NUCLEATION PHENOMENA IN DC HIGH PRESSURE ELECTRICAL DISCHARGES AND POST-PRODUCTION OF ULTRA FINE AEROSOL

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Abstract : The paper deals with the production of ultra fine particles by electrical discharges in point-to-grid configurations for centimetric gaps in controlled air (or nitrogen) at atmospheric pressure. Three different types of processes leading to a particle production are observed :

- A resuspension process shown by fugitive bursts of particles coming off from oxidized and /or contaminated electrodes when the voltage is switched on at values under the ionisation threshold or under discharge conditions.
- Nucleation processes occurring within the gap and initiated by the impact of streamers or sparks on the grid electrode.
- Gas-to-particle conversion processes obtained with all types of discharges except sparking discharges, by maturation (confining) of the gaseous effluents.

INTRODUCTION

The use of electrical point discharge systems is common to numerous applications such as corona chargers [10], ionizers [5], electrostatic precipitators [6] and more recently, depollution reactors [3, 7]. Firstly observed by Nolan [8], the production of very small nucleï in such systems has been afterwards reinvestigated in terms of resuspension and gas-to-particle conversion [9] as a function of the mean discharge current or of the applied voltage. But these parameters are known to depend on the electrodes geometry and arrangement, on the external electrical circuit of the discharge and on the gas composition [4, 7] ; and without more precise data on both the electrical behaviour variations on the one hand and on the UFA production on the other hand, it is hopeless to reach a good knowledge on the UFA production mechanisms which can prevail according to the different electrical discharge regimes which can be get.

The aim of this paper is to fulfil this goal while operating on an elementary point-to-plane electrical discharge with centimetric gaps in air (or N_2) at atmospheric pressure, under well-defined laboratory conditions.

EXPERIMENTAL SET-UP AND MEASUREMENTS

The experimental variables were electrode geometry, polarity and voltage, gas composition (dry or humid air, dry nitrogen) and flow-rate (i.e. maturation time) so as to produce and control different electrical discharge regimes. In practice, an electrode system consisting, on one side of a point electrode in tungsten-carbide or in stainless steel of variable radius ($50 < r < 100$ µm) and on the other side of a platinum grid grounded via an oscilloscope, was submitted to a ΔV_{gap} voltage in a -30kV/+30kV range, in various controlled gas flows (bottled air filtered on activated charcoal and 5 Å molecular sieves). Fine current measurements show the discharge regime and, through it, indirect informations on the ionisation and excited state of the gas in the interelectrodes space and on the chemical nature of the by-products concerned. The platinum grid used as a low field electrode enables particles characterisation (number and rough size distribution) by means of parallel analyses of the outlet aerosol flow with Condensation Nuclei Counters (models 3020, 3025 and 3760 T.S.I.Inc.) having different thresholds (respectively 3, 5 and 14 nm), an optical particle counter (OPC from 0.1 to 10 µm) and a differential mobility analyzer (DMA).

Chemical analyses of gaseous species produced by the discharge are performed by infra-red spectroscopy using a eight meters length-path cell and a Brücker IFS 48 spectrometer, while the post-production of UFA is studied by confining these gaseous species in a 10 litres maturation volume at the exit of the discharge vessel.

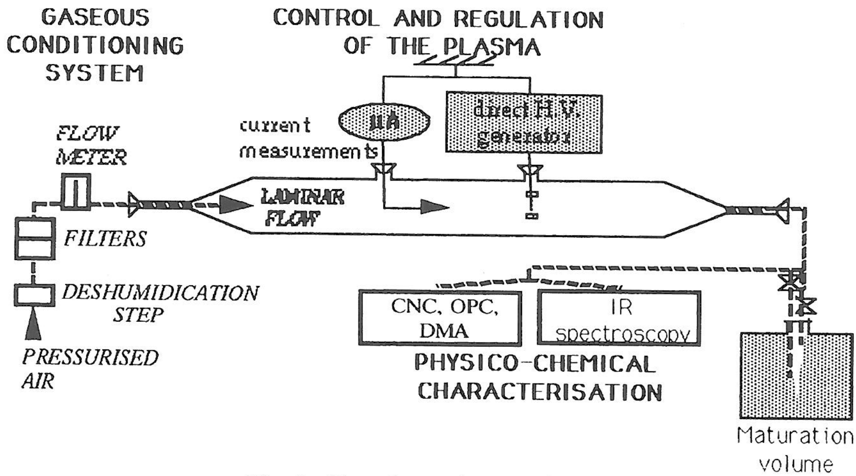

Fig. 1 : Experimental set-up (see text).

