Flowability Modification of Fine Powders by Plasma Enhanced Chemical Vapor Deposition

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ABSTRACT

The flowability of fine powders can be improved by surface morphology modification. Therefore, SiO_x-like nanoparticles were generated and attached to glass beads as a model substrate by plasma enhanced chemical vapor deposition (PECVD). A circulating fluidized bed (CFB) reactor with an integrated microwave plasma source was employed to realize the process. The surface of the treated substrate particles was analyzed by means of scanning electron microscopy (SEM). The size of the attached nanoparticles can be controlled by the operating pressure and the number of circulations of the CFB reactor. Nanoparticle diameters were determined in the range from 50 nm to 120 nm.

Keywords: PECVD, circulating fluidized bed, nanoparticles, flowability

1 INTRODUCTION

Handling and processing of solid powders or granules is widely used in a variety of sectors, including chemical, food and pharmaceutical industry. Delivery, dosage, and mixing require a movement of the bulk material. Therefore attractive inter particular forces have to be overcome. This might be accomplished by means of a gas stream, vibrations, or agitation tools.

As long as the gravitational force is dominating, the solid particles are able to flow. For fine powders with particle diameters smaller than 20 μm adhesive effects like liquid bridges, Coulomb or van der Waals forces are prevailing, leading to a decrease of the flowability [1]. These occurrences are associated with equipment clogging and deposition, which have to be avoided.

In dry powders, the attractive interactions between particles are mainly determined by the van der Waals force. According to Hamaker's law [2], for two spherical particles with equivalent radii this kind of force is proportional to the sphere radius R and inversely proportional to the square of the distance H between the particle surfaces:

$$F_{VdW} = \frac{A}{12}\frac{R}{H^2} \tag{1}$$

The constant of proportionality is given by the Hamaker constant A.

2 CONCEPT

Within the scope of this work, a novel process to improve the flowability of fine powders is investigated. Therefore, nanoparticles are generated by favoring homogeneous gas-phase reactions in a plasma enhanced chemical vapor deposition (PECVD) process and are simultaneously attached to the surface of the substrate particles. These nanoparticles act as spacers between the substrate particles and thus increase the distance between their surfaces. According to Hamaker's law, this leads to a reduction of the van der Waals forces. Figure 1 shows the theoretical values of the van der Waals forces as a function of the size of the attached nanoparticles. The attraction force can be reduced by a factor of 100 and higher, whereas the force reaches a minimum for a specific nanoparticle diameter (e.g. $3 \cdot 10^{-3}$ μm).

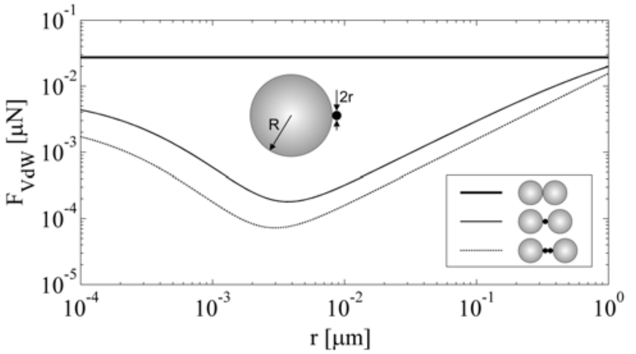

Figure 1: Calculated van der Waals forces acting between two spheres with the radius $R = 1.75 \cdot 10^{-6}$ m as a function of the nanoparticle radius r, distinguishing between no, one or two nanoparticles in-between the spheres (Hamaker constant $A = 3 \cdot 10^{-20}$ J)

The novel process shows some significant advantages compared to alternative methods [3], [4] for increasing the flowability of bulk solids. The process is a combination of the two stages of nanoparticle formation and attachment in one single step. Since a closed system is considered, additional handling of nanoparticles, associated with adhesion effects and health risks, is not required. Compared to alternative treatments, like nanoparticle attachment by mixing [1], remarkable time and cost savings can be obtained. Moreover, the application of a non-equilibrium plasma provides the opportunity to treat temperature sensitive materials.

