 lpm nitrogen which was selected as the carrier gas. With a power input of 150 Watt the whole system was running for an hour in which the copper oxide powder was circulated approximately 100 times through the plasma reactor.

Fig. 6 shows He-ion microscopic pictures of untreated (left) and treated (right) copper oxide particles.

6. Conclusions

The main potential and partly demonstrated benefits offered by the SDBD plasma reactor are: (1) undisturbed fluidized bed regime, low threshold gas flow rate where powder deposition on electrodes is avoided and more efficient cooling. A remarkable pressure difference caused by the plasma in combination with the CFB has been observed in case of the VDBD reactor. Preliminary results have been obtained with the coating of CuO particles.

It has been proven that cooling of the gas in the SDBD reactor is more effective. Further, due to the fact that the SDBD plasma can be initiated at much lower voltage, the power input in the SDBD reactor can be better controlled using both voltage and repetition rate. Further investigations are needed to find out whether the SDBD plasma has a similar effect on pressure drop as observed when using the VDBD plasma. Overall, this fluidized bed plasma treating system is expected to provide improved coating rates and better temperature control of the coating process.

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References