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Étude de la fluidisation d'une poudre de forte densité et dépôt d'un revêtement par CVD en lit fluidisé

Fluidization and coating of very dense powders by Fluidized Bed CVD

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Résumé

Dans le cadre d'une collaboration entre le CEA Cadarache et le Laboratoire de Génie Chimique de l'INP Toulouse, des études concernant la possibilité de fluidiser une poudre de très forte densité ont été réalisées. Pour ce faire, une poudre de tungstène commerciale (densité de grain = 19 300 kg/m³ ; diamètre moyen en volume : 75 µm) a été utilisée.

La fluidisation à température ambiante de cette poudre a été démontrée en utilisant de l'azote et de l'argon comme gaz vecteurs. Puis, des études à 400 °C ont également été réalisées et ont permis de dégager des conditions opératoires favorables pour la mise en fluidisation de la poudre de tungstène en vue de son revêtement par Dépôt Chimique en phase Vapeur (CVD) en lit fluidisé. L'influence du rapport H_0/D – hauteur initiale du lit fixe sur diamètre de la colonne de fluidisation – sur le comportement thermique du lit a été particulièrement étudiée.

Enfin, les premiers résultats concernant le dépôt d'alumine à partir d'aluminium acétylacéonate sur poudre de tungstène par CVD en lit fluidisé sont présentés. Ces derniers tendent à démontrer que la CVD en lit fluidisé est un procédé tout à fait adapté pour l'obtention d'un revêtement sur des poudres aussi denses.

Abstract

The feasibility of fluidizing very dense powders has been studied in a collaborative work between the French Alternative Energies and Atomic Energy Commission and the Laboratoire de Génie Chimique from INP Toulouse. For this work, a commercial tungsten powder, 75 µm in mean volume diameter and 19,300 kg/m³ in grain density, was used.

First, the fluidization of the tungsten powder has been attempted at room temperature using nitrogen or argon as carrier gas. Then, the fluidization was studied at 400 °C in order to investigate the subsequent coating of tungsten powder by Fluidized Bed Chemical Vapour Deposition (FBCVD). In particular, the influence of the H_0/D ratio (initial fixed bed height to reactor diameter) on the bed thermal behaviour was analysed.

Finally, the first results concerning the coating of tungsten powder by alumina FBCVD from aluminium acetylacetonate are detailed. These latter tend to show that FBCVD is a suitable process to uniformly coat so dense particles.

Mots-clés : poudre de tungstène, fluidisation, alumine, CVD, dépôt

Key-words : tungsten powder, fluidization, alumina, CVD, coating

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1. Introduction

The available literature concerning the fluidization of very dense powders is scarce. Itagaki (1995) reported the fluidization of tungsten powder with a mean diameter ranging between 3 and 5 μm and WC-Co composite powders with 200 nm mean grain size has been synthesized using high temperature fluidization technology (Ouyang, 1998; Gong and Ouyang, 2007). Nevertheless, these works concerned relatively small powders and we did not find reports concerning the fluidization of very dense particles with a mean diameter of several tens of microns. This fact is not really surprising because for particles with such characteristics contact between gas and particles is generally achieved in spouted bed instead of fluidized bed (Geldart, 1973; Kunii and Levenspiel, 1991). Fluidized Bed technology has long been recognized as an efficient technique to realize reaction between gas and particles and it has been employed in a wide range of industrial applications. Coupled with Chemical Vapour Deposition (CVD), Fluidized Bed technology has a great potential to modify the surface properties of particles or to create new materials (Caussat and Vahlas, 2007).

The present work deals with the hydrodynamic study of a tungsten powder in fluidized bed and its subsequent alumina coating by Fluidized Bed CVD. First, the fluidization of tungsten powder at room temperature and at 400 °C is discussed. Then, first results concerning the alumina coating of tungsten powder by Fluidized Bed CVD are described.

2. Experimental

The fluidization tests of the tungsten powder at room temperature were carried out in a cylindrical column made of glass with an internal diameter of 0.05 m and a height of 1 m. An Inconel™ porous plate was used for the gas distribution. Nitrogen carrier gas was supplied to the bottom of the bed through a mass flow controller. A differential fast response pressure sensor was used to measure the total pressure drop across the bed. A DasyLab® system enabled the on-line acquisition of the differential pressure.

