

# CVD of Aluminum Compounds on Carbon Materials in Microwave Plasma FBR

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## Abstract

Deposition of coatings of aluminum, aluminum nitride and aluminum carbide on particulate carbon materials by means of an atmospheric pressure microwave plasma fluidized bed process is reported. Two types of short carbon fibers and a monocrystalline diamond powder were used as substrate. As source of aluminum trimethylaluminum was utilized with nitrogen and argon/hydrogen (5 vol% H<sub>2</sub>) serving as fluidizing and carrier gas. Microwaves at 2.45 GHz frequency were used for heating the substrate materials and for establishing a plasma in an in-house built monomode cavity. For deposition of coatings the substrate surface temperature was varied between 600°C and 1100°C. Because of their microwave transparency, diamonds were mixed with fibers and heated indirectly in the bed. Coatings were characterized by means of SEM/FEM, EDX, XRD, TGA and BET surface area. The influence of processing parameters on the decomposition conditions of TMA and on the chemical composition of the composite coatings is discussed.

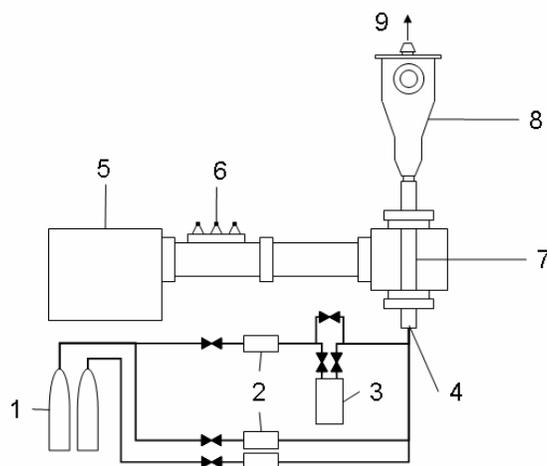
## Introduction

Chemical vapor deposition, CVD, based processes in fluidized bed reactors are known from e.g. synthesis of high purity silicon from silane [1], and CVD of TiO<sub>2</sub> at low pressure [2]. Application of plasma, particularly at atmospheric pressure for deposition of thin coatings on particulate materials is a topic of increasing interest, because of the substantial widening of the processing window in terms of temperature, coating composition, substrate material and deposition rate. Plasma fluidized bed processes are known for CVD of pyrolytic carbon on glass beads at low pressure [3], and for CVD of TiN and TiC on carbon fibers as substrate at atmospheric pressure [4]. Although ceramic coatings can also be deposited by electrophoretic and electrolytic processes [5], these processes are limited to electrically conductive substrates, e.g., carbon fibers, and cannot be applied on electric insulating materials, such as diamond.

In this study an in-house built laboratory scale microwave plasma fluidized bed is used, in detail described elsewhere [4] and shown schematically in Figure 1. One main advantage of microwave heating a fluidized bed is the direct heating of particles if the material is a good microwave absorber. As has been shown in the case of silicon and carbon fibers with chlorinated compounds as source of metal atom, this is the preferred place of precursor decomposition and coating deposition [4, 6]. The application of a metalorganic precursor for coating carbon fibers has been shown in a recent paper [7]. In the study presented here, the influence of plasma deposition conditions and the chemistry of precursor as well as properties of the carbon substrate on coating composition and morphology were investigated more thoroughly, in order to tailor the functional properties of the coating.

Carbon fibers and microdiamonds are promising materials for high performance heat sinks in copper metal matrix composites and thin coatings on carbon filler materials are known to influence contacting behavior towards copper and hence important

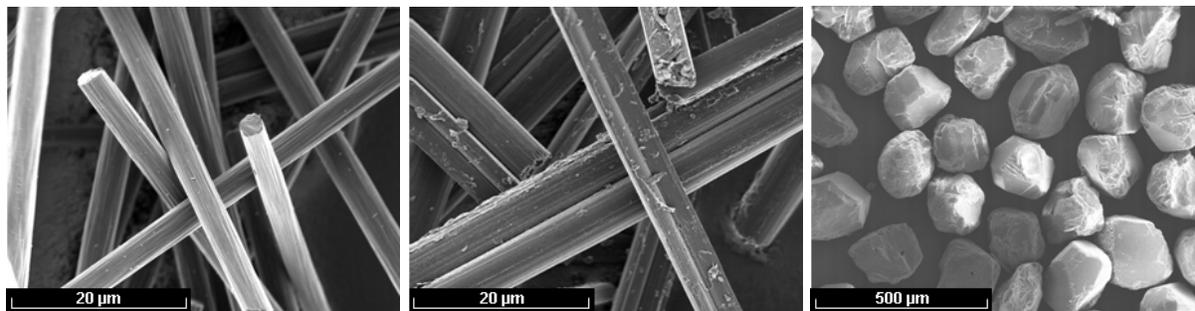
macroscopic properties of the composites such as heat conductivity and thermal expansion [8].



