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Alumina Coating on Dense Tungsten Powder by Fluidized Bed Metal Organic Chemical Vapour Deposition

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In order to study the feasibility of coating very dense powders by alumina using Fluidized Bed Metal Organic Chemical Vapour Deposition (FB-MOCVD), experiments were performed on a commercial tungsten powder, 75 μm in median volume diameter and 19,300 kg/m^3 in grain density. The first part of the work was dedicated to the experimental study of the tungsten powder fluidization using argon as carrier gas at room temperature and at 400 °C. Due to the very high density of the tungsten powder, leading to low initial fixed bed heights and low bed expansions, different weights of powder were tested in order to reach satisfactory temperature profiles along the fluidized bed. Then, using argon as a fluidized bed former and aluminium acetylacetonate $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ as a single source precursor, alumina thin films were deposited on tungsten particles at a low temperature range (e.g., 370–420 °C) by FB-MOCVD. The influence of the weight of powder, bed temperature and run duration was studied. Characterizations of the obtained samples were performed by various techniques including scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) analyses, Field Emission Gun SEM (FEG-SEM) and Fourier Transform InfraRed (FT-IR) spectroscopy. The different analyses indicated that tungsten particles were uniformly coated by a continuous alumina thin film. The thickness of the film ranged between 25 and 80 nm, depending on the coating conditions. The alumina thin films were amorphous and contained carbon contamination. This latter may correspond to the adsorption of species resulting from incomplete decomposition of the precursor at so low deposition temperature.

Keywords: MOCVD, Fluidized Bed, Alumina, Tungsten Powder, Aluminium Acetylacetonate.

1. INTRODUCTION

The Fluidized Bed Chemical Vapour Deposition (FB-CVD) process presents great potential for the formation of improved coatings on powder materials¹ and also for producing new materials.² For example, FB-CVD has been used to prepare supported catalyst, to improve surface properties of powders towards wear, oxidation and temperature resistance, to generate microelectronic and photovoltaic materials, to coat nuclear fuel particles and to produce multi- or single-walled carbon nanotubes.^{3,4} On the other hand, the FB-CVD process is generally limited to a narrow range of powders, approximately those with mean diameter between 50 and 800 μm and with grain density ranging between 1,500 and 4,000 kg/m^3 .^{5,6} For large and/or very dense particles, a derived technology, called spouted bed is used. Originally, this technique has been developed for wheat drying⁷ and, since, has been widely, but not

exclusively, used for nuclear fuel coating.^{8,9} The fact that fluidized bed processes are limited to a narrow range of powders explains why the literature concerning the fluidization of very dense powders is scarce.

In this work, we studied the fluidization of a tungsten powder and its alumina coating by Fluidized Bed Metal Organic Chemical Vapour Deposition (FB-MOCVD). First, the fluidization of tungsten powder at room temperature and at 400 °C using argon as carrier gas is described. Then, using aluminium acetylacetonate $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ as a single source metalorganic precursor, alumina thin films were coated on tungsten particles at a low temperature range (e.g., 370–420 °C) by FB-MOCVD. Characteristics of the deposits are discussed.

2. EXPERIMENTAL DETAILS

The Fluidized Bed Chemical Vapour Deposition reactor was made of a vertical cylindrical column of stainless

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steel with an internal diameter of 0.05 m and a height of about 1 m. The reactor was externally heated by a two-zone electrical furnace and the wall temperatures were controlled using two thermocouples. The bed temperatures were monitored at various heights using several thermocouples to measure the axial profile of temperatures in the bed. An Inconel™ porous plate was used for the gas distribution and argon was used as carrier gas. A differential pressure sensor measured the pressure drop existing between the bottom part of the reactor (under the distributor) and its top part. 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 temperatures. During MOCVD experiments, the precursor was evaporated from a stainless steel sublimator placed in a thermostated oil bath and was fed into the reactor through heated lines to prevent condensation. Argon flow rates, supplied directly to the bottom of the reactor or through the sublimator, were controlled by mass flow controllers. FB-MOCVD experiments were carried out at atmospheric pressure.

