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CVD and Powders: A Great Potential to Create New Materials

Powders play a major role in modern industrial activity. Approximately one-half of the products in the chemical industry and at least three-quarters of the raw materials nowadays are in granular form (Nedderman, 1992^[1]). During the very last years, these values have probably been further increased due to the spectacular development of nanomaterials and especially of nanoparticles.

Due to the high surface-to-volume ratio of powders compared with bulk materials, numerous challenges in surface functionalization exist, aimed at conferring useful properties on the final products at a high level of performance and/or in economically competitive way. Such properties include protection against corrosion or oxidation, wettability, toughness, catalytic activity, and biocompatibility, and also include durability issues. Indeed, controlling the surface characteristics of powders presents a huge interest in numerous fields, such as mechanics, transport, catalysis, energy, microelectronics, and the pharmaceutical and food industries.

Surface treatments of particles involve both wet and dry techniques. Among the former, one can mention sol-gels, impregnation, granulation, liquid coating. Milling, thermal annealing, hydrogen reduction, and chemical vapor deposition (CVD) are representative of the latter. The choice of technique depends on the requirements of the surface treatment and on the characteristics of the powders to be treated, e.g. chemical nature, size, size distribution, porosity, density, or shape.^[2]

Figure 1 presents the evolution of published papers dealing with CVD and powders as a function of the year of publication for a sample of 200 papers. Compared to the other techniques, CVD is a solvent free, “green” process; it is a versatile technology, allowing surface treatments or deposition of most of the chemical elements, either pure or alloyed, either in the zero valence state or in the form of compounds such as oxides, carbides, nitrides, or combinations thereof. CVD is most often a one-step process that does not require any activation or annealing post-treatment although this is not systematically the case. It implies the use of a reactive gas phase, involving heterogeneous and often homogeneous chemical reactions.

When treating powders, surface reactions often tend to be very intense, due to the high surface-to-volume ratio of the substrates. As detailed in a recent review,^[2] surface-to-volume ratios for

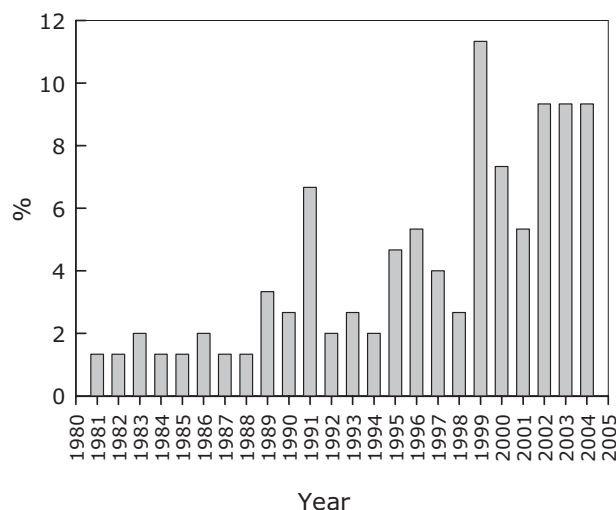


Fig. 1. Published papers dealing with CVD and powders as a function of the year of publication. A total number of 200 papers was considered in this compilation.

CVD on flat substrates like wafers do not exceed 100 m^2 per cubic meter of heated volume, whereas those for CVD on powders vary between 10^4 and $3 \times 10^7 \text{ m}^2/\text{m}^3$. To ensure satisfactory uniformity of deposits on powders, an efficient contact of particles with the reactive gas phase must be organized. Figure 2 schematically illustrates most common gas-powder contactors. It is noticeable that the simplest ones are fixed bed and flat hearth (figures 2a and 2b) where gas flows respectively through and over particles which remain motionless. These modes of contact have been used mainly for CVD processes devoted to catalyst preparation and carbon nanotube synthesis.^[3] Such processes are not adapted for the uniform processing of powders or for mass production; they present numerous drawbacks, among which are: i) the existence of radial thermal profiles spoiling