**Figure 1.** Microwave heated fluidized bed experimental setup: 1 – gas supply, 2 – mass flow controllers, 3 – precursor bubbler/evaporator, 4 – gas distributor, 5 – generator, 6 – 3-stub autotuner, 7 – plasma zone, 8 – cyclone, 9 – off gas washing

## Experimental

The microwave fluidized bed is equipped with a resonant monomode microwave cavity that promotes plasma ignition at atmospheric pressure by microwaves of 2.45 GHz frequency. Temperature in the reactor is measured contact-less through a small opening in the cavity by a high temperature pyrometer (Keller PZ20). Additionally the temperature is measured in gas phase a few centimeters above the cavity. A cyclone attached to the riser restrains carryover of particles but nevertheless a fraction of fines manages to escape. Off-gas is treated in gas washing bottles. All experiments were carried out at atmospheric pressure of 1 bar.



**Figure 2.** Substrate materials used, left to right: F1, F2, D1.

As substrates, commercially available carbon materials, namely short carbon fibers F1 (SGL Carbon, Sigrafil C25 M250 UNS, carbon content > 95%, amorphous, density  $\rho = 1790 \text{ kg/m}^3$ , average diameter  $d = 7.5 \text{ }\mu\text{m}$ , average length  $l = 135 \text{ }\mu\text{m}$ ), short carbon fibers F2 (Cytec, ThermalGraph DKD, carbon content > 99%, high degree of graphitization,  $\rho = 2200 \text{ kg/m}^3$ ,  $d = 10 \text{ }\mu\text{m}$ ,  $l = 200 \text{ }\mu\text{m}$ ) and a monocrystalline synthetic diamond powder D1 (AB Industrial Diamond,  $\rho = 3520 \text{ kg/m}^3$ , average particle size  $d_p = 150 \text{ }\mu\text{m}$ ) were used,

as shown in Figure 2. Due to its microwave transparency, diamond powder was mixed and fluidized together with 90 wt% of fibers. After processing the fibers were removed by sieving.

Trimethylaluminum (TMA;  $\text{Al}(\text{CH}_3)_3$ ; CAS 75-24-1; source: ABCR, min. 98% purity) was used as aluminum precursor. Carrier gases were argon-hydrogen (5 vol%  $\text{H}_2$ ) and nitrogen, respectively, while the main fluidizing gas was always nitrogen. TMA is a pyrophoric fluid – at room temperature it is a colorless liquid that reacts readily with oxygen. During the transfer of the chemical and preliminary experiments, it was confirmed that even at very low oxygen partial pressure (in range of  $1\text{-}5 \cdot 10^{-2}$  mbar) a white fume is easily visually observable, and it is known that in air it burns in a violent flame. This enabled an easy detection of TMA residue after it has left the reactor. TMA was evaporated at near-room temperature of  $22\text{-}24^\circ\text{C}$ , which corresponds to a vapor pressure of 13-15 mbar. Higher partial pressures lead to very high deposition rates and agglomeration of the coated substrate particles.

**Table 1.** Common processing parameters for both campaigns

	<b>Campaign 1</b>	<b>Campaign 2</b>
Material	10 g F2	20 g F1 + 2 g D1
Bed diameter	20 mm	41 mm
MW power	1000 W	600 W – 1100 W
Gas velocity	0.31 m/s	0.085 m/s
Pre-heating	8 min	8 min
Processing time (CVD)	20 min	10 min
Post-heating	10 min	10 min

Several preliminary experiments were conducted in order to determine preferable processing parameters. A summary of the common processing parameters is shown in table 1. The main parameter varied in campaign 1, is the TMA concentration. In order to modify it, gas was distributed in different ways between the main fluidizing supply and the precursor carrier gas. In campaign 2, the microwave power was varied, and hence plasma properties and particle temperature were different.

Particle geometry and surface morphology were examined by means of SEM (Jeol) and FEM (Zeiss-LEO). Elemental composition of the coatings was investigated with XRD (Philips X'Pert,  $\text{Cu}_{k\alpha}$ -) and EDX (INKA, Oxford Instruments) measurements. Specific surface area was measured using  $\text{N}_2$ -absorption (BET, Micrometrics, ASAP 2010). Weight fraction of aluminum in coatings was determined by TGA/DSC (Netsch STA449C), up to  $1500^\circ\text{C}$  with 10 K/min heating rate in synthetic air. For validation, a larger quantity (up to 2 g) of coated fibers was oxidized in a conventional furnace at  $800^\circ\text{C}$  with 8 h holding time in ambient air.

