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DETECTION OF SOOT PARTICLES USING A RESISTIVE TRANSDUCER BASED ON THERMOPHORESIS

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Abstract

A soot transducer based on the measurement of the electrical resistance value of the soot layer deposited on a finger structure was tested at different thermophoretic potentials. The soot, similar to that issued from the Diesel engines, in terms of particle number and size distribution, was obtained by the incomplete burning of propane and subsequent dilution. The decrease of the resistance value in time was directly proportional with the temperature gradient. Thus a soot transducer is aimed to be used in real Diesel exhaust, to monitor the particle release in the ambient air. An important practical aspect concerns the possibility to regenerate the sensorial system, when their resistance reaches a certain value corresponding to the sensor saturation. The soot can be removed by the burn off in atmosphere containing oxygen. The catalytic effect of platinum deposited on the finger structure as small isolated islands on the surface, was investigated. It was pointed out that the platinum islands are catalytically active, determining the soot removal at temperatures lower by 90 ^{o}C than in the case of the blank substrate.

Key words: catalytic effect, platinum, sensorial area regeneration, soot removal

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1. Introduction

Diesel engines gained during the latest decades a large popularity, due to some advantages connected to their high power, much lower fuel consumption for the same work than the gasoline engines, cheaper fuel (including the possibility to use biofuels from different sources), high reliability, longer lifetime in comparison with a gasoline engine, self-lubrication properties and lower hazards in fuel transportation, stocking and functioning (Ury, 2012). However, a major drawback of Diesel engines is their high particle emissions, i.e., soot.

The soot is the result of the association of rich carbonaceous nanoparticles formed as a consequence of the high temperatures developed during the combustion with sulphuric acid, water and unburned hydrocarbons from the fuel. A big number of studies prove the negative effects of the Diesel soot particles on human health (especially their carcinogen character) and on the environment in general (Arden Pope III et al., 2002; EPA, 2002; Valavanidis et al., 2008). The effects of the soot are more evident and dangerous in the high populated areas, where the amount of soot is higher. Their small sizes (hundreds of nanometers or less) as well as their chemical composition (hydrocarbons and sulphuric acid) make them responsible for respiratory diseases, cancer generation and esthetical degradation in long term processes.

The truck engines were especially proved to be responsible for high emissions. Since the fuel burning is not possible to perform in conditions to avoid soot formation, an alternative is its capture using Diesel Particle Filters (DPF) for both trucks and cars; these filters usually consist of cordierite, silicon carbide with controlled fine porosity (Prasad and Bella, 2010). When the pores are clogged, the

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soot has to be removed to regenerate the filters. This regeneration needs to be very well-planned, since it brings an extra-fuel consummation, necessary to initiate its burn off from the filter. If the regeneration begins earlier than necessary, there will be an unjustified fuel spare, while the late regeneration can lead to the irreversible filter damaging, due to the overpressure and high temperatures developed during the soot burning. The settlement of the moment when the regeneration should start can be performed by using soot sensors, able to show the moment when the amount of the soot amount reached the proper level.

The aim of our work is to establish the optimal parameters for obtaining soot particles with properties similar to those generated by real Diesel engines by the incomplete burning of propane, to prove the possibility to detect these particles using a simple and cheap resistive transducer, working on the thermophoresis principle and to discuss the possibilities for the sensorial area regeneration.

2. Experimental part

The soot particles were obtained while burning propane in a McKenna burner, in insufficient air volume compared to the stoichiometry of combustion. The burner was inserted in a vertical tube and the burning gas flow containing the soot particles quitted the tube by its upper part. This gas flow was diluted immediately with air in a horizontal tube, to quench the flow and dilute the soot, preventing the particle agglomeration which normally happens at high temperatures and high particle number per unit volume.

An extra dilution step using an ejector diluter (Dekati, Finland) at different ratios was applied in order to obtain a particle number per volume similar to usual, medium load Diesel emissions. The particles were measures using a Scanning Mobility Particle Sizer (SMPS) system, consisting of a Differential Mobility Analyzer (DMA) 3081 with classifier model 3080 and a Condensation Particle Counter 3010.