3 EXPERIMENTAL SETUP

To investigate the nanoparticle generation and attachment in the PECVD process, glass beads (120 μm) as a model substrate were treated in a circulating fluidized bed (CFB) reactor (Figure 2). This reactor concept provides a uniform particle treatment and a narrow residence time distribution. The substrate particles were conveyed through the plasma zone of the reactor by the process gas mixture, consisting of O_2, Ar and Hexamethyldisiloxane (HMDSO). The organosilicon monomer was used as a reactant for the formation of SiO_x nanoparticles.

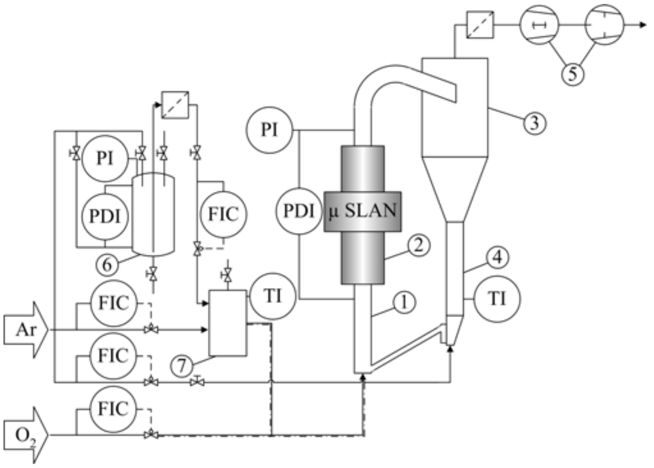

Figure 2: Scheme of the CFB reactor, 1: riser tube, 2: microwave plasma source, 3: cyclone, 4: feed section, 5: vacuum pump unit, 6: monomer tank, 7: evaporation module, FIC: flow indicator controller, PDI: pressure differential indicator, PI: pressure indicator, TI: temperature indicator

The glass beads were treated at microwave (MW) plasma powers of 1000 W and at an oxygen to monomer ratio of 6. By varying the residence time (number of circulations n in the CFB reactor) and operating pressure p, the effect of these process parameters on nanoparticle size distributions were investigated. Therefore, substrate surfaces were analyzed by means of scanning electron microscopy (SEM, Zeiss Leo 1530). Subsequently, the nanoparticle size was acquired by an image processing software (Scion Image, Beta 4.02).

4 RESULTS

In the upper part of Figure 3, the scanning electron micrograph of the surface of an untreated glass bead is shown. In the lower part, the surface of a plasma treated particle is depicted. The order of magnitude of the diameter of the attached nanoparticles is about 60 nm.

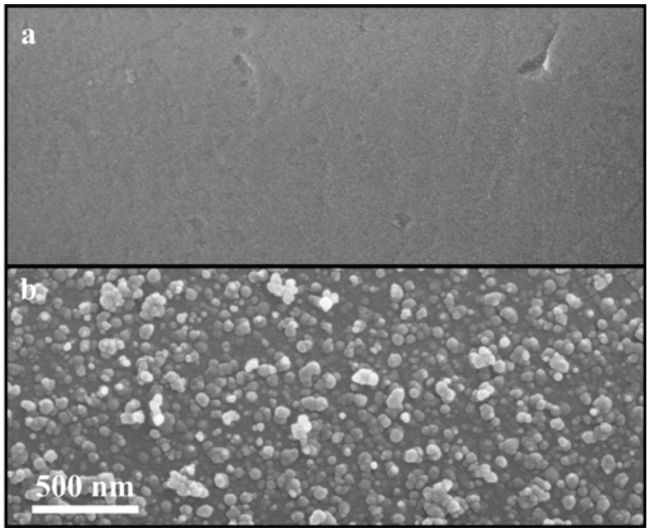

Figure 3: SEM analysis of the substrate surface: a) untreated glass bead, b) treated glass bead (operating pressure $p = 15.3\ mbar$, MW power $P = 1000\ W$, argon flow rate $V^*_{Ar} = 2000\ sccm$, oxygen flow rate $V^*_{O_2} = 200\ sccm$, HMDSO flow rate $V^*_{HMDSO} = 34\ sccm$, number of circulations $n \approx 5$)

