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PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION ON PARTICLES IN AN ATMOSPHERIC CIRCULATING FLUIDIZED BED

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ABSTRACT

Plasma-enhanced chemical vapour deposition is an attractive technqiue to provide particles with a thin film. Applying a cold plasma enables us to work with temperature-sensitive materials. Using a CFB with an incorporated volume dielectric barrier discharge reactor we coated 20-30 μm CuO particles with a thin SiO_x layer.

INTRODUCTION

Fluidized-bed coating of particles is widely applied in industry, for example for pharmaceutical and food applications. The applied coatings typically have a thickness of 10 micron or more. Recently, there is increasing interest in particle coatings in the order of just a few microns or smaller, for example for battery, pigment, and catalyst applications. Coating techniques originating from the semi-conductor industry, such as chemical vapour deposition (CVD) and atomic layer deposition (ALD) are used to obtain such coatings. It has been shown that both CVD and ALD can be applied to coat particles (e.g., 1,2).

While CVD and ALD for semi-conductor applications are typically carried out at vacuum, it is for fluidization operation more desirable to operate at atmospheric pressure. Werther and Czok (1) showed that CVD applied to particles can be carried out at atmospheric pressure, while Beetstra et al. (3) showed that also particle ALD can be applied at atmospheric pressure. Normally, these particle coating processes are carried out at elevated temperatures: for CVD, typically temperatures around 400°C are used, while ALD is typically carried out around 150°C. However, for several applications such a high temperature is undesirable. 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. This opens perspectives to coat materials that cause risk when heated too much, such as propellants, pyrotechnic materials, and

munitions, but also to put a film around compounds for food and pharmaceutical applications, that will degenerate at too high temperature.

Plasma-enhanced CVD (PECVD) in a fluidized bed using an inductive coupling of the electric field has been applied previously. For example, Sancheze et al. (4) applied PECVD in a spouted bed, while Jung et al. (5) proposed to coat particles by PECVD using capacitive coupling in a circulating fluidized bed reactor; both studies were carried out at atmospheric pressure. However, up to how little attention has been paid to the interaction between the plasma and the fluidized bed hydrodynamics. We applied a modified version of the latter configuration. The plasma can be operated at various frequencies and voltages to control power input and the reactor wall is efficiently cooled.

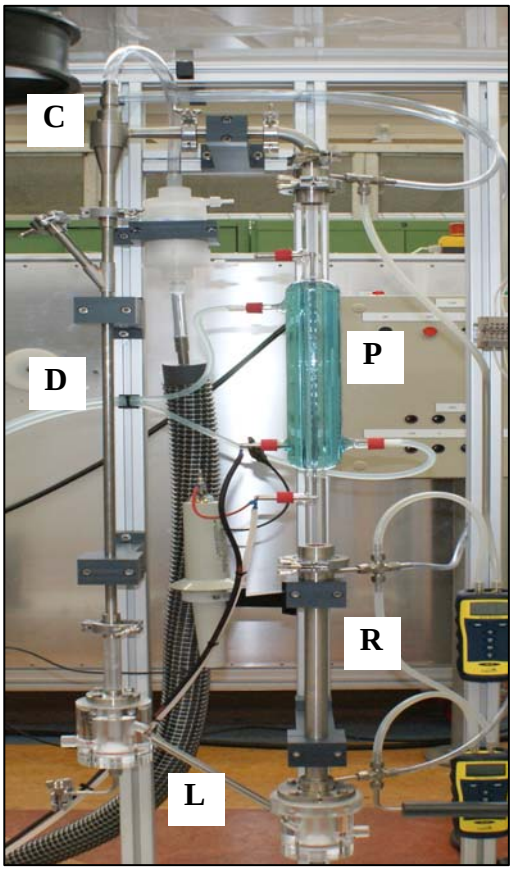

Figure 1. Experimental set-up for plasma coating in a circulating fluidized bed system. The set-up includes a plasma reactor (P), loop-seal (L), riser (R), cyclone (C) and downcomer (D).

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 recirculated 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. 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 (6).

In this paper, we investigate two novel lay-outs for creating dielectric barrier discharge plasma in combination with a circulating fluidized bed. The effects on the hydrodynamic behaviour will be investigated, and a proof-of-principle for coating cupper oxide particles with a layer of silica will be given.