The detection of the particles was performed by thermophoretic deposition in a sealed exposure cell, on a finger structure electrically connected to a multimeter device. The diluted soot gas flow was heated at different temperatures using an electrical heating coil surrounding a serpentine pipe hosting the soot gas flow, before entering the deposition cell, in order to settle a significant difference between the temperature of the gas and that of the sensor area (thermophoretic potential). At the exit of the gas, a T-shape ramification allowed analyzing the particle size distribution using the SMPS system, simultaneously with the deposition of soot in the sensorial cell (Fig. 1).

The soot sensorial area consisted of a finger structure of Au(200 nm)/Ti(5 nm), with 80 μm width metal contacts and gaps of 80 μm in between, obtained using the lift-off technology on a Si substrate, Si/SiO_2 (100 nm). Small (2 x 2 mm) parts of substrate were glued on a heater (Pt wire in an Al_2O_3 substrate from Heraeus), fixed on a 16 pin holder together with a Pt 100 sensor (Pt resistor with the resistance of 100 Ohm at 0 °C) to allow the continuous temperature measurement.

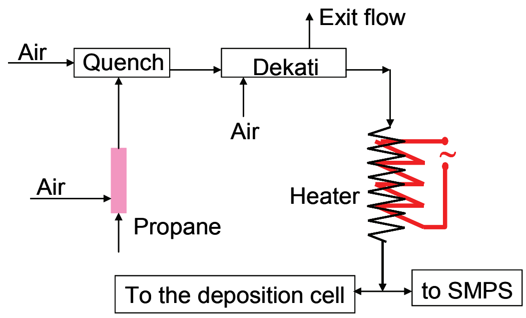


Fig. 1. Experimental setup for soot production, characterization and deposition in the sensorial cell

Two of the pins were connected to the finger structure and to a multimeter device (TTI 1604), to measure the resistance of the soot layer (the instrument measurement range: 1 kOhm - 40 MOhms). The 16-pin holder was placed in a sealed cell and exposed to a gas flow rate of 100 mL/min with soot content (Fig. 2) (Lutic et al., 2010).

The regeneration of the sensorial area was performed by heating the substrate for 30 – 240 minutes in air flow, at high temperatures, in order to burn off the deposited soot. The catalytic effect of platinum in fastening the sensor regeneration was tested by depositing small Pt islands (by vapour deposition of a 85 Å layer followed by heating at 600 ^{o}C) on the finger structure. The examination of the sensorial surface state in order to check the regeneration degree was investigated by the SEM technique, using a Leo 1550 VP emission field scanning electron microscope.

3. Results and discussions

3.1. Soot generation

Several organic species were tested for their adequacy to generate soot by thermal treatments. Benzene or toluene mixed with n-propanol (1/3 mole ratio) were vaporized by bubbling nitrogen or 2 % O_2 in N_2 through a glass bubbler, at room temperature, and the resulted gas mixture was flown through a horizontal tubular oven heated at temperatures ranged between 800 and 1100 ^{o}C.

However, the resulted particles were too big (over 1 μm), with a tar-like consistency. Also the ethylene (4 % in nitrogen) mixed with 2 % oxygen was subjected to pyrolysis to generate soot particles, but the results were not either satisfactory. The use of propane gas born in air proved to generate soot particles quite similar to Diesel soot, when the appropriate ratios were chosen. The stoichiometric molar ratio for the propane total burning is 5/1 (oxygen/propane), respectively 23.8/1 (air/propane).