In this study, tungsten powder (T-1220) produced by CERAC, Inc. and supplied by NEYCO was used as a model powder. According to the characteristics provided by the producer, the grain density is 19,300 kg/m³. The particle size distribution 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 μm/105 μm with a median diameter of the particles (D_{50}) of about 75 μm. Scanning Electron Microscopy (SEM) observations highlighted that particles are non spherical and faceted, as shown by Figure 1.

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 purchased from Strem Chemicals, Inc.

The morphology and the composition of the tungsten powder and the coated particles were studied by Field Emission Gun Scanning Electron Microscopy (FEG-SEM)

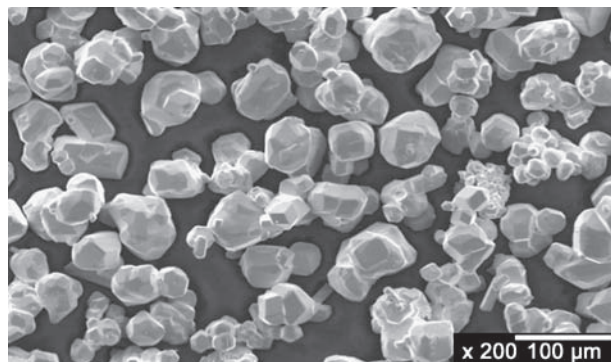


Fig. 1. FEG-SEM micrograph of the tungsten powder.

coupled with Energy Dispersive X-ray Spectroscopy (EDS) analyses (Philips XL 30 FEG) and by FEG-SEM (JEOL JSM 6700F). Moreover, the chemical composition of the films were analysed by Fourier Transform InfraRed (FT-IR) spectroscopy using a Thermo Nicolet Nexus 470 FT-IR spectrometer. The IR spectra were recorded under diffuse reflection conditions in the 4,000–400 cm⁻¹ region. For each spectrum, the number of scans was 100 and the resolution was 4 cm⁻¹. Film spectra were obtained by subtracting the spectrum obtained for uncoated powder (reference) to spectra obtained for coated powders. Thus, obtained spectra only correspond to the deposit and not to a combination of the deposit and the substrate.

The fluidization hydrodynamics was studied by plotting the bed pressure drop 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). In addition to this study performed in the FB-MOCVD reactor, observations of the hydrodynamics of the bed were made in a transparent glass column having the same dimensions.

3. RESULTS AND DISCUSSION

3.1. Fluidization Study of Tungsten Powder

Before performing the MOCVD experiments, a hydrodynamic study was performed at room temperature and at 400 °C in order to (i) demonstrate the ability to fluidize of the tungsten powder and to (ii) identify optimal experimental conditions to obtain uniform alumina coating by MOCVD.

Figure 2 details the fluidization results obtained at room temperature.

These results, coupled with observations of the hydrodynamics of the bed through the glass column, highlighted that the fluidization of the tungsten powder was achieved. Using argon as carrier gas, the measured minimum fluidization velocity (U_{mf}) is close to 2.6 cm/s. Even if fluidization was reached, this latter remained difficult as shown by the hysteresis observed for normalized bed pressure drops between increasing and decreasing gas velocities. The fact that fluidization was not easy was confirmed by the very low bed expansion measured thanks to the observations through the glass column: only about 10% for a fully fluidized bed of tungsten particles whereas standard values obtained for more conventional powders generally range between 30 and 40%.⁶

In a second step, optimal experimental conditions were found to obtain: (i) a fluidized bed with a temperature stabilized at least at 400 °C, which is the lowest temperature limit to obtain a significant decomposition of the single-source MO precursor and (ii) an isothermal bed of tungsten particles. This second point is a key parameter to obtain