EXPERIMENTAL

A circulating fluidized-bed set-up with a riser diameter of 20 mm and a riser height of 1170 mm has been used in the study. A plasma reactor of 0.30 m length has been incorporated into the riser (see Fig. 1). The bed is fluidized using nitrogen. During

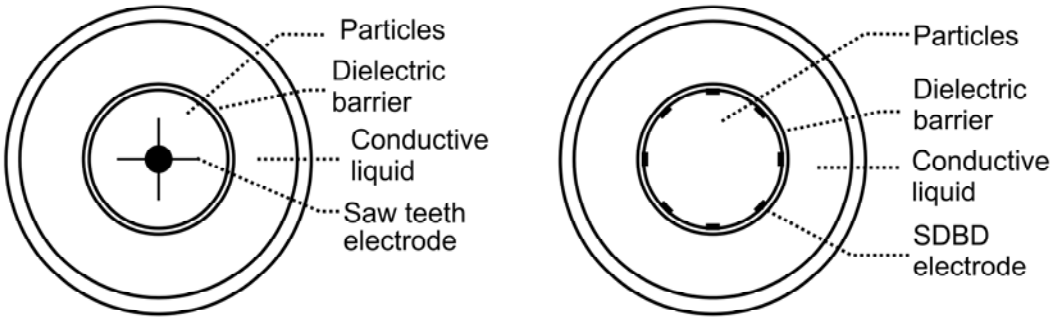

Figure 2. Cross sections of the Volume Dielectric Barrier Discharge reactor (left) and Surface Dielectric Barrier Discharge reactor (right).

the coating process, gaseous coating precursors are added to the main gas stream. By adjusting the riser gas flow and the gas flow through the L-valve the solid hold-up as well as the solid mass flow rate can be controlled. While the mass flow rate was not measured in the experiments, it was visually observed that the material in the riser had a relatively short residence time. No dense bed was present in the riser. The 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 not be captured by the cyclone.

Two types of dielectric barrier discharge plasma reactors have been tested. A horizontal cross section of both reactors is schematically represented in Figure 2. 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 sulphate. The VDBD reactor is used in most experiments presented in this paper. In a later stage, the VDBD reactor was compared to the Surface Dielectric Barrier Discharge (SDBD) reactor. This 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. In both cases, a liquid electrode is used, 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 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 W (by means of controlled repetition rate and voltage).

The gas flow is controlled by a set of mass flow controllers. The gaseous coating precursors are introduced in the CFB together with the main flow stream. A

controlled quantity of liquid precursors can be evaporated using a Bronkhorst evaporation and precursor delivery system. Hexamethyldisiloxane (HMDSO) was using as the precursor to form SiO_x coatings. The temperature of the reactor is monitored by means of a thermocouple which is placed in the center of the gas stream 15 cm downstream of the plasma section. The pressure inside the system is monitored by differential pressure meters measuring the pressure drop over the bottom zone of the riser and the plasma reactor.

The tests which have been performed with this experimental setup can be summarized as:

- Visual study of the fluidization regime in combination with VDBD plasma formation using glass beads (60 μm diameter).
- Measurement of the pressure drop with and without VDBD plasma formation, and with and without CuO particles 20-30 μm diameter).
- Initial tests of powder coating using the VDBD reactor with CuO particles (20-30 μm) and HMDSO coating precursor.
- Measurements of power dissipation and gas heating in both VDBD and SDBD plasma reactors.

RESULTS AND DISCUSSION

Fluidized bed and plasma formation

Some preliminary fluidization tests have been carried out using glass beads (60 μm diameter) to investigate the influence of the superficial gas velocity. When the gas velocity 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, too high a gas velocity will lead to very low particle fractions in the riser and thus low coating efficiencies. 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.

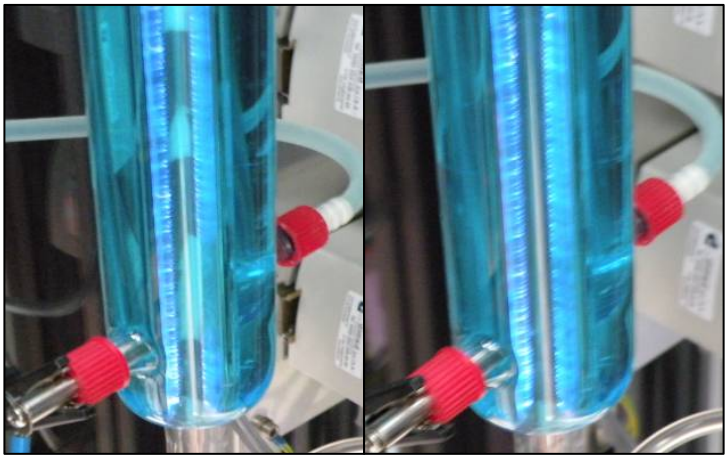

Figure 3. Picture of the VDBD plasma with fluidized glass beads (left) at 1.4 m/s and (right) at 2.3 m/s

Figure 3 shows two pictures of the VDBD plasma reactor obtained at different gas velocities. The left-hand picture shows that for a relatively low gas velocity the particles are not homogenously distributed: a local build-up of particles on the electrodes was observed. An increase of the superficial gas velocity to approximately 2.3 m/s 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 about 4 hours.