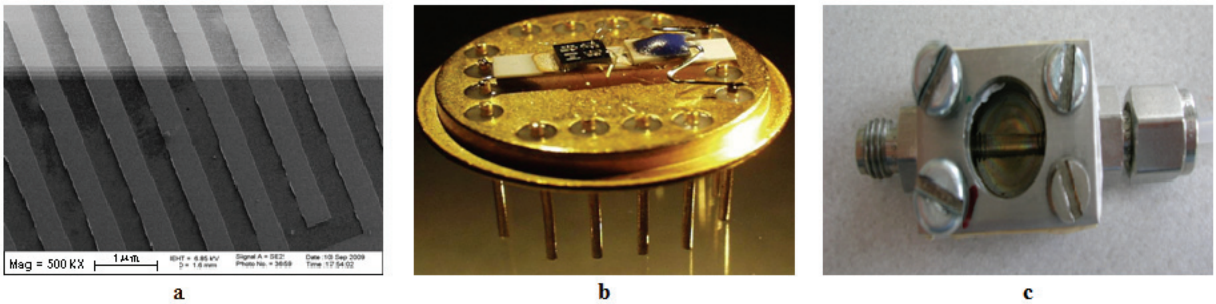


Fig. 2. Experimental setup for soot sensing: a – SEM image of the finger structure (light grey: finger structure, dark grey: gaps); b- 16-pin holder; c – exposure cell.

Several ratios O_2/propane were tested; the optimal value in terms of flame and particle size stability as well as particle size was ranged between 3.9 and 4.1. The soot gas flow was quenched with air, at a 3/1 volume ratio, then another dilution at a 7/1 volume ratio was applied using the Dekati diluter. The typical particle size distribution curves in terms of particle number for the quenched soot and for the soot diluted heated are presented in Fig. 3.

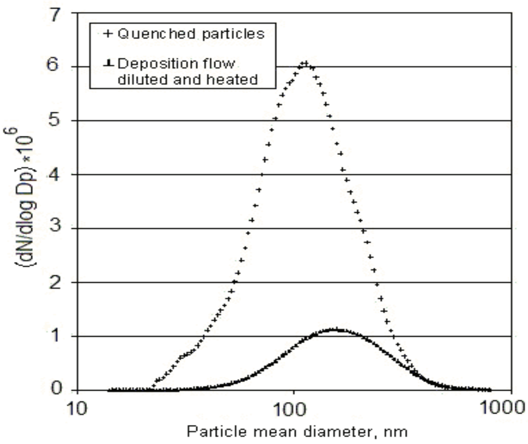


Fig. 3. Soot particle size distribution in terms of particle number

The presented curves show gaussian-type size distribution, with the maximum of the particle number situated between 110-140 nm mean diameter, similar to those typically emitted by the Diesel engines (Rose et al., 2006; Kittelson, 1998; DieselNet Technology Guide, 2002). The imperfections in the particle size distributions can be attributed to small flow fluctuations which occur during the several measurements of particle number and size were performed before using the particles for the deposition tests. The fine regulation of the flow rates of propane and air was a basic condition for obtaining soot having constant parameters, also mentioned by Malik et al. (2011).

3.2. Soot deposition

The chemical composition of the soot recommends it as a highly conductive material, due to the big proportion of carbon-rich materials with multiple chemical bondings, somehow similar to fullerenes or graphite (Burtscher, 2005; Liang et al., 2005; Maricq, 2007; Prasad and Bella, 2010).

The soot deposition on the finger structures occurs due to the thermophoretic force, associated with the temperature differences between the soot from the gas flow and the sensorial surface (Hinds, 1999; Malik et al., 2011). The soot particles adhere to the substrate surface or to each others. Thus, a net of non straight wires constructing bridges between the fingers progressively appears. The soot layer formation can be explained by the percolation theory (Hagen et al., 2010); the percolation time is defined by the time needed until the first conducting continuous lines made of deposited soot particles appear between the gaps from the finger area and close the electrical circuit between them.

The first values of the measured resistance values are in the range of tens of hundreds of MOhms (Hagen et al., 2010, Lutic et al., 2010) and depend strongly on the size of the gap between the finger electrodes. After the percolation time is reached, the continuation of the soot deposition on the surface determines the fast settlement of a stable, multilayered connection between the fingers. The resistance value decreases also fast, in relation with the deposition potential of the soot, i.e., the difference between the sensorial surface and the soot gas flow temperature. The time dependence of the resistance value is displayed in Fig. 4.

