Nanoparticle Synthesis in a Tubular Plasma Reactor – From Plasma Parameters to Nanoparticle Properties

Extended abstract for
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1 Introduction

In the presented study a tubular plasma reactor is investigated, which is normally used for the continuous plasma surface modification of fine-grained powders. The plasma reactor basically consists of a 1.5 m long glass tube with a gas and precursor feed unit at its top and a particle-gas separation unit at the lower end. The power is coupled inductively into the plasma via a coil which is wrapped around the reactor tube.

Substrate powders normally pass the discharge tube with high velocity and are functionalized on their way through the plasma in approximately 0.1 s. Possible plasma surface functionalization processes for powders are illustrated in Figure 1.1. The wettability of powders is increased by the formation of polar groups on the surface [1]. Films are deposited on particle surfaces to protect the substrate from harsh environments [2] or for catalytic applications [3]. In recent years, also a new plasma process, which increases the flowability of fine-grained powders, gained increasing attention. Nanostructured SiO_x is formed in the plasma and directly deposited on the substrate particle surface [4]. These nanoparticle structures increase the surface roughness of the substrate particles. Thus, the interparticle van der Waals forces are reduced, which leads to a major improvement of the powder flowability [5]. This process shows promise for companies dealing with cohesive granular materials.

The feasibility of this process was shown in the past, but at the same time the need for fundamental research in this field was recognized. Which ion density is required to yield in an effective surface modification? What is the thermal load of a substrate particle during the treatment? Which precursor should be used for a maximum improvement of the flowability?

In order to answer such questions, we measured axial profiles of plasma parameters in this continuous reactor and studied the nanoparticle synthesis in detail. No substrate powder was fed during these investigations to facilitate probe measurements and to focus on the produced nanoparticles.

Silica-like nanoparticles were produced from the four organosilicon monomers hexamethyldisiloxane (HMDSO), tetramethyldisiloxane (TMDSO), tetraethyl orthosilicate (TEOS), and tetramethyl orthosilicate (TMOS) in argon-oxygen gas mixtures. The chemical composition and morphology of the emerging particles and its production rate were studied as a function of process pressure (100 – 400 Pa), plasma power (200 – 350 W), gas velocity (5 – 16 m/s) and gas composition. Langmuir double probe and calorimetric probe measurements allowed determining the axial profiles of electron temperature, positive ion density, and energy influx along the vertical axis of this tubular reactor.