Pressure differences

Differential pressure measurements have been performed with the VDBD reactor, using copper oxide (20-30 μm) as the bed material. The superficial gas velocity was 2.3 m/s. During these measurements, no precursor was added. Table 1 shows that for the empty columns without plasma the pressure drop per unit length is slightly higher in the bottom zone of the reactor; this is probably due to the acceleration of the gas. When the plasma is generated, the pressure drop over the riser slightly increases. When particles are added, the pressure drop over both zones increases. Remarkable is however, that the pressure drop over the plasma zone increases stronger than that over the bottom zone, while one would expect a higher or at least the same particle concentration in the bottom zone. 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) or the electric wind.

Table 1. Pressure drop in the circulating fluidized bed.

	No plasma, no particles	Plasma, no particles	No plasma, with particles	Plasma with particles
$\Delta p_{(1,2)}/\Delta h$ [Pa/m]	102	135	112	142
$\Delta p_{(2,3)}/\Delta h$ [Pa/m]	70	103	113	211

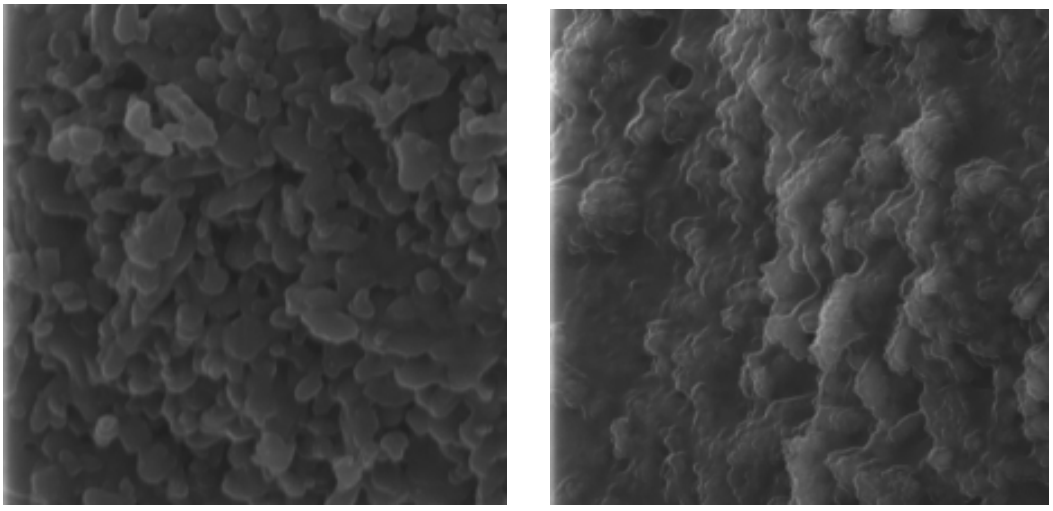

Figure 4. He-ion microscopy image of the surface of untreated (left) and treated (right) copper oxide particles of 20-30 μm size. The area shown on each picture is 2 μm x 2 μm.

Coating of particles

Experiments in which copper oxide particles (20-30 μm 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 $[(CH_3)_2\text{-Si-O}]_n$. However, with increasing oxygen content, a gradual change is observed from organic polydimethylsiloxane-like coatings to inorganic quartz-like deposits (7). In this experiment 20 gram per hour of HMDSO was added to 44 l/min nitrogen (superficial gas velocity 2.3 m/s). With a power input of 150 W the whole system was running for an hour in which the copper oxide powder was circulated dozens of times through the plasma reactor. Figure 4 shows He-ion microscopic pictures of untreated and treated copper oxide particles. The pictures show a detailed part of the surface of a CuO particle, consisting of small, primary particles. The treated CuO particles show an irregularly shaped “collar” which is typically observed for coated materials. Figure 5 shows a droplet of water on a bed of coated copper oxide particles. While uncoated CuO is perfectly hydrophilic, the picture clearly shows that the coated material has become strongly hydrophobic. X-ray micro-analysis of the coated material shows indeed a silicon peak (the most right-hand peak in Fig. 6).

Figure 5. A water droplet on a bed of the coated copper oxide particles.