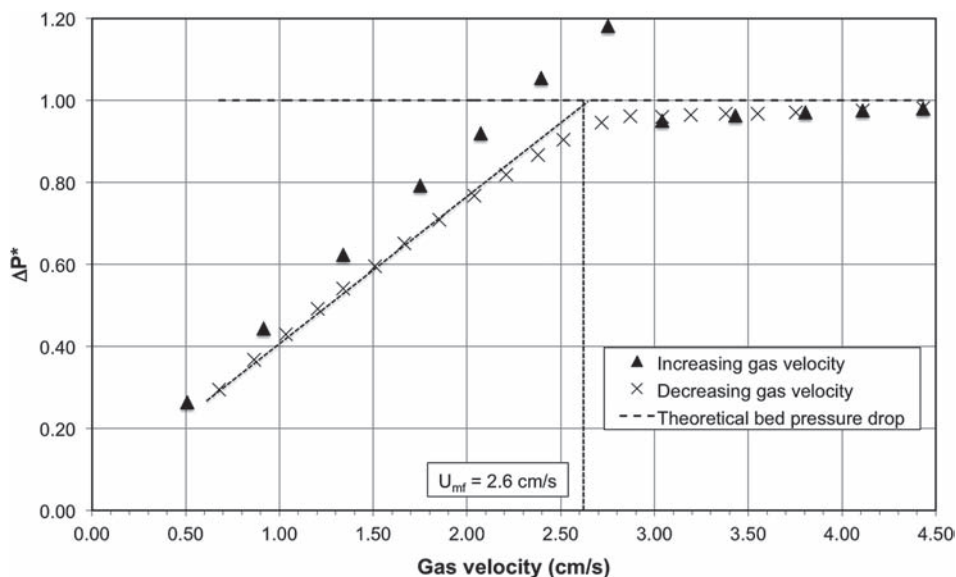


Fig. 2. Tungsten powder bed normalized pressure drop versus superficial gas velocity at room temperature.

uniform coatings by MOCVD. Moreover, for our application, low bed weights are required. Then, the aim of this experimental part was not only to obtain an isothermal and fully fluidized bed of particles but with the lowest possible bed weight as well. 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. It is well known that the higher the H_0/D ratio is, the better the thermal and mass transfers are and that H_0/D ratios up to 4–5 are generally used for FB-CVD coatings.³ In our case, such values correspond to bed weights ranging between 3.4 and 4.2 kg, which are not conceivable for our further application. Then, experiments were carried out using ratios between the gas velocity and the minimum fluidization velocity (U_g/U_{mf}) close to 3.5 and thermal profiles were recorded for H_0/D ratios ranging between 0.5 and 2. The analyses of bed thermal profiles showed that for the lowest H_0/D ratios, the target bed temperature (400 °C) could not be reached even with an important overheating of the reactor walls. Only H_0/D ratios higher than or equal to 1 allowed to reach a bed temperature around 400 °C and only H_0/D ratios higher than or equal to 1.2 allowed to obtain very low thermal gradients (ΔT) between the bottom and the top of the bed (i.e., isothermal beds). These experiments allowed to find a compromise 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, satisfactory thermal profiles were obtained with bed temperatures stabilized around 400 °C after 2 h of heating process. However, the furnace set point had to be fixed at 750 °C. The important gap between the furnace and the bed temperatures might be explained by the very low bed expansion described in the previous paragraph, which leads to low thermal transfers between particles and reactor walls. For these experimental conditions, the particle

bed was fully fluidized and isothermal: ΔT between the bottom and the top of the bed was less than 2 °C. These optimal experimental conditions were used for performing FB-MOCVD experiments.

3.2. FB-MOCVD of Alumina on Tungsten Powder

FB-MOCVD of alumina was studied by varying different experimental parameters such as bed temperature, carrier gas flow rate sent through the sublimator line and coating duration. The results obtained are discussed below.

Different thermocouples, placed inside the particle bed at different heights, indicated identical values during all the MOCVD process, which confirmed that the bed was fluidized and isothermal. During the first minutes of the coating procedure, we noticed a slight decrease of the bed temperature. This latter may be related to the introduction of the precursor into the reactor and its further decomposition that requires energy supply. At the beginning of the coating, the necessary energy is provided by the bed, leading to a slight decrease of its temperature (e.g., 5–6 °C). Then, after a few minutes of heating regulation, the particle bed is stabilized. The comparison of the experimental normalized bed pressure drop with the theoretical one confirmed that the tungsten particle bed was fully fluidized during all the experiments.