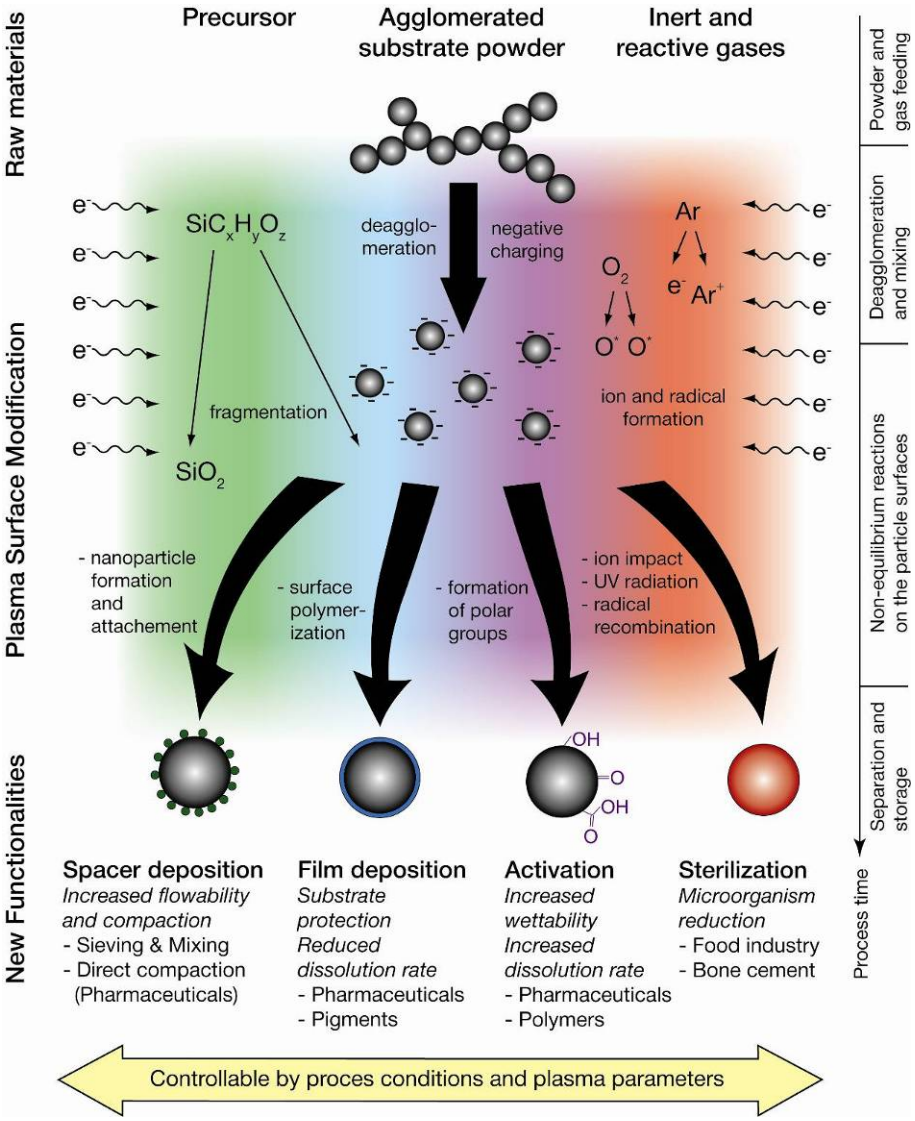

Figure 1.1: Overview of plasma-assisted surface modification processes for fine-grained powder substrates.

2 Experimental

The process scheme for the nanoparticle production in the tubular plasma reactor is shown in Figure 2.1. The plasma chamber (1) consists of a 1.5 m long double wall glass reactor with an inner diameter of 40 mm. Thus, a high surface-to-volume-ratio of 100 m^{-1} is provided. The gap between inner and outer glass tube was flushed with deionized water (2) of 20 °C to ensure a constant reactor temperature.

The discharge was driven with radio frequency (RF) of 13.56 MHz. The RF-generator (3) was connected over a matching network (4) with the water cooled copper coil (5) on the outside of the cooling jacket. The flow rates of oxygen, argon and the organosilicon monomers were adjusted by flow controllers. The liquid monomers were fed through a controlled evaporation mixing device (6) and stored under a 2 bar argon atmosphere (7) to prevent monomer degradation.

Below the plasma zone the produced nanoparticles were separated from the gas stream by a downcomer (8), cyclone (9) and filter unit (10) and collected in the solid collection vessels (11). Since the produced silica structures are very small, all powder was collected from the polyester filter. A constant pressure in the reactor was maintained during the process by a butterfly control valve (12) in front of the two stage roots and rotary vane vacuum pump (13).

