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Gravimetrical and chemical characterization of SiO_x structures deposited on fine powders by short plasma exposure in a plasma down stream reactor

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ABSTRACT

The surface of lactose particles was modified by a plasma-enhanced chemical vapor deposition process to improve the flow behavior of the powder. For this, the particulates were treated in a plasma down stream reactor which provides a short (50 ms) and homogeneous exposure to the capacitively coupled RF discharge. The organosilicon monomer hexamethyldisiloxane (HMDSO) was used as a precursor for the formation of SiO_x which is deposited on the substrate particle surface. For varying process gas mixtures (O_2/Ar/HMDSO) and RF power applied, the amount of the deposited material was determined gravimetrically after dissolution of the lactose substrate particles and the chemical composition of the accumulated deposition material was investigated by means of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The concentration of the deposited SiO_x relating to the substrate material was found to be in the range of 0.1 wt.%. Based on the ATR-FTIR analysis, the inorganic, i.e. oxidic SiO_x fraction of the obtained deposits was shown to be controllable by varying the process parameters, whilst a relatively large amount of organic structures must be considered.

1. Introduction

In many industrial applications dealing with bulk solids, such as delivery, dosage and mixing, the flow behavior of the powder is a critical factor in terms of clogging and malfunction of the equipment. To prevent such events, an adequate flowability of the bulk solid is required. This parameter is mainly determined by the particle size distribution, particle shape, bulk density and moisture content of the bulk solid.

In fine powders, the attractive interparticle forces have a significant impact on the flow behavior. If the powder is dry and thus, the effect of potential capillary forces can be neglected, cohesion between the particles is then dominated by the van der Waals forces [1].

Hamaker [2] derived a correlation (Eq. (1)) to determine the van der Waals force between two equal-sized spherical particles as a function of the particle radius R, the shortest distance between the particle surfaces H and the Hamaker constant A_H which quantifies the atom–atom pair van der Waals interaction.

$$F_{\mathrm{VdW}} = \frac{A_H}{12}\frac{R}{H^2} \quad (1)$$

One method to improve the flowability of cohesive powders is the addition and dispersion of nanoparticles ('glidants', 'flow agents' and 'flow conditioners') on the surface of the substrate particles to be treated [1]. The idea of dispersing nanoparticles on the surface of the substrate particles to reduce the van der Waals forces is based on observations made by Rumpf [3]. He has shown that the van der Waals interaction is strongly dependent on the surface roughness of the substrate particles. By attaching nanoparticles to the substrate particle, the distance between the substrate particle surfaces is increased. According to Eq. (1), this leads to a reduction of the van der Waals force between the substrate particles and hence, improves the flow behavior of the powder. The principle of reducing the van der Waals attraction by the attachment of nanoparticles is described more explicitly in Ref. [4], where we

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have also shown that a similar effect is obtained when very shortly exposing the substrate particles to the low-pressure discharge in a plasma-enhanced chemical vapor deposition (PECVD) process. For that, we have treated lactose powder with a median particle diameter of 5.5 μm in a RF discharge by adding a gas mixture of argon, oxygen and hexamethyldisiloxane (HMDSO). It was shown that the flow behavior of the powder can be significantly improved by the plasma treatment.

The implied plasma surface modification comprises the formation of nanoparticles by favoring homogenous gas-phase reactions and their simultaneous attachment to the substrate particles surfaces [5]. Due to the increase in surface roughness, the van der Waals interactions between the particles are reduced and thereby, the flowability of the powder is enhanced.

However, because of the small amount of deposited material and the use of particulate substrates, it is challenging to characterize the deposition on the substrate particle surface. Furthermore, the nanoparticle like deposition complicates the chemical analysis by means of conventional methods such as X-ray photoelectron spectroscopy which is often applied for the analysis of dense and coherent films deposited by PECVD on macroscopic substrates. Thus, within the scope of this work, a new method to characterize the deposited material was applied. By dissolving the substrate material and accumulating the residue of the deposition on a filter paper, the amount and the chemical composition of the deposition was analyzed gravimetrically and by means of ATR-FTIR.

Depending on the process conditions and the monomer used for silicon-containing depositions, the stoichiometry may differ from pure silica (SiO_2). Silicon-containing organic compounds, such as HMDSO are preferentially used as monomers in low-pressure plasma deposition of silica-like (SiO_x) and silica films. Since non-stoichiometric SiO_x films have varying hydrocarbon content, the proper empirical formula would be $SiO_xC_yH_z$. For the purpose of simplification, in this work SiO_x will be used as a general expression for the deposited material.