At the macroscopic scale, the difference between coated and uncoated particles is obvious. Whereas uncoated particles are metallic grey, the coated particles exhibit a brown tint. This latter could be surprising for alumina coatings. However, several works, in which alumina coatings were obtained from aluminium acetylacetonate precursor in our range of temperature, i.e., 390–450 °C, reported that the obtained films exhibited orange-claret,¹⁰ golden brown¹¹ or tan and dark tan¹² tints. These colours could be explained

by an alumina film contamination due to carbon and pyrolysis by-products incorporation.^{10,12} The uniform tint of particles after MOCVD tends to indicate that all particles were uniformly treated. This has been confirmed by the SEM-EDS and FEG-SEM analyses performed and discussed below.

The difference between coated and uncoated tungsten particles has been studied at microscopic scale by SEM-EDS analyses and FEG-SEM observations. The surface morphology of uncoated particles is relatively smooth as shown by Figure 3(a). Moreover, EDS analyses (not shown

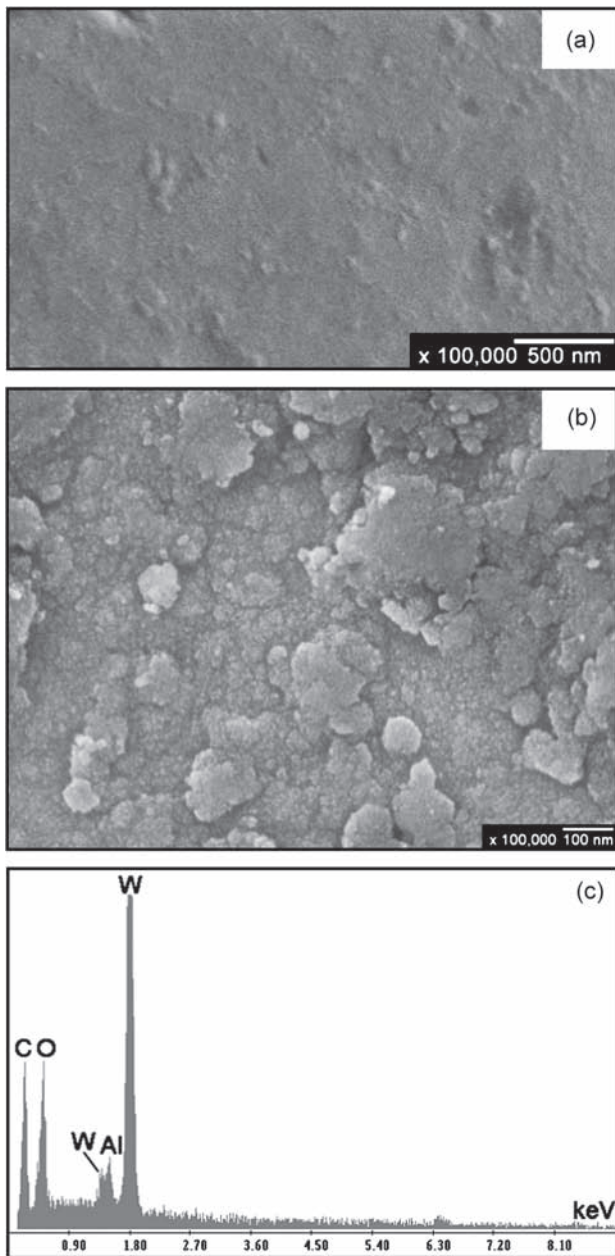


Fig. 3. FEG-SEM micrographs of (a) an uncoated tungsten particle and (b) tungsten particle coated by alumina; (c) EDS analysis of tungsten particle coated by alumina.

