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Liquid spray vs. gaseous precursor injection — Its influence on the performance of particle coating by CVD in the fluidized bed

Gregor S. Czok, Joachim Werther *

Hamburg University of Technology, Particle Technology, D-21073 Hamburg, Germany

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Abstract

Aluminum coatings were created onto glass beads by chemical vapor deposition in a fluidized bed reactor at different temperatures. Two different routes were examined. First, tri-isobutyl-aluminum (TIBA) vapor was enriched in nitrogen and thermally decomposed inside the fluidized bed to deposit elemental aluminum. On the other hand, liquid injection of TIBA via a two-fluid nozzle directly into the fluidized bed was tested. To ensure homogeneous coating on the bed material, the fluidizing conditions necessary to avoid agglomeration were investigated for a broad range of temperatures. Also, different glass types and pretreatments of the substrate surface were investigated to elucidate the influence of the surface chemistry on the growth and morphology of the layers deposited.

Keywords: CVD; Precursor; TIBA; Liquid spray injection; Fluidized bed

1. Introduction

For various applications in modern powder technology coatings help to produce desired solids properties. Most pigments for metallic color paints consist of a core particle surrounded by a well-defined layer of a certain refraction index to give the impression of a certain color, depth and shine [1]. While wet processing of pigments requires solid–liquid separation, drying, destruction of agglomerates and often subsequent tempering of the fine solids, the combination of chemical vapor deposition (CVD) and fluidized bed technology facilitates coating without additional process steps.

The fluidized bed provides incentives for powder coating due to intense solids mixing, excellent heat and mass transfer and homogeneous temperatures. Although there are already industrial applications of chemical vapor deposition in the fluidized bed reactor (CVD-FBR) for pigment coating [2], investigations in the open literature are scarce and the governing mechanisms in the fluidized bed are not yet fully understood. The technology is further mentioned for the production of noble metal catalysts [3,4], where metal organic precursors are either decomposed thermally or by micro wave or radio frequency plasma. In the patent literature CVD-FBR can be found for the production of layered luminescent pigments [5,6]. Here, one or more very thin but closed protective coating layers of alumina or SiO_2 are applied to prevent moisture contact and the hereby caused decay of brightness.

A first pioneering work was carried out by Liu et al. [7], who investigated the thermal decomposition of tri-isobutyl-aluminum (TIBA) for the coating of glass beads with high refractive index. The application – although not named explicitly – seems to be the production of color pigments with angle-dependant change in color. Although the temperature range investigated was almost the same than in the present work, the focus was on the surface chemistry of the reaction pathways, the carbon incorporation into the surface layer and the layer quality for different temperatures and operation times from a chemist's point of view. The fluidizing conditions, the agglomeration tendency and the homogeneity of the coated material were not further discussed. In the present paper the fluidizing conditions and solids mixing rates were systematically studied. Special focus was set on the mode of precursor injection. Two routes have been investigated; one being the injection of vaporized precursor in a carrier gas stream, the

* Corresponding author.
E-mail address: Werther@tuhh.de (J. Werther).

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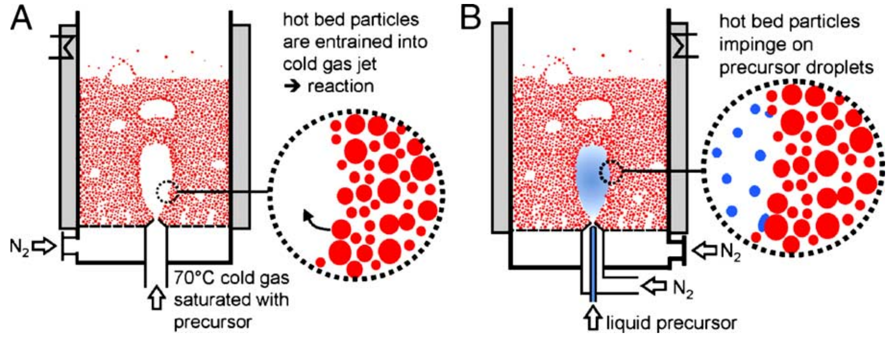

Fig. 1. Injection mechanisms of A) gaseous and B) liquid precursor injection.