2. Experimental part

2.1. PDSR set-up and treatment

In Fig. 1, the plasma down stream reactor (PDSR) [4] for the particle treatment is shown. Its main part is a glass tube, wherein a low-pressure glow discharge is generated. For this, an RF signal at the frequency of 13.56 MHz and a power of 50, 100 and 200 W, respectively, is capacitively coupled into the plasma by means of two copper electrodes mounted on the outer tube wall. A metering screw is used to provide a steady particle feed (2.4 kg/h) from the substrate particle storage container to the diverging nozzle device at the upper end of the tube. Here, thus prior entering the plasma zone, the substrate particles become accelerated downwards and simultaneously disagglomerated and dispersed over the entire tube cross-section by the process gas stream. The gas mixture jetting through the nozzle consisted of Ar (430–995 sccm), O_2 (170–685 sccm) and HMDSO (17–68 sccm). The organosilicon monomer was added to promote the formation of SiO_x nanostructures which are subsequently attaching the substrate particle surfaces. Furthermore, to provide a constant particle residence time in the plasma zone for all experiments, the process gas was complemented with argon. Consequently a constant total gas flow rate of 1180 sccm was obtained. Keeping the process pressure at 2 mbar, the corresponding superficial velocity was 8.7 m/s. Assuming that the substrate particles follow the gas flow, the plasma exposure time can be estimated to be in the range of 50 ms.

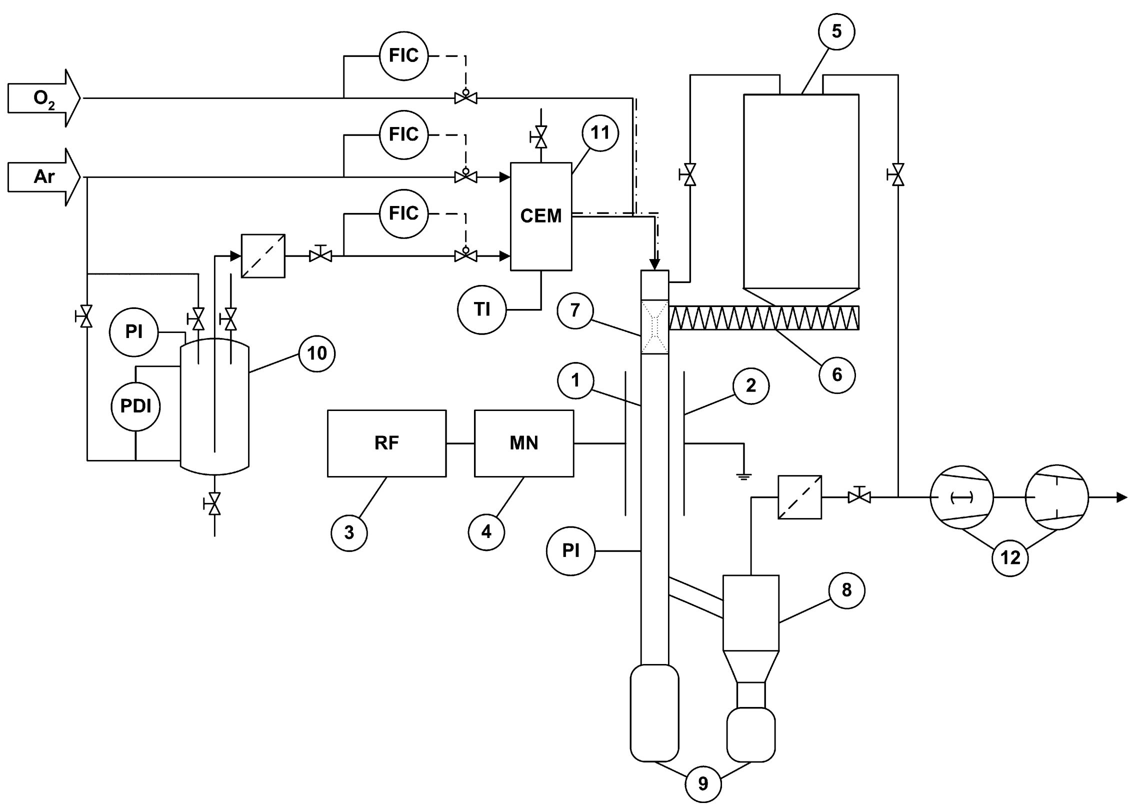

Fig. 1. Scheme of the plasma down stream reactor: (1) downer tube, (2) capacitively coupled electrodes, (3) RF generator (13.56 MHz), (4) matching network, (5) solid storage container, (6) metering screw, (7) nozzle device, (8) cyclone, (9) solid collecting vessels, (10) monomer tank, (11) temperature-controlled evaporator mixer device and (12) vacuum pump unit, FIC: flow indicator controller, PDI: pressure differential indicator, PI: pressure indicator and TI: temperature indicator.