here) 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. For all experiments, the examination of coated particles exhibited pronounced morphologic differences. SEM and FEG-SEM observations, at relatively low magnification, show that all particles were uniformly covered by a continuous film. At higher magnification, the presence of a coating film is obvious (Fig. 3(b)). The coating increases the surface roughness and its morphology appears tortuous with hollows and bumps. Moreover, the film surface seems to be composed of a multitude of nodules as illustrated by Figure 3(b). EDS analyses on coated samples (Fig. 3(c)) exhibit oxygen, carbon and aluminium peaks. Tungsten is also detected because EDS analyses concern thicknesses higher than those of alumina deposits. The comparison of the EDS spectra of coated and uncoated particles suggest that an alumina film with carbon impurities was obtained for all experiments.

Several attempts to estimate the coating thickness have been realized. According to approximate calculations based on precursor consumption, the film thickness is probably lower than 100 nm. Experimental evidences have been obtained by SEM observations of crushed coated particles using backscattered electron (BSE) detector to highlight the contrast between areas with different elemental

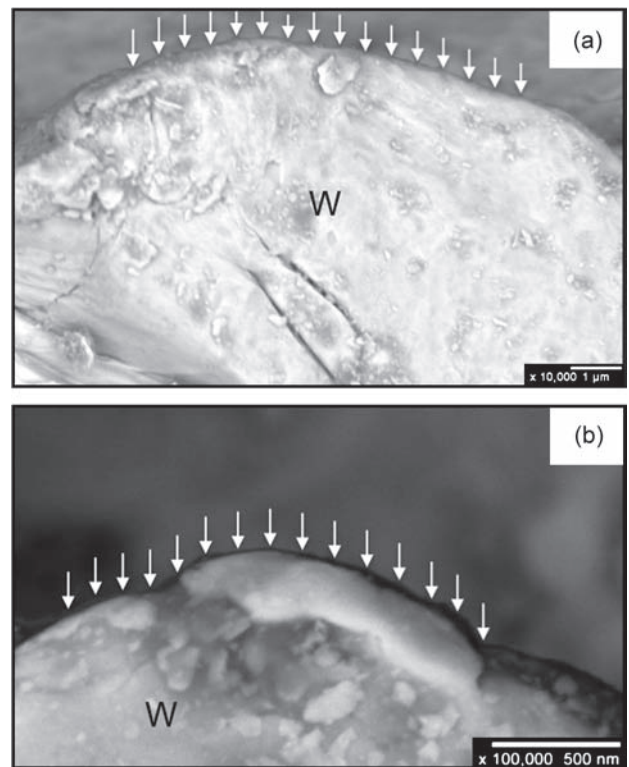


Fig. 4. FEG-SEM micrographs of crushed tungsten particles coated by alumina (BSE mode).

compositions. Preliminary results showed that film thickness is ranging between 25 and 80 nm depending on the coating conditions. An example of film thickness observation is shown on Figure 4.

The Figure 4(a) allows showing the uniformity of the deposit all around the tungsten particles. Because heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), tungsten particles appeared brighter than alumina films. To facilitate the micrograph interpretation, white arrows highlight the alumina film. The FEG-SEM micrograph exhibited on Figure 4(b) was taken on another particle and at higher magnification than the one shown on Figure 4(a). This kind of micrograph allows measuring the coating thickness. On this sample, the estimated average thickness was close to 40 nm. The coating thickness appeared to be regular from one particle to another.

The chemical composition of the coatings has been determined by FT-IR analyses; a representative spectrum is shown in Figure 5. FT-IR spectra exhibit several bands corresponding to different vibrational transitions; certain ones are relatively easy to identify, whereas others could have different origins.