In Figure 4, the influence of the operating pressure on the nanoparticle diameter d_{np} is shown. $E(d_{np})$ is the expected value of the measured nanoparticle size distribution. Lower pressure favors heterogeneous reactions and thus causes SiO_x-layer deposition on particle surfaces, leading to an increase of the mean nanoparticle sizes. By increasing the pressure, homogeneous gas phase reactions are promoted. This leads to an increase of the number of created particles and a decrease of the particle size due to lower deposition rates.

The residence time of the process was controlled by the number of circulations n in the CFB reactor. The effect of this parameter is depicted in Figure 5. By elevating n, the expected vaulue of nanoparticle diameter is increased. This is caused by an increase of the thickness of the deposited layer due to longer deposition times.

5 CONCLUSION AND OUTLOOK

The study demonstrates that our process enables the nanoparticle generation by PECVD and subsequent attachment to substrate particles in one single step.

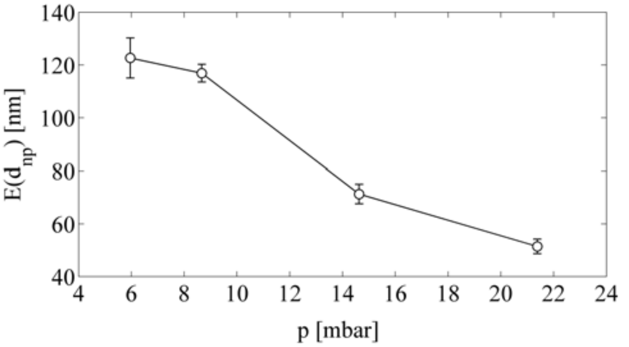

Figure 4: Expected value of the nanoparticle diameter d_{np} as a function of operating pressure p (MW power $P = 1000\ W$, argon flow rate V^*_{Ar} = 3000-7000 $sccm$, oxygen flow rate $V^*_{O_2} = 200\ sccm$, HMDSO flow rate $V^*_{HMDSO} = 34\ sccm$, number of circulations $n \approx 4.5$)

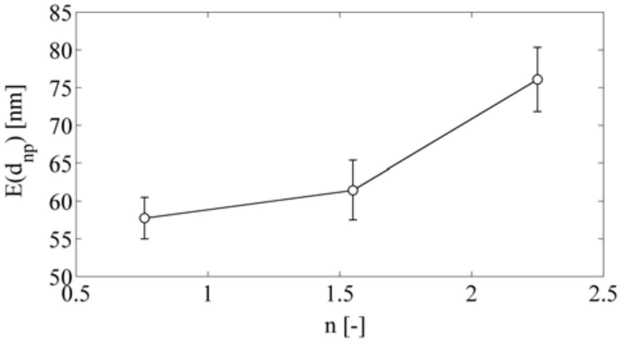

Figure 5: Expected value of the nanoparticle diameter d_{np} as a function of number of circulations n (MW power $P = 1000\ W$, argon flow rate $V^*_{Ar} = 2000\ sccm$, oxygen flow rate $V^*_{O_2} = 200\ sccm$, HMDSO flow rate V^*_{HMDSO} = 34 $sccm$, operating pressure $p = 16\ mbar$)

The experimental study shows that the diameter of the attached nanoparticles can be controlled by the number of circulations and the operating pressure of the CFB reactor. Theoretical considerations confirm that the nanoparticle sizes lie in a range, where the van der Waals forces between the substrate particles can be reduced significantly.

First experiments with a cohesive substrate material show that the process enables to increase the flowability up to a factor of 300 % compared to the untreated material. The flow factor was measured by a ring shear tester (RST-XS, Schulze, Germany) [5].

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