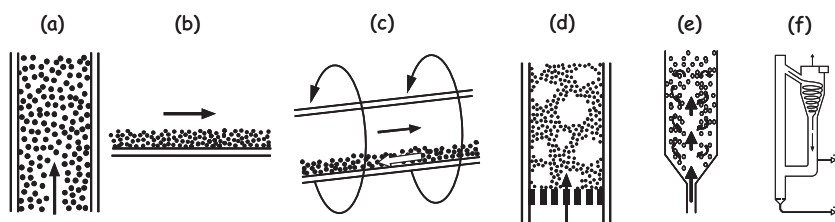


Figure 2: Schematic of the most common gas-powders contactors: (a) fixed bed, (b) flat hearth, (c) rotary cylinder, (d) fluidized bed, (e) spouted bed, (f) circulating fluidized bed.

ing the uniformity of treatment; ii) the impossibility of performing deposition over the entire surface of particles due to contact points among them and with reactor walls; and iii) the occurrence of clogging phenomena when high deposition rates and/or high thickness are required. To limit these drawbacks, it is necessary to levitate or at least to apply a relative motion among the particles in the reaction volume. A first alternative technology concerns rotary cylinders (figure 2c), in which the particles are put into motion by the rotation of the horizontal cylindrical reactor walls. However, the previously mentioned drawbacks are not fully eliminated; in particular, the particles are often quite diluted in the gas phase, which leads to the existence of radial thermal heterogeneities, and clogging phenomena can occur on reactor walls where the temperature and then the deposition rates are the highest.

One of the best-known and most efficient gas-solid contactors is fluidization. As illustrated in figure 2d, it consists of putting the powders above a grid (also called gas distributor) in a vertical cylindrical column. An ascending gas flow is organized such that the powders behave like a liquid: gas bubbles appear in the bed of particles and a vigorous mixing of powders is created by the rising, coalescence and collapsing of bubbles. Intense thermal transfers exist in a fluidized bed (FB) between the powders, the gas phase, and the reactor walls; this is the reason why a FB is known to be isothermal, which constitutes a medium very well suited to performing thermal CVD. Mass transfers in FB are also very high, which most often ensures both a good uniformity of CVD treatment and also a high conversion rate of the gaseous precursors.

A shadow cast over this very promising description of CVD in FB is that only a limited range of powder sizes can be fluidized, roughly those with mean diameter between 50 and 800 μm and with grain density between 1500 and 4000 kg/m^3 .^[4] Attempts to fluidize powders composed of millimeter-sized particles yield no expansion of the bed due to gas flow, and consequently poor gas-solid contact. To address this problem of the fluidization of large particles a derived technology was proposed in the fifties, called spouted beds (SBs). As illustrated in figure 2e, the gas distributor is replaced by a cone generating a spout of gas through the particles and convenient thermal and mass transfers are thus created between the gas and the particles with, however, a lower residence time for the gas, and then in general, lower conversion rates for the CVD precursors.

The treatment of individual micrometer or sub-micrometer particles by CVD is more difficult because for these fine powders, the interparticle forces, especially the Van der Waals ones, are higher than the forces exerted by gas flow. Consequently, either particles do not fluidize at all or they can fluidize under the form of millimetre-sized agglomerates. The formation of such agglomerates prevents uniform deposition around each individual particle and CVD consolidates the agglomerates both externally and in the voids of the inter-grain porosity. To face these problems, external

energy can be applied to the FB to partly overcome the interparticle forces, for instance either by vibrating the reactor or by mechanical stirring.^[5] Alternatively, powders can be treated in diluted phase contactors, such as circulating fluidized beds (CFBs), schematically shown in figure 2f, which consist of transporting the particles in a closed loop. But it must be emphasized that, due to the formation of agglomerates, deposition on each individual grain of powders of mean diameter lower than 5 μm remains an unsolved problem.