RESULTS

1- Resuspension phenomena already observable under the onset voltage of ionisation processes. Whatever the polarity, when the voltage is switched on, or even only increased, short events of few nuclei generation can be observed, even when the applied electrical field is too low to set ionisation in the point-to-grid gap. This gives bursts of sub-micronic particles ($0.1 < D_p < 1$ µm), which can be avoided by an ultrasonic cleaning of the electrodes and are thus attributed to an electrostatic resuspension of particles from the surfaces of both the point and the grid (crystallized oxides formed on the electrodes by the oxidizing plasmas and/or mineral dust brought by contamination).

2- Nucleation phenomena monitored by discharge-surface interactions. Apart from the erratic bursts discussed above, which correspond to an electrostatic resuspension of particles only weakly tight to the electrode(s) surface(s), cathodic points lead to a particle production only in the spark regime.

On the contrary, with a positive point polarity, under both auto-stabilisation and corona glow regimes, i.e. regimes characterized by a localised activation volume in the point electrode vicinity, only these initial bursts of particles are observed, but UFA are generated as soon as the applied voltage becomes sufficient to develop streamers from the point to the grid (also referred to as crossing streamers hereafter).

2-a Streamer induced UFA generation. When operating at the threshold voltage for streamer initiation, only some of the streamers generated reach the grid, developing a luminous filamentary link between the electrodes and a cathodic spot at their arrival on the grid. Actually, it has been observed with different electrodes spacings, that the production of UFA is only observed when the streamers reach the grid.

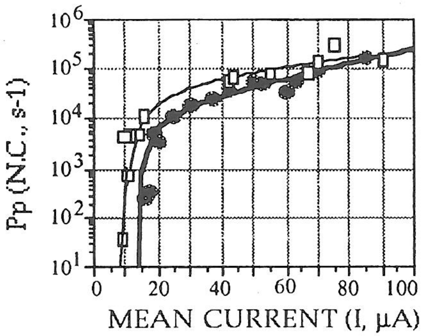

Fig. 2 : The threshold mean current of UFA production depends on geometrical configuration ; d = 1 cm (●), d = 2 cm (□), Q = 2.5 l/min, r = 50 μm.

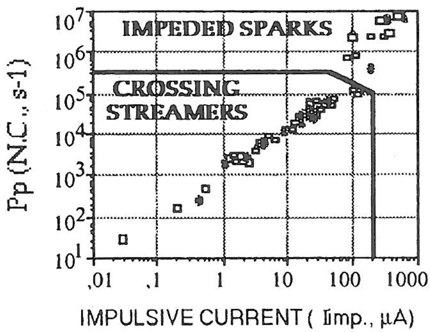

Fig. 3 : The UFA production is linked to the mean value of the impulse current component due to streamers.

The threshold discharge current for UFA generation is linked to the interelectrode distance (see figure 2), only reflecting the shifting of phenomena which occurs, for gaps of different lengths. Nevertheless, from figure 3, it is clear that, whatever the shape of the electrodes is, and the distance between them, the mean value of the impulse component of the discharge current is the only reliable electrical parameter when dealing with UFA production by streamers.

When counted at the exit of the discharge vessel only a few seconds after their generation, the main fraction i.e. 95% of the UFA have diameters laying under 14 nm (figure 4). This probably means that we are dealing with a nucleated aerosol, originating from the interaction of the cathodic spot created by the impinging streamers with the grid, either through thermal effects (sublimation of the metallic grid) and subsequent homogeneous nucleation of metallic vapors or through sputtering effects with the ejection of metallic atoms, as already observed [1] and able to serve as embryos of condensation in the interelectrode space. Local enhancement of the electrical field close to the grid at the point of impact of the streamers [2] leads to an increased velocity of the oncoming positive ions reaching high kinetic energies, around 10 eV. It should be underlined that new chemical species can be produced by the cathodic spot.

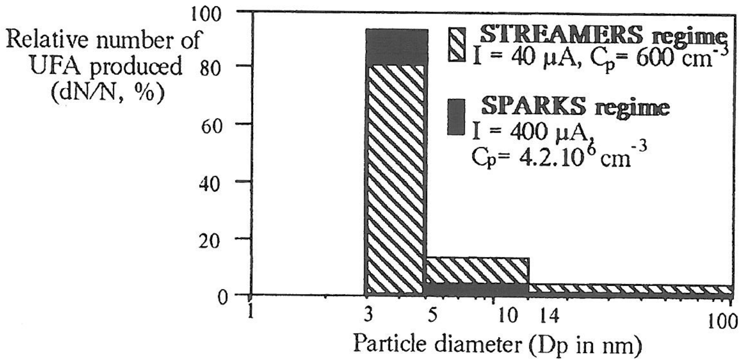

Fig . 4 : Size distribution of the Ultra Fine Aerosol produced with positive point discharges in the streamers mode and in the sparking mode.