## Results

SEM pictures of typical coatings are shown on Figure 3. EDX scans confirmed Al on powder surface. Preliminary experiments showed that initial (pre-CVD) plasma treatment etches the fiber surface, removes small irregularities and hence lowers the BET

surface area, which is in agreement with previous results [9]. The surface area after coating is significantly increased, as already reported in [7].

**Table 2.** Details of presented experiments from both campaigns

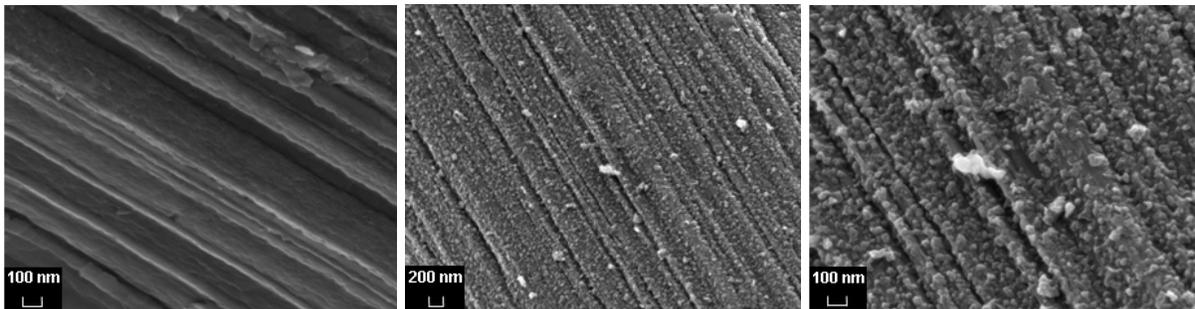
Experiment	C1-1	C1-2	C1-3	C2-1	C2-2	C2-3
$P_{MW}$ [W]	1000	1000	1000	600	850	1100
$T_{pyro}$ [°C]	875	875	875	400	560	600
$T_G$ [°C]	345	335	350	218	237	270
$m_{TMA}$ [mg]	140	300	730	760	950	940
$m_{Al,f}$ [wt%]	0.46	1.28	3.10	0.59	1.05	1.58
$m_{Al,d}$ [wt%]	-	-	-	0.58	0.67	1.02

Three experiments per campaign are presented in detail. Table 2 shows the applied microwave power, average processing temperature reached (pyrometer, plasma zone), average temperature in the gas phase (thermocouple, 10 cm above the plasma zone), quantity of TMA spent, resulting weight content of Al in the coating on fibers and weight content of Al in the coating on diamonds, designated as  $P_{MW}$ ,  $T_G$ ,  $T_{pyro}$ ,  $m_{TMA}$ ,  $m_{Al,f}$  and  $m_{Al,d}$ , in that order.

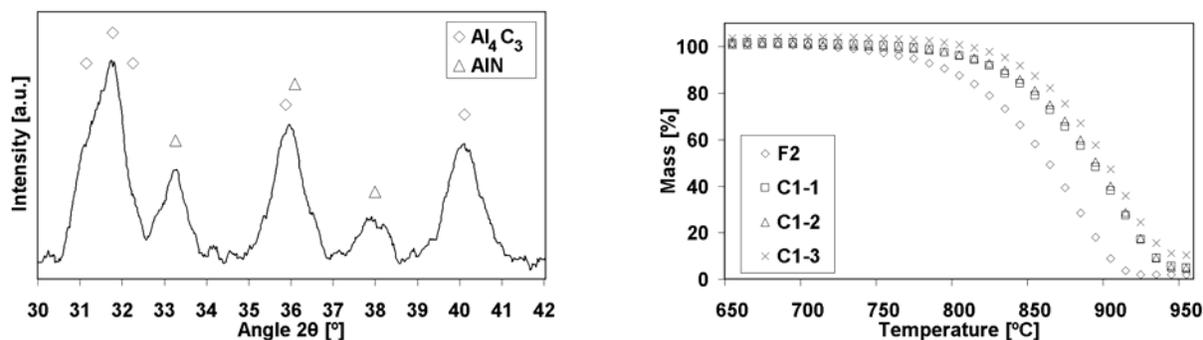
In experimental campaign 2 the coatings were found to be a mixture of AlN and  $Al_4C_3$ . From XRD measurements shown in Figure 4 it is clear that the carbide is the dominant phase in the coating. Based on TG and XRD measurements the AlN content in the coating was estimated to be in range of 15-35 wt%.