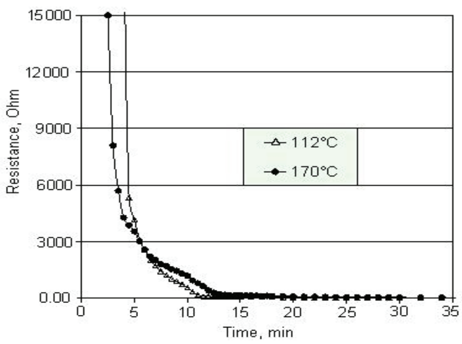


Fig. 4. Evolution of resistance value of the deposited soot layer in time at two different ΔT

The deposition of the soot on the sensorial surface is due to the thermophoresis mechanism, consisting in the thermal force determining the particle settlement on the colder surface of the resistive sensor (Lutic et al., 2010; Malik et al., 2011; Visser et al., 2011).

The delay between the admission of the soot flow through the cell and the moment when the resistance of the deposited layer enters in the measurable range clearly depends on the ΔT between the gas flow and the sensorial surface, the higher temperature difference being favourable for the deposition.

As expected and observed previously in similar works (Lutic et al., 2010; Malik et al., 2011; Visser et al., 2011), the resistance value of the conductive soot layer decreases steeply after some minutes, due to the fast multiplication of the number of conductive bridges deposited on the surface and to the increase of the conducting layer depth. After 10-12 minutes, a relatively continuous soot layer deposited on the surface involves a measured resistance value in a range between 100-1000 kOhms, for both tested temperature differences between the "cold surface" and the "hot particle". It means that even a relatively low temperature difference of 112^{o}C makes possible to use this device for the soot detection and, after a proper calibration, measuring the soot amount from the gas stream (Visser et al., 2011).

The simple construction and low price of this transducer make it an interesting device to be installed on Diesel engines vehicles as on-board diagnostic (OBD) tools. It is important to manufacture devices able to work a long time as OBD and detect, in the same time, very fast the moment when the regeneration of the DPF should start in the safety way, in order to avoid the damage and to prolong its lifetime.

3.3. Sensorial area regeneration

The finger sensorial area needs to be subjected to an efficient regeneration procedure after being covering with soot particles, in order to re-start the sensorial procedure. The simplest way to remove of the soot from the sensorial surface is its burning in air flow; the usual temperature for this operation is around 550-600 ^{o}C, in order to complete in a reasonable time duration (several minutes). This method is efficient, but the fragility of the finger structure and the thin connecting wires do not recommend repetitive cycles of sensor heating in this temperature range.

The catalytic high efficiency of platinum in organic matter (including soot) burn off in air is well documented (Liu et al., 2013; Oi-Uchisawa et al., 2003; Stanmore et al., 2001). Therefore, we tested the effect of "islands" of Pt deposited on the sensor surface for the faster and more gently removal of the soot form the sensor surface. In this respect, a platinum layer with 85 Å was deposited by evaporation on the finger structure before the mounting and soot deposition. Previous studies from literature (Lundström et al., 2007; Salomonsson et al., 2005) indicate that the thin platinum layers suffer structural changes while heating at temperatures above 500-600 ^{o}C, consisting in a strong trend of sintering. The continuous Pt layer is transformed in low surface islands, located at bigger distances in between, as the temperature values increase.

In our study, we used the SEM technique to investigate the modification of the thin Pt layer (85 Å) morphology when heating in air the substrates at temperatures comprised between 480-600 ^{o}C, for one hour. The SEM images (Fig. 5) shows that the platinum layer occurs only slight, insignificant cracking when heated at 480 ^{o}C. Starting from 500 ^{o}C, the layer structure becomes discontinuous and the surface still covered by platinum diminishes to an important extent. At 600^{o}C the platinum islands are very small grains found on the surface. In order to determine the role of the Pt islands in the removal of the deposited soot, we used samples heated at 580 ^{o}C as a substrate for the soot deposition and regeneration test. The same soot flow was sent to two deposition cells, one hosting a simple, blank finger, another finger with Pt islands on the surface. After 30 minutes of exposure to soot-containing gas flow, the samples were examined by SEM. A thick layer of soot, consisting in primary almost spherical particles assembled in branched, disordered chains was deposited (Fig. 6). On the big magnification degree image, one can observe that the primary particles have around 100 nm in diameter, in line with the SMPS measurements.