The Fluidized Bed Chemical Vapour Deposition (FBCVD) reactor was made of a vertical cylindrical column of stainless steel and had the same dimensions as the glass column used for fluidization tests. The reactor was externally heated by a two-zone electrical furnace and the wall temperatures were monitored using two thermocouples. Several thermocouples were also bundled into a 6 mm diameter stainless steel tube and placed inside the reactor in order to monitor the bed temperature at various heights. An Inconel™ porous plate was used for the gas distribution and argon was used as carrier gas. During CVD experiments, the precursor was evaporated from a stainless steel vaporizer placed in a thermostated bath and was fed into the reactor through heated lines to prevent condensation. The argon flow rates supplied directly to the bottom of the reactor and through the vaporizer were controlled by mass flow controllers. Coating tests were carried out at atmospheric pressure. A differential fast response pressure sensor with taps under the distributor and top of the column was used to measure the total pressure drop across the bed. Moreover, an absolute pressure sensor allowed monitoring the total pressure above the distributor. A DasyLab® system enabled the on-line acquisition of the differential pressure, the total pressure and the axial profile of bed temperature. The FBCVD reactor was also used to perform tungsten powder fluidization tests at room temperature and at 400 °C using argon as carrier gas.

In this study, tungsten powder (T-1220) produced by CERAC, Inc. and supplied by NEYCO was used. According to the characteristics provided by the producer, the grain density is 19,300 kg/m³. The particle size distribution (PSD) values measured by laser scattering (performed with a Beckman Coulter LS™ 13 320 particle size analyser) indicated that the distribution of the particle diameters D_{10}/D_{90} is 50 $\mu\text{m}/105 \mu\text{m}$ with a mean diameter of the particles (D_{50}) of about 75 μm ; the corresponding results are shown on Figure 1b. Scanning Electron Microscopy (SEM) observations highlighted that particles are non spherical and faceted as shown by Figure 1a.

The alumina coatings were performed using aluminium acetylacetonate $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ (99%) as a single-source MetalOrganic (MO) precursor. The precursor was purchased from Strem Chemicals, Inc. The fluidization hydrodynamics were studied by plotting the bed pressure drop and expansion versus increasing and decreasing gas superficial velocity. A normalized bed pressure drop ΔP^* was calculated by dividing the bed pressure drop measured experimentally by the theoretical bed pressure drop (equal to the

bed weight per column surface area). A normalized bed expansion H^* was also measured as the ratio between the expanded bed height and the fixed bed height.

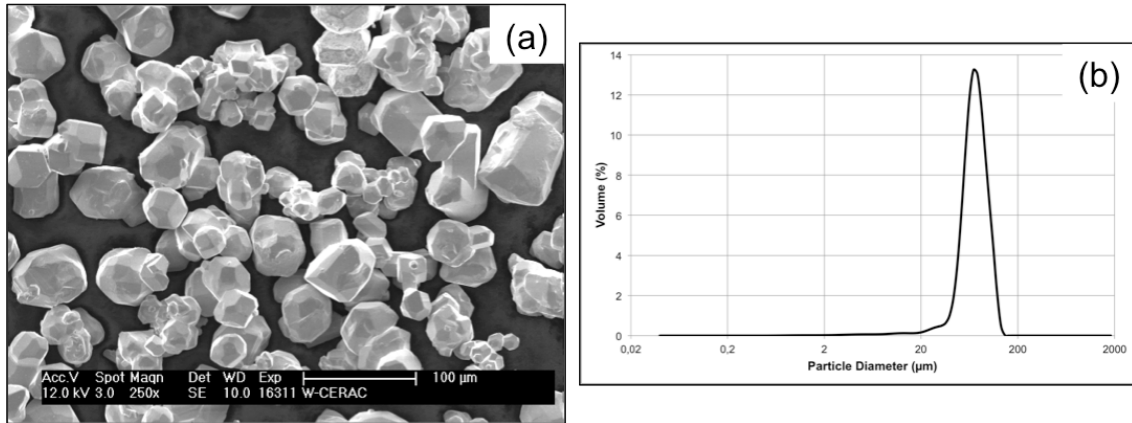


Figure 1. Characterization of the tungsten powder used in this study: (a) SEM micrograph and (b) PSD.

The morphology and the composition of the initial powder and the coated particles were observed by Scanning Electron Microscopy coupled with EDS analyses (Philips XL 30 FEG and LEO 435 VP).