The broad band observed in the 520–960 cm^{-1} region could be due to the presence of aluminium oxide in an amorphous state.¹³ This fact is not surprising because at these relative low processing temperatures (370–420 °C), aluminium oxide films obtained by MOCVD are mainly amorphous.¹⁴ This band is composed of the contribution of the bending vibration mode of the O–Al–O bond that is located at 650–700 cm^{-1} and the stretching vibration mode of the Al–O bond located at 750–850 cm^{-1} .¹⁵ The different bands observed in the 1350–1650 cm^{-1} region could be representative of carbon impurities in the samples; these bands are characteristic of C=C and

C–O vibrations.¹² These bands could also be attributed to non-decomposed aluminium acetylacetonate molecules. Indeed, the literature data for $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ indicate matching peaks in this region.¹² The peaks located at 1010 cm^{-1} and 1160 cm^{-1} could also be attributed to the incomplete decomposition of the MO precursor and related to the $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ molecule vibrations.¹² Moreover, the peak located at 1590 cm^{-1} could be related to the acetylacetonate ligand vibrations.¹⁶ Finally, the broad band in the 3200–3700 cm^{-1} range corresponds to O–H bond vibrations. This latter is characteristic of adsorbed water molecules on the film surface.

FT-IR analyses tend to confirm that obtained coatings are alumina films with carbon impurities as indicated by EDS analyses; they also suggest that alumina films are amorphous as previously reported in literature for this low temperature of deposition.¹⁴ Moreover, these analyses highlight that aluminium acetylacetonate molecules and acetylacetonate ligands are probably adsorbed on or incorporated in the alumina film during the coating process. This suggests that the deposition temperature is undoubtedly too low to allow the complete decomposition of the MO single-source precursor.

Concerning the influence of the experimental conditions on the film characteristics, first trends can be drawn from experimental observations. The particle bed temperature has been varied in a very low range; so, first results about film thickness variations observed from one experiment to another might not be assigned to temperature influence. We believe that the film thickness is rather governed by the carrier gas flow rate sent through the sublimator line. Indeed, significant variations of the precursor consumption have been noticed when increasing this flow rate. This result has to be confirmed by a systematic observation of corresponding film thicknesses (work currently in

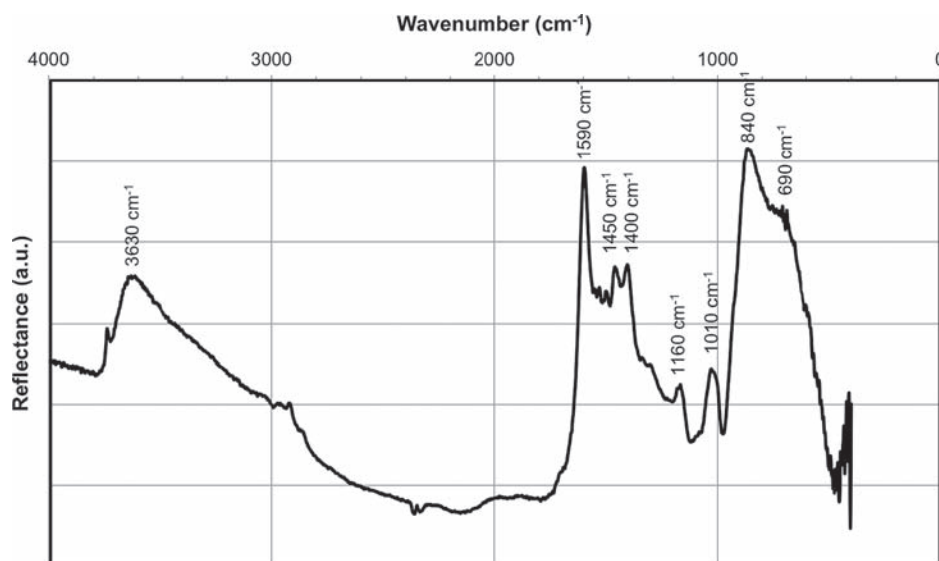


Fig. 5. FT-IR spectrum of alumina film coated on tungsten particles.