The comparison concerning the removal of the soot from the simple substrates and the ones with Pt islands in the regeneration was performed by heating them in ambient air at temperatures range between 400 and 600 ^{o}C and time duration comprised between 30 – 240 minutes. When heating the simple substrate covered with soot at 510 ^{o}C, the amount of soot remaining on the surface after 2 h is still important (Figs. 7a, b) and the remaining layer resistance is of 2.2 kOhm. The removal of the soot was not total either at 600 ^{o}C, even if the heating time was 4 h (Fig. 7c). However, the soot looks like some isolated agglomerations unable to generate a conductive layer; the attempt to measure the resistance indicated that its value is over the detection limit of the device.

The contribution of the Pt islands in decreasing the temperature for the advanced soot removal is confirmed by the SEM image of the sample, Fig. 8. When heated at 510 ^{o}C for 30 minutes, the soot had been burn off almost totally, only scarcely flakes remain on the sensorial surface. This temperature value can be considered the proper regeneration temperature, so a lowering of 90 ^{o}C is noticed due to the platinum presence.

3.4. Practical applications for soot monitoring

Monitoring of soot emitted in automotive applications, could be carried out at the pollution sources (located in the vehicle driven by the engine) and also along the route for vehicle moving.

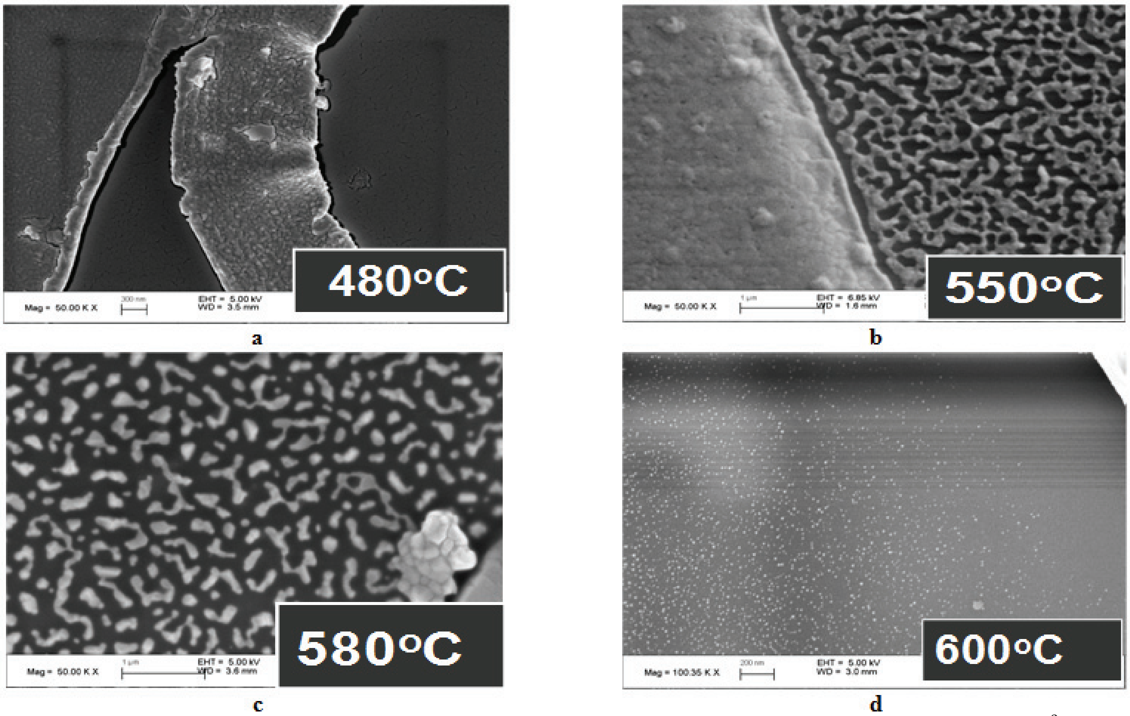


Fig. 5. SEM images showing the thin Pt layer morphology modifications on heating between 480-600 °C