Other applications of FBCVD processes are thermal and thermochemical treatments as well as formation of wear- and corrosion-resistant protective coatings on metals. In the case of thermochemical treatments (carburizing, nitriding, carbonitriding, and nitrocarburising), the gas mixture consists of reactive gases such as methane and ammonia, and inert gases, such as argon or nitrogen. These mixtures serve for the fluidization of an inert powder, mainly alumina, and as a medium for the transition of, for example, carbon and/or nitrogen into the surface of the material to be treated.

Last but not least, the potential of the CVD technology devoted to powder production should also be mentioned. In contrast to wet chemistry or classical mechanical milling, this processing route involves gaseous precursors and is thus cleaner, more energy-efficient, and environmentally sounder. It provides high-purity metallic, oxide and non-oxide powders and more recently nanoscale materials formed by a catalytic mode, such as carbon nanotubes. Laboratory-scale production has been easily mastered but with the exception of catalytic routes, up-scaling towards industrial exploitation seems difficult because of the large number of parameters that have to be considered.

In order to take advantage of the above mentioned possibilities for surface treatment or processing of powders, it is necessary to deal with the recurrent constraints associated with CVD processes such as side deposition, precursor handling, or homogeneous nucleation. This can only be achieved through an integrated, interdisciplinary approach with inputs from chemistry, chemical engineering, and materials science.

In the present special issue of Chemical Vapor Deposition eight papers report on the different aspects of powders involving CVD processes. Von Rohr and Borer (ETH Zürich) summarize specific design and operational features for a CFB system with a non thermal plasma. They exemplify their approach with coating results of glasslike material on salt particles considered as model substance. McCormick et al. (University of Colorado and Physical Electronics, Chanhassen, MN) combine atomic layer deposition (ALD) and a rotary reactor to deposit alumina thin films on zirconia nanoparticles. Serp et al (Institut National Polytechnique de Toulouse, CEMES and Arkema) present the current state of art in FB catalytic CVD as a process for large-scale industrial production of carbon nanotubes. Suffner et al (Technische Universität Darmstadt, Forschungszentrum

Karlsruhe and SusTech GmbH) present a synthetic route for the preparation of nanoscale oxide/polymer composites consisting of a silica core coated with either methylmethacrylate or ethyl-2-cyanoacrylate by Chemical Vapor Synthesis. Sánchez et al (Universidad Complutense de Madrid) provide a general review on the deposition, co-deposition or modified deposition by FBCVD of several coatings such as Al, Si, Al/Si, Al/Hf, on ferritic steels at temperature below 600 °C. In the last paper on processing science, Moravec et al (Institute of Chemical Process Fundamentals, Prague, Tampere University of Technology, and Luikov Heat and Mass Transfer Institute, Minsk) synthesize binary ZrO₂/SiO₂ fine particles by simultaneous decomposition of zirconium tetra-*tert*-butoxide and tetraethyl orthosilicate in an externally heated tube flow reactor under oxidizing atmosphere. Two papers on modelling complete the contributions: Pannala et al (Oak Ridge National Laboratory, TN and National Energy Technology Laboratory, Morgantown, WV) describe simulation studies of the dynamics of spouted beds used for CVD coating of nuclear fuel particles. Finally, White et al (Carnegie Mellon University) use a multi-scale framework for modelling the dynamic particle size distribution in a FBCVD process.

Although it was the growth of the nuclear power industry in the 1960s that provided the drive for the development of FB reactors to coat large volumes of powders, there are not yet any major industrial processes operating with such technology. The current applications of FBCVD concern the manufacture of advanced engineering materials and it is worth mentioning that an extensive patent literature ex-

ists on the subject and that some SMEs are already using this technology to manufacture custom powders. It can be reasonably expected that in the near future, nanotechnologies will contribute to intensifying the industrial development of powder synthesis and treatment by FBCVD and the other CVD processes mentioned in this special issue.

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