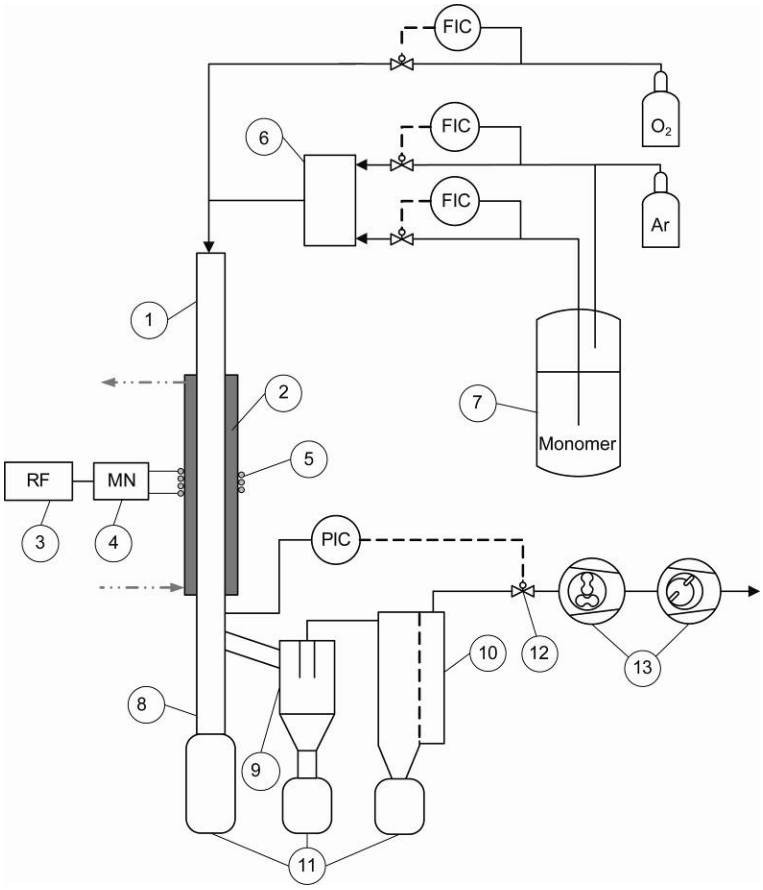

Figure 2.1: Process scheme of the tubular plasma reactor adapted for nanoparticle production, PIC:flow indicator controller, PIC: pressure indicator controller, numbers are indicated in the text, taken from [6].

3 Analytical methods

The plasma was characterized by a tailor-made Langmuir double probe and a calorimetric energy influx probe. In addition, photographs of the discharge were taken to discuss characteristic differences in optical emission of the plasma as a function of the process parameters. The morphology of the emerging nanoparticles was investigated by transition electron microscopy (TEM). For the determination of the mass production rate of nanoparticles the filter weight was measured before and after each experiment. Information about the bond structure of the produced particles was gained by Fourier transform infrared (FTIR) spectroscopy, whereas the chemical composition of the particles was studied by X-ray photoemission spectroscopy (XPS).

4 Results

The electron temperature reached its maximum in the domain of the inductive coil and values up to 17 eV were measured. The positive ion density featured as well maximum values in the region of the helical coil. Densities up to approximately $2 \cdot 10^{11}$ cm^{-3} were found and the positive ion density as well as the energy influx rose with increasing plasma power. The measured energy influx was additionally strongly influenced by the mean gas velocity in the reactor.

The carbon content of the orthosilicate derived particles was generally lower compared to disiloxane derived particles. Furthermore, the carbon content decreased with rising oxygen to monomer ratio, plasma power, and process pressure. The conversion from monomer to nanoparticles was favoured by high pressure, short residence time, and high monomer content in the process gas. The morphology of the produced amorphous particles was similar to fumed silica, with primary particles in the size range of 10 nm, building hard-agglomerates of several

hundred nanometres during the synthesis. Finally, an adapted particle growth model for a continuous plasma reactor, illustrated in Figure 4.1, was introduced which explains the influence of the different process parameters on the particle evolution.

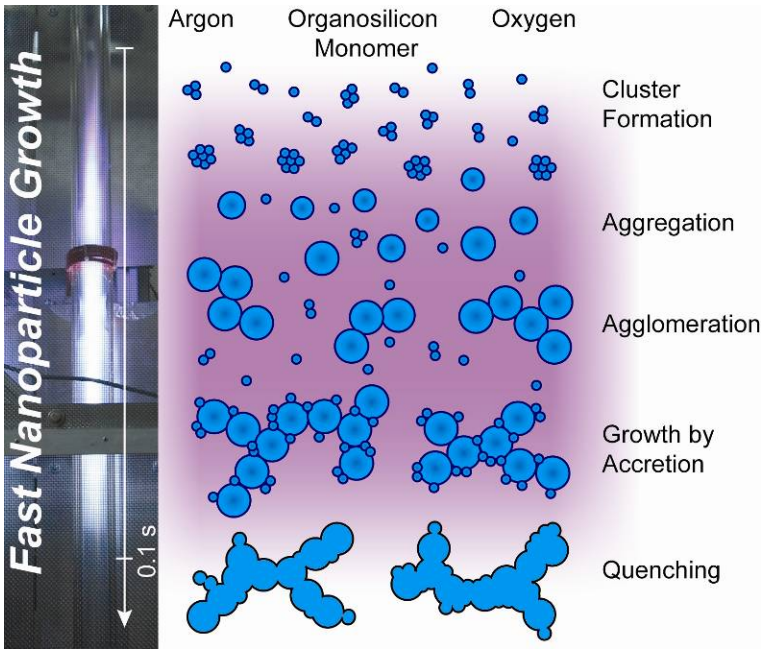

Figure 4.1: Adapted particle growth model for this tubular plasma reactor, taken from [6].

5 References

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