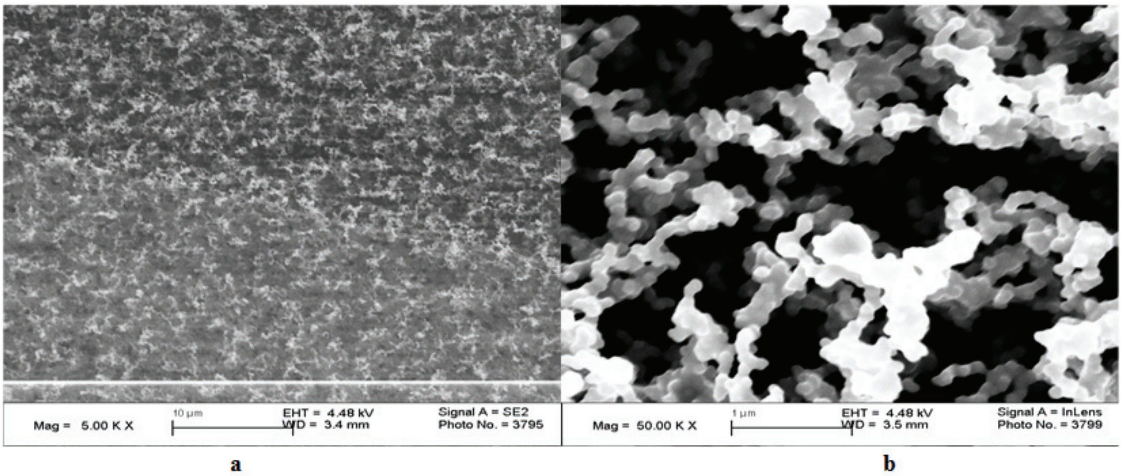


Fig. 6. Soot layer deposited on the finger structure a – 5000 x; b – 50000 x

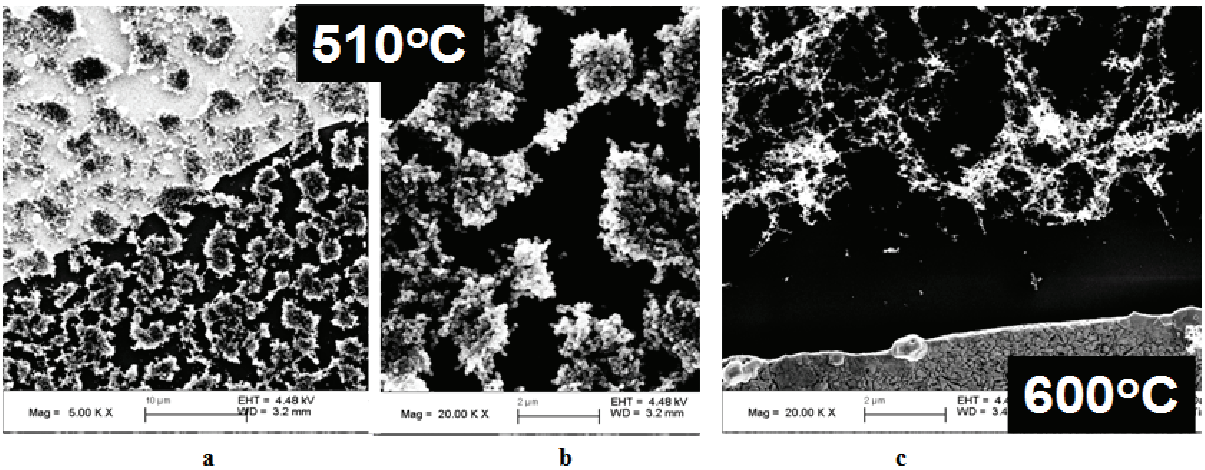
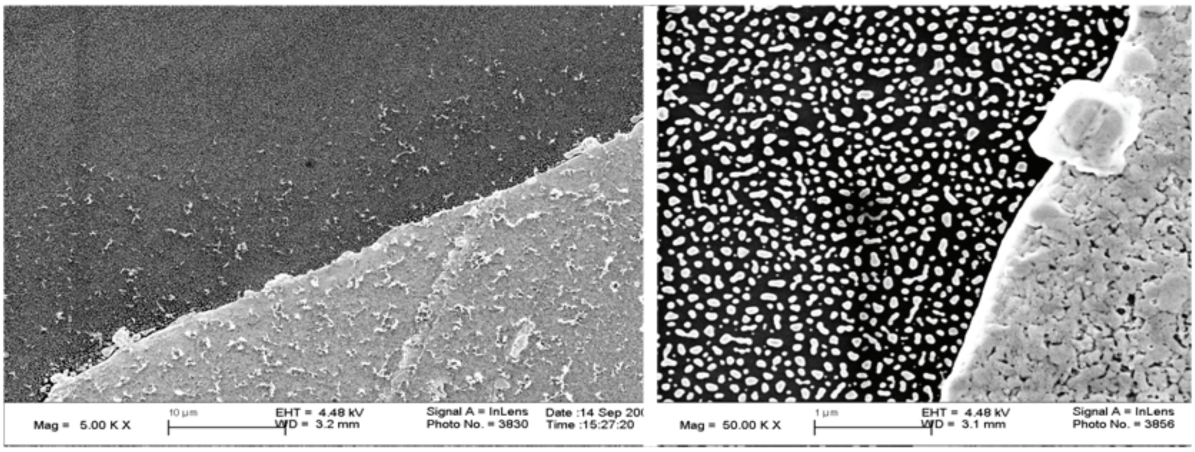


