The Characterization of Thin Layers of Carbon Particulate Deposited in Rich Premixed Flames

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Introduction

In the energy production and transport field, fuel-rich combustion has to be avoided to limit environmental impact related to the formation/emission of undesired carbonaceous species [1]. On the other side, fuel-rich combustion features some pyrolytic processes used to produce carbon materials as carbon black, and is currently studied as a source of advanced graphene-like materials [2-3]. The fuel-rich combustion process is a peculiar "self-sustaining system" for carbon material production, being both a heat and carbon source since most of the hydrocarbon reactant oxidizes generating the high temperature environment necessary to the surplus of hydrocarbons for producing carbon-based nanostructures.
Metal or silica-based grids are mainly used for deposition and growth of thin layers [2-3]. The morphology and thickness of the thin layers are among the parameters important to be measured to verify the quality of the deposited material. To this aim, in the present work techniques as surface profilometry and atomic force microscopy (AFM) have been implemented on carbon layers deposited in a fuel-rich ethylene flamer. The results have been compared with those obtained by UV-Visible and ellipsometry spectroscopic measurements obtaining information about the density of the arrangement of the particles in the deposited layer.

Experimental

The carbon particulate, produced in an ethylene-oxygen premixed laminar atmospheric flame burning on a water-cooled sintered bronze McKenna burner (d=60mm) (Holthuis & Associates), was deposited on fused silica plates at two heights above the burner (HAB) using different deposition times. The flame parameters and deposition conditions in which the two carbon particulate samples, named test1 and test2, were collected, are reported in Table 1.

Tab. 1 Flame parameters and deposition conditions.

Flame				Test Conditions		
Fuel	Oxidant	C/O ratio	v_o, cm/s	Test no.	HAB, mm	Deposition time, ms
Ethylene	Oxygen	0.8	4	1	8	240
				2	14	120

The set-up for the deposition into the flame was constituted of a fused-silica plate driven by a gear motor, which regulates the insertion/deposition time of the plate to 60ms per lap.

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UV-Visible absorption spectra were measured directly on the fused silica plates by an HP8452A spectrophotometer.
Ellipsometric measurements were performed using a phase modulated spectroscopic apparatus (UVSEL, Jobin Yvon Horiba) with a wavelength scanning range from 300 to 1600 nm at variable incident angle between 55° and 75°. Acquired data were fit to an optical model of the sample in which the dispersion of the soot layer was assumed to follow a modified version of the Forouhi-Bloomer dispersion relation [4] leading to film thickness and complex refractive index $\tilde{n}(\lambda)$. The film structure used in the model consists of an inhomogeneous soot layer, described by a Bruggeman effective medium approximation (BEMA) [5] mixture of bulk material and voids, with a lower density.
The sample height longitudinal profiles were measured by a KLA Tencor P-15 profiler (tip radius: 0.05 μm; tip angle: 95°) able to analyze substrates up to 8 inches.
2D/3D-topological maps (20x20μm) of the sample were obtained by a Scanning Probe Microscope NTEGRA Prima from NT-MDT, using NOVA SPM post-processing software. The AFM was operated in semicontact mode in air, using NANOSENSORSTM SSS-NCHR supersharp silicon probes with nominal tip radius of 2 nm, a 125-mm long cantilever with a spring force constant of 42N/m, and a range of resonance frequency 204–497kHz.
The carbon particulate thickness was evaluated from UV-Visible measurements by the equation $\mathbf{t=A/\varepsilon/\rho}$, where t is the layer thickness, A the absorbance of the sample measured directly on the fused silica plate, ε the specific absorption of the sample measured in DCM solution and ρ the bulk density of the carbon particulate [6].

Results and discussion

Before of describing the results, it is worth to give some information about the typical size distribution of the flame-formed carbon particulate, in order to establish the minimum limit of monolayer thickness. Considering the bulk density of carbon particulate ranging from a minimum of 1.2g/cm3, typical of particulate components having low molecular weight (200-300u), up to a maximum of 1.8g/cm3 [6], featuring the high molecular components (1E8-1E9u), the bulk diameters of the particles, considered in form of spheres, vary from about 2 to 60nm [7].
Fig. 1 reports the height profiles measured by stylus profilometer for test1 and test2. It can be noticed that samples showed a strong inhomogeneity in the height range, from a few tens up to hundreds of nanometers.
The measurements spans were enough wide, namely 1.3mm and 0.8mm of surface length investigated, for test 1 and test 2, respectively, allowing to start the measures from the "void zone" of the fused silica plates. In this way, it is possible to evaluate a sort of "background thickness" of the sample, then treating separately the peaks emerging after the background subtraction. The thickness evaluated for the background was about 70+/-20nm for both the test1 and test2.
Fig. 2 reports the normalized peak height distributions evaluated from profilometry and grain analysis of AFM 2D maps. It has to be underlined that the AFM measurements are limited to much smaller portions of sample in respect to profilometry, so the zero level (i.e. the void zone) could not be recognized. In order to evaluate the peak heights distributions by AFM the grain analysis function of the NOVA SPM software was used using a threshold on the 2D map that minimizes the difference of the distributions obtained from AFM and from profilometry. The agreement between the two sets of measures appears rather satisfactory. Specifically, the mean values of the peak heights above the background values are 40nm and 60nm for test1 and test2, respectively.

Considering the background of 70nm as above mentioned, the overall mean heights of the carbon particulate deposited therefore result about 110nm and 130nm for test1 and test2, respectively.

