FLUIDIZED BED CHEMICAL VAPOR DEPOSITION : STATE OF THE ART AND MAIN CHALLENGES

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Fluidized bed chemical vapor deposition (FBCVD) is one of the most efficient techniques to functionalize, to deposit on, or to coat each individual particle of a powder from gaseous species. FBCVD combines two processes. One is the deposition itself, the other aims in suspending the particles in the deposition zone, most often by flowing a gas upwards through the powder. In contrast to CVD on flat surfaces which often operates in a surface kinetics limited regime, FBCVD is generally transport limited. This is due to the extremely high available growth surface to heated volume ratios (S/V) in the deposition area. Consequently, gaseous precursors are very often totally consumed a few centimeters after their entrance into the fluidized bed reactor, but the high degree of gas solid mixing compensates for this discrepancy, and ensures isothermal conditions as uniform deposition.

Thermal or plasma assisted FBCVD has been initially used in the sixties for the deposition of pyrolytic carbon and of silicon carbide on radioactive particles for the primary containment of nuclear fission products. But, the most numerous reports concern the protection of powders against oxidation and corrosion, the production of monolithic materials (diamond, Si, AlN), the fabrication of composites and of finely dispersed nanoparticles or, by means of surface treatments, the improvement of the wetting between matrix and reinforcement (1-3 and references therein). Another important application of FB reactors is the preparation of supported catalysts, either through a direct one-step CVD process, or through the adsorption from the gas phase onto the inert support of metal precursors followed by a decomposition on the surface to yield the finely dispersed catalyst.

FBCVD has been investigated in the authors research groups since the early nineties (2,3). Based on these activities, the present paper will draw the main potentialities and bottlenecks associated with this technology. We will first focus on silicon deposition from silane, one of the rare FBCVD materials for which kinetics are known. Another school case concerns the preparation of platinum finely dispersed supported catalysts, useful to emphasize the importance of surface chemistry to drive the process towards deposits with desired morphology. Then, two more recent activities will be used to illustrate the potentiality of fluidized beds to deal with powders of particular morphology, density and/or size distribution. These are the massive production of carbon nanotubes and the doping with Pt-group and refractive metals bond coats in thermal barriers applied to gas turbine engine blades and vanes.

Let us focus on the production of multi-wall carbon nanotubes, from the decomposition of ethylene on Alumina/Fe supported catalysts. The bottlenecks of this FBCVD process are linked to the accurate mastery of the catalyst characteristics and of the operating conditions, necessary so as MWNT grow.

The remarkable features of this process are a selectivity in MWNT close to 100% (neither soot nor encapsulated particles detected by TEM), a carbon conversion into MWNT always greater than 85%, and an excellent reproducibility of experiments. This process presents another specificity, concerning the huge bed expansion during runs. Indeed, the initial nominal bed height is about 3 cm; it can exceed 50 cm after two hours of run, corresponding to about 50 g of MWNT formed. This spectacular expansion is due to the formation of 3D randomly oriented jumbles, in which the initial catalytic particles are embedded, as shown in figure 1. Some first hydrodynamic studies have been performed concerning the fluidization quality of the bed for various run durations. It appears that the bed remains fully fluidized till 60 minutes of run. After 60 min, slugs and preferential channels co-exist, apparently ensuring a sufficiently high gas solid contact, since no clogging phenomena occur and material homogeneity is good. In fact, in this FBCVD process, the size, morphology and density of powders notably change all along the deposit duration. So, another challenge to take up for this technology concerns the mastery of the fluidization quality of a bed composed of evolutionary powders.

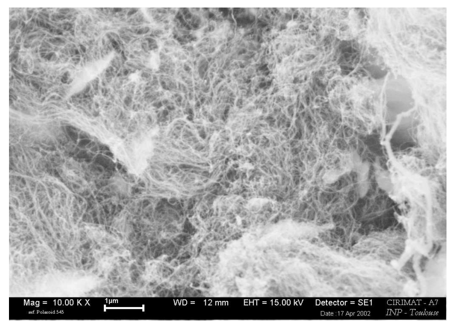

Figure 1.

The advantages of the FBCVD technology are important: high versatility, high gas conversion into solid on powders, good homogeneity of products, possibility of continuous operations, technology easy to use and to rescale, low costs in equipments, ...

The bottlenecks today identified essentially concern identification of conditions ensuring high deposition rates to perform thick continuous deposits on non porous powders, since clogging phenomena and parasitic fine particle formation can occur. For some FBCVD processes, another challenge to take up is relative to the mastery of fluidization quality for either lowly fluidizable initial powders or particles of evolutionary morphology due to the deposit. Finally, the FBCVD process seems to be perfectly suited to perform discontinuous deposits on non porous powders, as to treat porous powders in all possible conditions.

The versatility of this process in terms either of powders able to be treated or of materials to be deposited is very high. A huge field of potential applications is then opened for this very promising technology.

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