2-b Increased production of UFA in the spark regime. As shown in figure 3, the UFA production in sparking positive discharges increases by one or two orders of magnitude and is no more correlated to the impulse component of the current as in the streamer regime. It is clear that this sudden increase of UFA production is due to the thermal properties of the plasmas generated in this regime.

By changing the gas composition from dry air to dry nitrogen, the production is unaffected. We have thus demonstrated that the UFA production is not linked to the adiabatic expansion associated with the transition from streamer to spark and to the gaseous activity induced by such a thermal plasma, but rather to highly energetic exchange processes between the spark and the grid, which are less sensitive to the gas nature than the preceding gaseous process.

At last, impeded sparks were obtained by modifying the external electrical circuit of the discharge, thus controlling the dynamics of energy injection and the thermalisation phase duration. This allowed us to show that the UFA production rate increases with the spark repetition rate but is not correlated to the total energy injected in the sparks. Actually, the UFA production is shown to be independent of the thermalisation phase duration and seems more closely related to the intensity of the initial phase of the spark, which has been proved to depend on the interelectrode space capacitance [7].

3- Maturation (or confining) effects. Under positive point polarity, for slow flow rates, the UFA concentration in a 10 litres maturation volume placed at the exit of the discharge vessel increases up to values depending on the impulse current component mean value, and on the maturation time. One observes that a few minutes are necessary to see an effect and that the post-maturation UFA concentration then increases exponentially with time, before a quasi-static equilibrium plateau is reached. There is thus a gas-to-particle conversion from gaseous products of slow kinetics chemical reactions between oxidized species created by the streamers propagation. During the maturation time, not only the number of UFA varies, but also their size distribution which implies that condensation occurs on pre-existing nuclei produced by discharges.

It has to be underlined that post-discharge production phenomena are also observed with the localised discharge regimes (i.e. autostabilisation and glow regimes), whereas by maturation of gaseous effluents from sparks, only condensation processes are shown to play a significant role, without generation of new particles. Table 1 indicates that one of the common points between streamers and localised discharges is the production of ozone which is destroyed by high temperature arc phenomena. We can thus confirm that the confining effect could be in particular linked to the ozone production, as already mentioned [3, 9].

Table 1 : Gaseous species, main characteristics and mechanisms of ultra fine aerosol production in dry air, with positive point-to-grid discharges according to the discharge regime.

DISCHARGE REGIMES	DISCHARGES LOCALISED AT THE POINT	STREAMERS PROPAGATING TILL THE GRID	STREAMER-TO-SPARK TRANSITION
MEAN IMPULSE CURRENT(Iimp. μA)	$0\text{-}10^{-1}$	$10^{-1}\text{-}10^{2}$	$10^{2}\text{-}10^{3}$
GASEOUS SPECIES CREATED	O_3, NO_x, HNO_3	O_3, NO_x, HNO_3	N_yO_x, HNO_2
Particle concentration cm^{-3} without maturation	bursts of particles	$10^{2}\text{-}10^{3}$	$10^{4}\text{-}10^{6}$
MECHANISMS OF NANO-PARTICLES GENERATION AT THE EXIT OF THE DISCHARGE VESSEL	**FIELD INDUCED RESUSPENSION** of surface contaminants and unadherent corrosion products	- **INDUCED BY PLASMA/ ELECTRODES INTERACTIONS :** -**ELECTROEROSION & RESUSPENSION** of surface products (metallic oxides and/or contaminants) - **GAS-TO-PARTICLE CONVERSION** of very locally sursaturated metallic vapours	
AFTER MATURATION	**GAS-TO-PARTICLE CONVERSION** of ternary species created by slow reactions between secondary gaseous species (i.e. O_3 and NO_x)		

CONCLUSION

Our main results concerning the production of particles by positive point-to-plane discharges in air at atmospheric pressure have been summarized on table 1. We see that, within the discharge gap, one may find three different classes of particles :

(i) some particles of contaminants and/or oxidation and corrosion products which may leave the electrodes simply by field effect when the voltage is switched on or increased,

(ii) ultra-fine nucleated aerosol originating from sursaturated metallic vapours produced by the impact of streamers or sparks on the grid electrode,

(iii) ultra-fine nucleï formed by slow reactions between secondary gaseous species and afterwards revealed by maturation in a post-discharge step.

Concerning the negative point-to-plane discharges, the results obtained on the production within the discharge gap are not fundamentally different as far as the only regime with plasma-grid interaction lies on the spark regime. Nevertheless, the post-production phenomenon still remains to be investigated in this polarity, even if the present study already underlines the need of taking into account the particles to understand the physico-chemical properties of high pressure electrical discharges.

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