In all three experiments the temperature in the gas phase was well above 300°C, the decomposition temperature of TMA. Although no TMA was observed leaving the reactor, it was found that the quantity of Al deposited on carbon fibers correlates with its concentration in the gas phase, as shown on Figure 5. The residual TMA was deposited on the reactor wall and on the particles carried over with the gas stream during processing (the average effective product yield in these experiments was about 85%).

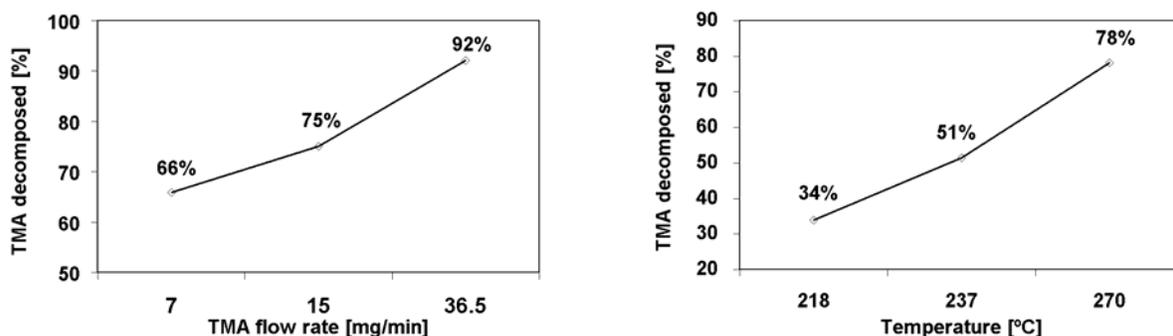
TG measurements (Figure 4) showed that these fibers have higher oxidation resistance than the original, uncoated material. Upon oxidation of the fibers, first the ceramic coating oxidizes to  $Al_2O_3$  which gives carbon some protection from oxidation.



**Figure 3.** SEM pictures of typical coatings on F2 fibers from coating campaign 1, left to right: uncoated, coated 25000x magnification, coated 50000x magnification.

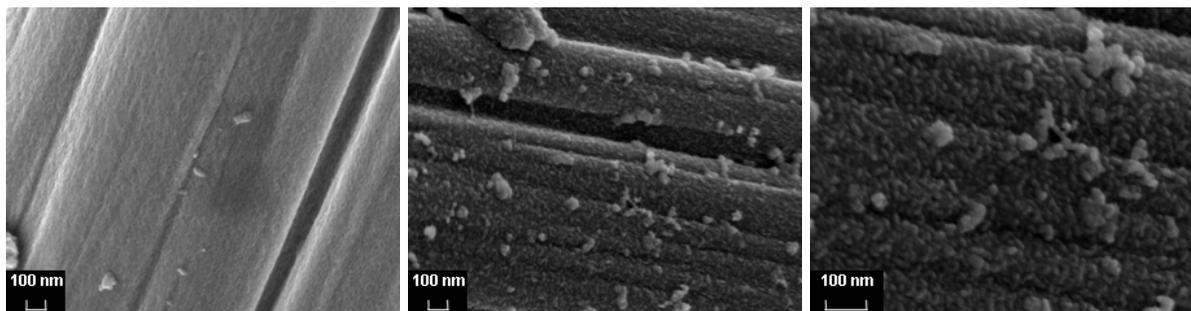


**Figure 4.** Typical XRD scan from coating campaign 1 (left); TG measurements of the product materials from campaign 1 (right)

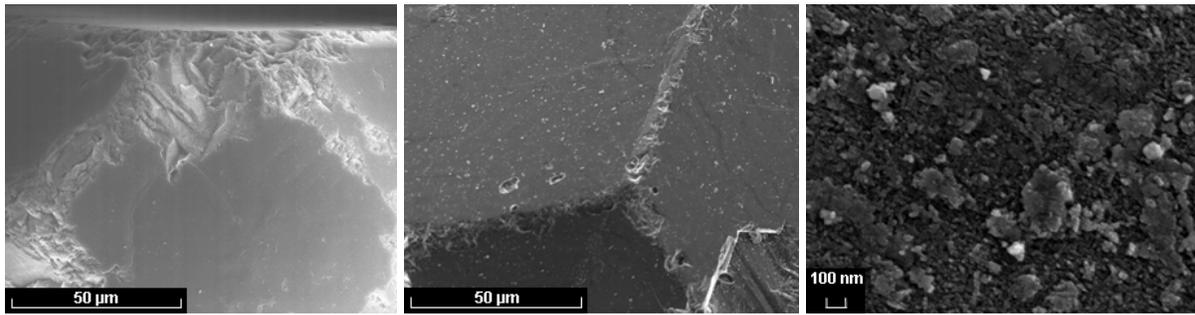


**Figure 5.** Percent of TMA given deposited on carbon fibers, in campaign 1 (left) as a function of concentration, in campaign 2 (right) as a function of temperature