3. Fluidization study of tungsten powder

The hydrodynamic study of the tungsten powder had two main objectives. First, we had to answer the following question: “Is it possible to fluidize a powder with such characteristics?” Indeed, due to its very high density, this powder can be classified into Geldart’s Group D (Geldart, 1973) and it is well known that contact between gas and such particles is generally achieved in spouted bed instead of fluidized bed (Kunii and Levenspiel, 1991). Second, and after validation of the first point, we had to determine the necessary experimental conditions to obtain a fluidized bed with a temperature stabilized at least at 400 °C which was the lower temperature limit to obtain an efficient decomposition of our single-source precursor. For this point, we carefully studied the influence of the H_0/D ratio (initial fixed bed height to reactor diameter) on the bed thermal behaviour. Our aim was to obtain bed temperatures as isothermal as possible since temperature is a key parameter to obtain uniform coatings by CVD.

An example of the fluidization results obtained at room temperature is illustrated by Figure 2.

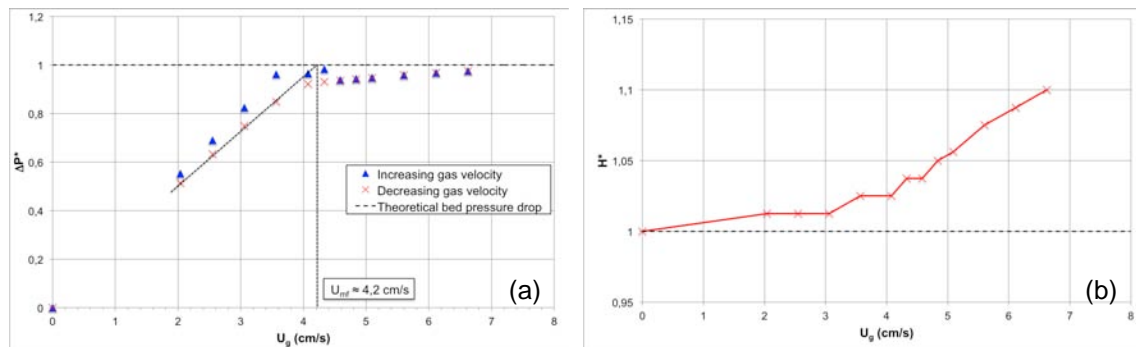


Figure 2. Tungsten powder bed (a) normalized pressure drop and (b) expansion versus gas velocities.

These results, coupled with observations of the hydrodynamics of the bed through the glass column, highlighted that the fluidization of our tungsten powder was achieved. The experimental plots obtained for normalized bed pressure drop versus decreasing gas velocity (Figure 2a) prove that fluidization was achieved (Kunii and Levenspiel, 1991). Using nitrogen as carrier gas, the measured minimum fluidization velocity (U_{mf}) is close to 4.2 cm/s. Even if fluidization was reached, this latter remained difficult as highlighted by the hysteresis observed between experimental plots obtained for normalized bed pressure drop versus increasing gas velocity and versus decreasing gas velocity. The fact that fluidization is not easy was confirmed by the very low bed expansion observed and illustrated by Figure 2b: only 10% for a

fully fluidized bed. As shown on Figure 2a, for the tests realized in glass column with nitrogen as carrier gas, ΔP^* has never reached the theoretical bed pressure drop plateau. This phenomenon could be explained by the fact that a low percentage of tungsten particles were deposited onto the glass column walls and, due to the very high density of tungsten particles, this might have significantly changed the bed weight and the corresponding theoretical bed pressure drop. Moreover, in order to obtain a representative H_0/D ratio, experiments were carried out with more than 1.3 kg of tungsten powder thus leading to a theoretical bed pressure drop closed to the differential fast response pressure sensor upper limit. This technological limitation might have increased the experimental measure errors for the highest gas velocities. Nevertheless, for all the experiments carried out in the stainless steel reactor with argon as carrier gas and without experimental limitation concerning the differential pressure sensor, a fluidization plateau, close to the theoretical value, was observed. Using argon as carrier gas, the average measured minimum fluidization velocity (U_{mf}) is close to 2.5 cm/s. This value is lower than the one obtained with nitrogen gas, which can be explained by the difference between gas densities and viscosities.

Once we have demonstrated that it was possible to fluidize this tungsten powder, the second step of the hydrodynamic study was to determine the optimal experimental conditions to obtain a fluidized bed with a temperature stabilized at least at 400 °C. For our application, low bed weights are required. Then, the aim of this experimental part was to obtain an isothermal and fully fluidized bed of particles with the lowest possible bed weight. Thermal profiles were recorded for various bed weights as detailed in Table 1. Experiments were carried out in the FBCVD reactor using preheated argon at 120 °C as carrier gas.

Table 1. Correspondence between bed weight, bed height and H_0/D ratio.