Fig. 7. SEM images after heating the simple substrates with deposited soot a. 510 °C, 5000 x, 2h; b. 510 °C, 50000 x, 2h; c. 600 °C, 20000x, 4h



a b

Fig. 8. SEM images of the regenerated substrates with Pt islands heated at 510 ^{o}C a. 5000x, b. 50000x

In the first case all technical problems could be easer solved, because the electrical power and data transmission are assured in the frame of the vehicle electrical system. In the second case, the energy must be distributed or in situ generated at each location, where soot transducer is installed, but the most important aspect is data acquisition and transmission. Currently, wireless sensor networks (WSNs) have been used for environmental monitoring and real-time event detection because of their low implementation costs and their capability of distributed sensing and processing.

A similar application was developed for fire detection using special transducers which are enabling to measure the environmental parameters and can decide about the fire occurrence using specific software. Such kind of methods was evaluated in terms of detection accuracy rate and computational complexity in the specific literature (Bahrepour et al., 2009). Also some specific problems and limitations of a WSN designed for an environmental protection/wildlife tracking application were presented (Badescu et al., 2011; Marmureanu et al., 2012).

In the case of soot monitoring located in different sampling points of a monitoring network the main problem is the air sampling due to the influence of meteorological parameters changes. Some researches, based on the field sampling were carried out using models and software for data processing and interpretation.

Beside the detection part which was in detail presented in this article, a smart sensors located on different sites, must have its own network address, accessible for any location. They can be programmed to send an alarm signal when the soot concentration is increasing in the air flux collected from the traffic roads. In order to incorporate all these functions, an electronic chip should be designed, accomplishing the transmission and reception of signals from the sensor (Iordache and Dunea, 2012; Statescu et al., 2011).

4. Conclusions

The generation of soot with similar particle size distribution as the Diesel particle emissions was performed by propane burning in insufficient volume ratio as regarded to the stoichiometric ratio. The deposition of the soot on a finger structure was possible in a good extent at thermophoretic potentials comprised between 112-170^{o}C, resulting in the formation of a soot layer compact enough to allow measuring its electrical resistance in a relatively short time duration (some minutes).

The regeneration of the sensor was performed by heating in air. The heating temperature decreased in an important extent if on the sensorial area exist sub-micrometer size Pt islands resulted from the sintering of a an 85 Å evaporated layer. Thus, the finger structure can be protected further and can be used a longer time than in the case of the undoped structure.

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