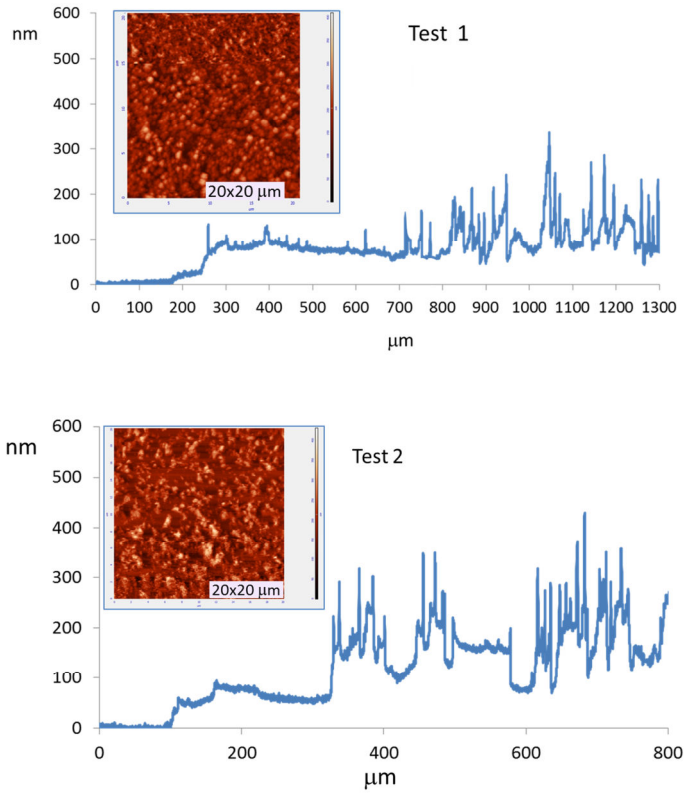

Fig. 1 Height profiles measured by profilometry of particulate carbon deposited at 8mm HAB with 240ms deposition time (Test 1) and at 14mm HAB with 120ms deposition time (Test 2). AFM 2-D topological maps obtained on the same samples (insets).

The carbon particulate thickness has been also evaluated from UV-visible spectroscopy and ellipsometry. Table 2 reports the results of the UV-visible and ellipsometric analysis which appears to be similar (column 4 and 7), provided the correction of ellipsometric value for the carbon particulate content (column 6 of Tab. 2).

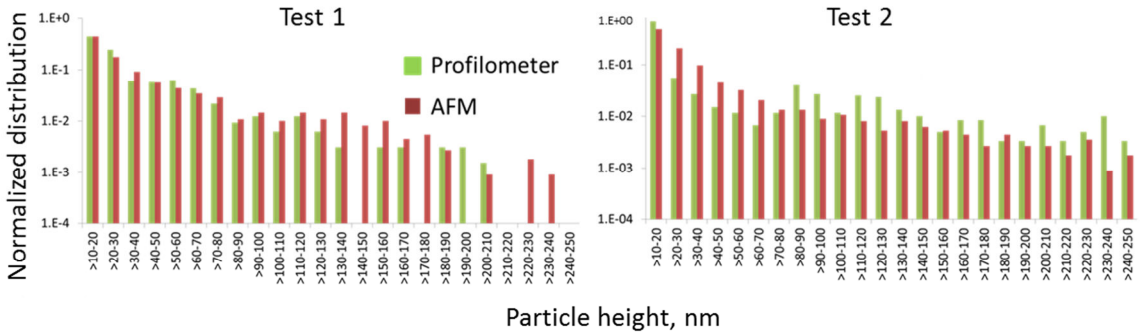

Fig.2 Normalized distributions of the heights of the particles/aggregates found by surface profilometer compared with those estimated by AFM measurements.

It is noteworthy that the thickness values are about one order of magnitude lower in respect to those evaluated by profilometry and AFM above reported. Responsible for this

difference is the much lower density of the arrangement of the carbon particulate deposited on the fused silica plate in respect to the bulk density. Actually, the material density of primary soot particles constituting the soot core is ~2g/cm^3 [6], but the effective density of the agglomerated soot particles is lower, and substantially decreases with size.
Another parameter that can be derived from the AFM measurements is the grain volumes (above the threshold). The sum of the grain volumes are equal to 35μm^3 and 45μm^3 for the test1 and test2, respectively. If we assume the same density of the arrangement through the whole carbon particulate layer, the overall volumes are about equal to 100μm^3 for both test1 and test2. The overall volumes for the test1 and test2 are equal to 3.3μm^3 and 2.4μm^3 as derived from UV-visible and 10μm^3 and 15μm^3 as derived from ellipsometry measurements. Hence the volumes obtained by profilometry/AFM are about 30 and 40 times greater than those obtained by UV-visible for test1 and test2, respectively.

Table 2 Absorption coefficients and thickness obtained from UV-visible spectroscopy and ellipsometric analysis.

	UV-visible Absorption			Ellipsometry		
Test no.	Absorbance @400nm	Mass absorptivity @400nm, l/(cm*g)	Carbon particulate thickness, nm	Thickness, nm	Carbon particulate fraction, %	Carbon particulate thickness, nm
1	3.40E-02	23	8.3	24.7	26.2	6.5
2	5.90E-02	69	4.8	37.2	26.2	9.8

Conclusions

Surface profilometry and atomic force microscopy (AFM) were implemented on carbon layers deposited in a fuel-rich ethylene flame. The results were compared with those obtained by UV-Visible and ellipsometry spectroscopic measurements. The density of the particle arrangement in the deposited layer, as estimated by the profilometry/AFM measurements, appears to be about 30 and 40 times lower than the bulk density of the carbon particulate for the two test cases considered.

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