Power dissipation and temperature rise

As an alternative to the volume DBD reactor used in the presented coating experiments, we investigated the use of the surface DBD reactor (See Fig. 2). Its

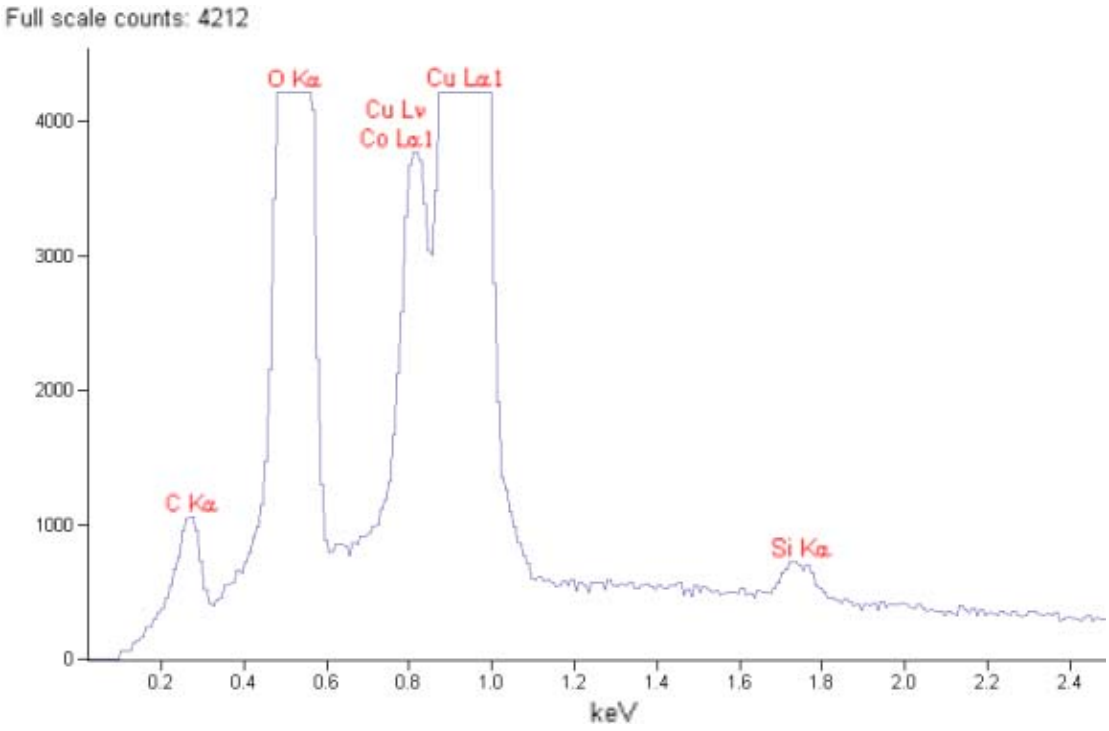

Figure 6. X-ray micro-analysis of the coated copper oxide.

potential advantage is that the geometry poses less obstruction to the gas-solid flow. Because of the different electrode placement, different heat transfer behaviour is expected as well. To investigate this, 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. The experiments are carried out with an empty column (i.e., no particles present) at a superficial gas velocity of 2.1 m/s. Figure 7 shows the measured temperature of the gas as a function of power input in the plasma for both VDBD and SDBD reactors.

The figure shows that in the SDBD reactor heat is more efficiently transported to the surrounding cooling fluid which is held at 20°C 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 cooling is most efficient. 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. Because of the fact that the SDBD plasma can be initiated at much lower voltage, and because of the more efficient cooling, this system is expected to provide improved coating rates and better temperature control of the coating process. In near future, we will carry out additional experimental work in order to confirm this.

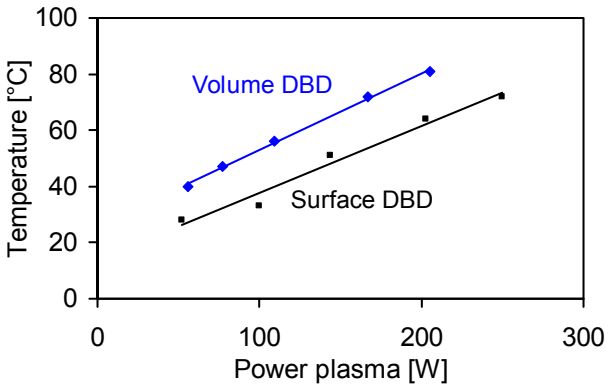

Figure 7. Temperature versus power in plasma. At the same power input, the gas temperature in the SDBD reactor is about 15° C lower than in the VDBD reactor.

CONCLUDING REMARKS

Plasma-enhanced chemical vapour deposition (PECVD) is an attractive technique to provide particles with a thin film. By applying a cold plasma, temperature-sensitive powder materials can be treated and temperature-sensitive coatings can be obtained. We showed that using a CFB with an incorporated volume dielectric barrier discharge reactor 20-30 μm CuO particles can be provided with a thin SiO_x film. It has been shown that a certain minimum superficial gas velocity is needed to overcome the resistance created by the plasma; the plasma is shown to generate an additional pressure drop.

It has been proven that for placing all electrodes at the column wall, a so-called surface dielectric barrier discharge, the deposition of powder on the electrodes is avoided and the cooling is more effective. 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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KEYWORDS

Coating, thin films, plasma, chemical vapour deposition, circulating fluidized bed, cold plasma.