Bed weight (g)	Bed height (cm)	H_0/D ratio
400	2.4	0.48
600	3.6	0.72
850	5.1	1.01
1,000	5.9	1.19
1,500	8.9	1.78
1,700	10.1	2.02

Analyses of thermal profiles showed that for the lowest bed heights, i.e. H_0/D low ratios, the target bed temperature (400 °C) could not be reached. Even after 2 h 30 of heating process and furnace set point fixed at 800 °C, the bed temperature stagnated at about 330 °C. Only H_0/D ratios higher than or equal to 1 allowed reaching a bed temperature around 400 °C. Nevertheless, for H_0/D ratios of 1, the furnace set point had to be fixed at 850 °C and the particle bed was not isothermal. Indeed, thermal gradients ΔT between the bottom and the top of the bed reached 50 °C which is unacceptable for subsequent CVD coating. It is well known that higher the H_0/D ratio is, better the thermal and mass transfers are and that H_0/D ratios up to 4-5 are generally used for FBCVD coatings. Such values were obviously impossible to carry out because a H_0/D ratio of 4 corresponds to a bed weight as high as 3.4 kg, which was not conceivable for preliminary tests and our further application. Nevertheless, a compromise had been found between an acceptable thermal behaviour and a reasonable bed weight. For bed weights of 1,500 g corresponding to H_0/D ratios of 1.8, a satisfactory thermal profile was obtained with a bed temperature stabilized around 400 °C after 2 h of heating process and furnace set point fixed at 750 °C. The ratio between the gas velocity at 400 °C and the minimum fluidization velocity (U_g/U_{mf}) was fixed at approximately 3.5. For such experimental parameters, the bed was isothermal: ΔT between the bottom of the bed and the top of the bed was less than 2 °C. The important gap between the furnace temperature and the bed one might be explained by the very low bed expansion measured: only 10% of expansion for a fully fluidized bed of tungsten particles whereas standard values obtained for more conventional powders generally range between 30 and 40%. This very low bed expansion implies low thermal transfers between particles and reactor walls.

4. FBCVD of alumina on tungsten powder

Using the experimental parameters described in the previous section, we successfully performed the FBCVD of alumina coating on several sets of tungsten powder by varying bed temperature, carrier gas flow rate sent through vaporizer line and coating duration. All the results detailed below are representative of the whole results obtained.

Figure 3 shows a typical thermal profile obtained during coating tests. Heating process was realized respecting two steps of 1 h in order to progressively increase the powder temperature and obtain an isothermal particle bed. This latter factor is highlighted by the fact that the four thermocouples, placed inside the particle bed at different heights and denoted TC_x on Figure 3, indicated the same temperature values. Indeed, on all the thermal profiles, the corresponding data were mingled. Once the desired coating temperature was reached, the coating procedure began. We noticed a slight decrease of the bed temperature during the first minutes of the coating. This latter may be related to the precursor decomposition that requires energy supply. At the beginning of the coating, the necessary energy is provided by particle bed, leading to a slight decrease of its temperature. Then, after a few minutes of heating regulation, the particle bed temperature is stabilized.

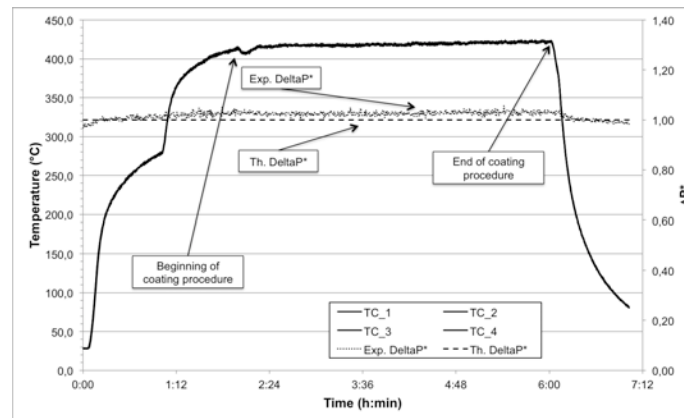


Figure 3. Typical thermal profile obtained for FBCVD of alumina coating on tungsten powder.

The experimental normalized bed pressure drop (denoted *Exp. DeltaP** on Figure 3) was calculated and compared with the theoretical normalized bed pressure drop (denoted *Th. DeltaP**) during all test duration. The obtained results clearly indicate that the tungsten particle bed is fully fluidized during all the experiment duration.