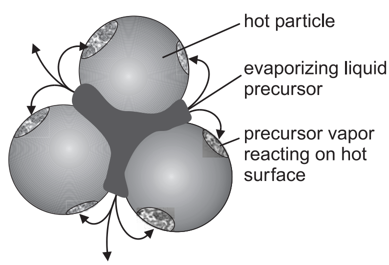

Fig. 2. Scheme of liquid precursor forming an agglomerate with particles.

other being liquid spray injection of TIBA directly into the fluidized bed.

2. Theory

The transfer of the coating process from classical semiconductor production at clean vacuum conditions to the coating of powders with a high volume specific surface in the fluidized bed requires a higher throughput of precursor, since, for example, 1 g of 60 μm glass beads has a total surface area of already $3.8 \cdot 10^{-2}$ m^2. Therefore, a high feed rate of precursor is required to shorten operation times and thus to keep attrition effects as low as possible. Following classical CVD processes, the precursor can be introduced into the reaction zone by a carrier gas. The precursor feed rate is limited by the saturation capacity of the carrier gas in this case. The enriched carrier gas is usually kept well below the reaction or decomposition temperature of the precursor to prevent gas phase reactions. Inside the fluidized bed, the precursor gets in contact with hot particles that are entrained into the cooler gas jet (Fig. 1A). The decomposition reaction will preferably take place at the hot particle surfaces, as long as the reaction is fast compared to the mass transport. Thus, gas phase nucleation can be suppressed largely.

To increase the precursor dosage, liquid spray injection can be considered. The mechanisms here are displayed in Fig. 1B for the application with a two-fluid nozzle. Those hot bed particles, which are entrained in the jet, impinge onto liquid precursor droplets or ligaments. Although the vaporization of the liquid precursor is very fast (Leclère et al. [8] found a vaporization time of 16 ms for a 300 μm FCC feedstock droplet), according to Bruhns and Werther [9] some neighboring particles will be sticking to the droplet to form an agglomerate (Fig. 2). Heat supply by the hot particles of the agglomerate will cause the precursor to vaporize and since this occurs locally very close to the particle surface, the gaseous precursor decomposes on the neighboring particle surface. Since each agglomerate acts as local source of gaseous precursor with locally high vapor concentration near the liquid surface, it can be expected that this mode of precursor supply will cause a layer structure which differs from the morphology caused by gaseous precursor injection into the fluidized bed.

Bruhns and Werther [9] have shown, that the agglomerates formed in the spray jet easily fell apart after evaporization of the liquid. In the present application it could be necessary to agitate the bed to such an extent, that the formation of permanent agglomerates is suppressed. This question is also subject of the present experimental investigation.

3. Experimental

3.1. Experimental setup

The fluidized bed reactor for the injection of gaseous precursor had a cross-section area of 8×8 mm^2, a height of 200 mm and an enlarged freeboard section of 45 mm inner diameter for gas solids separation (Fig. 3). The fluidized bed reactor was built with these small dimensions in order to be operated with a solids inventory of 4 g only. This made it possible to simulate the deposition process in the fluidized bed reactor based on a discrete particle simulation, which is subject of another publication [10].

High-purity nitrogen (>99.99990%) was used as a carrier gas to be saturated with TIBA vapor. The gas flow rate was adjusted by a mass flow controller (FIC) that was connected to a pressure controller to prevent over pressure (>150 kPa) at the precursor flask. The precursor bottle was placed into a heated oil bath and used as a bubbler by inserting an immersible pipe. The oil bath was kept at 82 °C to gain a TIBA temperature of (80 ± 0.5)°C, measured by a Pt100 temperature probe (TI-1). The saturated nitrogen was transported in pipes, which were heated to a temperature of 85 °C, to the fluidized bed reactor and entered the reactor through a four-hole nozzle. The diameter of the four holes was 0.8 mm each. The geometry of this four-hole nozzle is given in detail in Fig. 4.