In campaign 2, the coatings on carbon fibers as well as on diamonds were found to be composed mainly of Al<sub>4</sub>C<sub>3</sub>. By XRD scans neither Al nor AlN reflections could be detected. SEM pictures of typical coatings are shown in Figures 6, 7. It was found that the weight percent of the coating, hence coating process efficiency correlates with the temperature, as shown in Figure 5. The fraction of aluminum from TMA decomposed on diamonds was around 5% in all three experiments.



**Figure 6.** SEM pictures of typical coatings on F1 fibers from coating campaign 2, left to right: uncoated, coated 50000x magnification, coated 100000x magnification.



**Figure 7.** SEM pictures of typical coatings on D1 diamonds from coating campaign 2, left to right: uncoated, coated 1000x magnification, coated 50000x magnification

Upon investigation of the weight fraction of coating by oxidation of the carbon, XRD showed that it was always possible to burn out all carbon from fibers but not from diamonds – in some cases traces of diamond remained after heat treatment at 950°C. As shown in Figure 6 in comparison to Figure 7, there is clear evidence that the coatings on diamonds are thicker.

## Discussion

By varying the substrate particle temperature, evidence is found, that AlN is formed in the coating at higher temperature than  $\text{Al}_4\text{C}_3$ . High temperature experiments in campaign 1 yielded some AlN in the coating, while lower temperature experiments in campaign 2 yielded none. The formation of AlN might occur by direct nitridation of Al deposited from TMA or by nitridation of the  $\text{Al}_4\text{C}_3$  already deposited on the substrate particle surface. Thermodynamical calculations by HSC software [10] suggest rather that the  $\text{Al}_4\text{C}_3$  is the least stable phase in this system, which is not in agreement with the observed results.

Formation of  $\text{Al}_4\text{C}_3$  in carbon fiber Al metal matrix composites is known to occur at 500°C [11]. We assume that the carbide is not a product of reaction between aluminum and the carbon substrate, but rather a product of the TMA precursor decomposition at the surface of the substrate. From the results obtained so far, it can not be distinguished, whether TMA yields directly AlC-fragments or first carbon is deposited followed by a reaction between this carbon deposit and aluminum atoms provided from the precursor TMA. Although it is known that upon Plasma Enhanced CVD graphite is formed from hydrocarbons at low pressure at a temperature as low as 300°C [12], at atmospheric pressure plasma CVD conditions facilitate formation of pyrolytic carbon from hydrocarbons at much higher temperature, above 1100°C [13]. The influence of atmospheric pressure on this reaction is unknown for TMA.

Additional support for  $\text{Al}_4\text{C}_3$  formation from the gas phase precursor comes from the comparison of coating composition between carbon fibers and diamond as substrate. Because of the much lower reactivity of diamond a larger difference in coating composition would be expected between carbon fibers and diamond, if the substrate would contribute to the coating reaction.

The large difference in coating thickness between carbon fibers and diamonds can be due to the different fluidizing properties of these two particle types. Minimal fluidization velocity is much higher for diamonds than for carbon fibers, and hence they tend to stay near the bed entrance while fiber bed expands much more. TMA concentration is highest at the entrance, therefore less TMA is left for the carbon fibers to be coated in one run of the mixture.

Whether the microwave transparency of diamonds makes them colder than the carbon fibers during processing, or their higher thermal conductivity makes up for this can not be distinguished from the present study.

## Conclusion

An atmospheric pressure PECVD fluidized bed process for coating of short carbon fibers and of micro diamonds with Al-AlN-Al<sub>4</sub>C<sub>3</sub> composite coatings has been developed. The primary goal to produce pure AlN coatings had just a limited success due to the decomposition chemistry of the organometallic precursor TMA. On the other hand, with this precursor deposition rates are high and on high enough temperatures the percent of TMA decomposed on the substrate materials can be well over 90%. All coated materials show significantly improved resistance to oxidation on air at high temperatures, with the onset of oxidation shifted by up to 50°C to higher temperature.

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