At macroscopic scale, the difference between coated and uncoated particles is obvious. Whereas uncoated particles are metallic grey, the coated particles exhibited a brown tint. This latter could be surprising for alumina coatings. Nevertheless, several works, in which alumina coatings were obtained from aluminium acetylacetonate precursor in our range of temperature, i.e. 390-450 °C, have reported that obtained films exhibited orange-claret (Minkina, 1993), golden brown (Nable et al., 2003) or tan and dark tan (Nguyen et al., 2002) tints. These colours might be explained by an alumina film contamination due to carbon and pyrolysis by-products incorporation. This contamination probably corresponds to (i) the condensation and adsorption of carbonaceous species resulting from incomplete decomposition of the precursor, (ii) from the formation and deposition of species from secondary reactions during the chemical reactions, or (iii) from a combination of these processes (Minkina, 1993; Nguyen et al., 2002). Moreover, at these relative low temperatures, aluminium oxide films obtained by MOCVD are mainly amorphous (Nable et al., 2003a). The uniform tint of particles after deposition indicates that all particles were uniformly treated. This has been confirmed by the numerous SEM-EDS analyses performed.

In order to study the difference between coated and uncoated particles at microscopic scale, all the samples have been observed by SEM coupled with EDS analyses. The surface morphology of uncoated tungsten particles is relatively smooth as shown on Figure 4a. Moreover, EDS analyses performed on uncoated samples showed the different characteristic peaks of tungsten and, for some particles, the peak of oxygen. This latter is probably due to a partial oxidation of tungsten powder during handling under air.

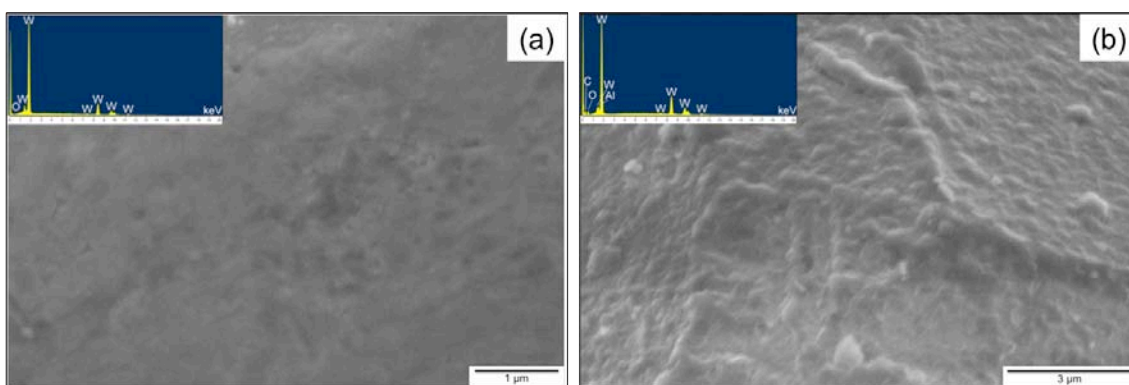


Figure 4. SEM micrographs and corresponding EDS analyses of (a) uncoated and (b) alumina coated tungsten powder.

The SEM analyses of coated particles (Figure 4b) exhibited pronounced morphologic differences: the surface roughness had clearly increased and the presence of a coating film was obvious. Even if Al K_{α} peak is partially overlapped by W M_{α} peak and that alumina films are very thin (probably less than 100 nm according to calculated film thicknesses from mass balances and to first characterizations), EDS analyses on coated samples showed oxygen, carbon and aluminium peaks. Tungsten was also detected because EDS analyses concern thicknesses higher than those of alumina deposits. The relative comparison of the EDS spectra of uncoated and coated particles indicated that, on these latter, an alumina film with carbon impurities was obtained. This result is in good accordance with previous works reported in literature and already cited. In order to confirm these first results, further characterizations are currently in progress.

5. Conclusion

The fluidization of very dense powder, using tungsten particles (75 μm in mean diameter and 19,300 kg/m^3 in grain density), was successfully demonstrated. The obtained results showed that, even if the powder is fully fluidized, the bed expansion is very low, involving low thermal transfers between powder and reactor walls. The analysis of axial thermal profiles for different bed weights allowed finding experimental parameters compatible with Fluidized Bed Chemical Vapour Deposition of alumina at 400 °C. First characterizations of samples after CVD suggest that alumina films formed from aluminium acetylacetonate $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ as single source precursor are probably amorphous and carbon contaminated. Results obtained in this study suggest that FBCVD is a suitable process for coating very dense particles with uniform deposits. Additional experiments are planned to test higher deposition temperatures in order to limit carbon contamination.

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