progress). Surprisingly, the increase of coating duration did not lead to a significant increase of precursor consumption. We believe that aluminium acetylacetonate state is damaged after a few hours of heating and that the gaseous concentration of sublimated precursor decrease with run duration. This assertion is supported by the fact that the precursor physical state changes during the MOCVD process. Whereas the initial powder is white and relatively fluid, the powder recovered after deposition exhibits a yellowish tint and forms compact aggregates. This physical change probably lowers the precursor sublimation efficiency. So an increase of run duration is not a solution to increase deposit thickness. Finally, additional experiments are planned to test higher deposition temperatures in order to limit carbon contamination of alumina films. Indeed, increasing coating temperatures should favour MO precursor decomposition into the bed and decrease the adsorption of carbonaceous species in alumina film. Moreover, after coating process, we noted that cold parts located near the exit of the reactor were covered with yellowish deposit. This is probably due to the part of non-decomposed precursor that condenses on cold zones. This phenomenon could be limited by increasing bed temperature thus leading to an increase of precursor decomposition yield on the tungsten powder.

4. CONCLUSION

After having demonstrated the ability to fluidize very dense tungsten particles with a median volume diameter of 75 μm and a grain density of 19,300 kg/m^3 , we have successfully achieved the Fluidized Bed MetalOrganic Chemical Vapour Deposition (FB-MOCVD) of alumina on this powder. Aluminium acetylacetonate $\text{Al}(\text{C}_5\text{O}_2\text{H}_7)_3$ was used as single-source precursor.

Microscopic characterizations after experiments indicate that all the particles were uniformly treated. The alumina coatings have thicknesses ranging between 25 and 80 nm depending on the samples. Their chemical composition of the film has been studied using FT-IR spectroscopy.

Aluminium oxide films are amorphous and contain carbon impurities. We have found evidences that the processing temperature is probably too low for obtaining the total decomposition of the precursor. Additional experiments are in progress in order to perform the coatings at higher temperature. Finally, the results obtained in this study suggest that FB-MOCVD is a suitable process for coating very dense particles with uniform deposits.

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References and Notes

1. S. Kinkel, G. N. Angelopoulos, D. C. Papamantellos, and Winfried Dahl, *Steel Res.* 66, 318 (1995).
2. B. Caussat and C. Vahlas, *Chem. Vap. Deposition* 13, 443 (2007).
3. C. Vahlas, B. Caussat, Ph. Serp, and G. N. Angelopoulos, *Mater. Sci. Eng. R* 53, 1 (2006).
4. R. Philippe, A. Morancais, M. Corrias, B. Caussat, Y. Kihn, Ph. Kalck, D. Plee, P. Gaillard, D. Bernard, and Ph. Serp, *Chem. Vap. Deposition* 13, 447 (2007).
5. D. Geldart, *Powder Technol.* 7, 285 (1973).
6. D. Kunii and O. Levenspiel, *Fluidization Engineering*, 2nd edn., Butterworth-Heinemann Ltd, Newton, MA, USA (1991).
7. K. B. Mathur and P. E. Gishler, *AIChE J.* 1, 157 (1955).
8. J. M. Blocher, US Patent 3,249,509 (1966).
9. F. Charollais, C. Perrais, D. Moulinier, M. Perez, and M.-P. Vitali, *Nucl. Eng. Des.* 238, 2854 (2008).
10. V. G. Minkina, *Inorg. Mater.* 29, 1400 (1993).
11. J. C. Nable, M. K. Gulbinska, M. A. Kmetz, S. L. Suib, and F. S. Galasso, *Chem. Mater.* 15, 4823 (2003).
12. Q. T. Nguyen, J. N. Kidder, Jr, and S. H. Ehrman, *Thin Solid Films* 410, 42 (2002).
13. M. Aguilar-Frutis, M. Garcia, C. Falcony, G. Plesch, and S. Jimenez-Sandoval, *Thin Solid Films* 389, 200 (2001).
14. J. Nable, M. Gulbinska, S. L. Suib, and F. Galasso, *Surf. Coat. Technol.* 173, 74 (2003).
15. A. Ortiz and J. C. Alonso *J. Mater. Sci.: Mater. Electron.* 13, 7 (2002).
16. J. Ahenach, P. Cool, and E. F. Vansant, *Phys. Chem. Chem. Phys.* 2, 5750 (2000).

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