

Plasma – surface interaction phenomena induced by corona discharges. Application to aerosols detection and to diagnosis on surface layers

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Abstract - Atmospheric glow-like discharges can be powerful for gas and for surface diagnoses in gaseous environment. This paper deals specifically with interaction phenomena between such type of discharges and surfaces, which have proved their efficiency either for detection and diagnoses on gas polluting particles or for diagnoses on some characteristics of surface layers, especially on metals, but also on insulating materials.

1. INTRODUCTION

Thanks to its non-uniform gap geometry which provides an important space-charge build-up developing in the low-field region, corona is probably one of the best and surely the easiest way to obtain glow-like discharges in gaseous media at atmospheric pressure or around, let us say from a few 10^2 Pa to a few 10^5 Pa, referred to as atmospheric glow discharges in this text. This explains the large amount of fundamental and applied work published on this aspect of coronas. Actually, applications mainly lie on the electrostatical (or more properly now called electrofluidodynamical) properties or on the chemical properties of the discharge, or, in other terms, on the discharge acting either as a source of electrical charges or as a source of reactive species for plasma chemistry (ref.1).

In the case of plasma chemistry applications, the main uses of discharges are for the production of chemicals of direct industrial interest as ozone or of interest for surface treatments, in particular for improvement of wettability and adhesion properties of plastics (ref. 1) and also, more recently, for corrosion studies (ref. 2). But in another way, for any factor influencing the properties of a discharge, this discharge may provide an appropriate tool to perform diagnoses on it, that can be of interest for different plasma chemistry purposes. It is a field which was not much explored till now and for which atmospheric glow discharges can be useful, as well self-sustained discharges, such as coronas, as not self-sustained discharges, as developed in the Townsend regime. Our aim here is to give an insight on such possibilities, while dealing exclusively with processes where surface phenomena are involved, either as a means or as a goal. In a first step, will be treated gas pollution diagnoses and surface diagnoses where the discharge will act as an electron multiplier, while, in a second step, the discharge will be used as an source of species providing, by their internal energy, surface potential variations useful for diagnoses on properties of surface layers.

2. CURRENT AMPLIFICATION PROCESS PROVIDED BY CHARGED PARTICLES APPROACHING A SURFACE (AND ITS USE FOR GAS POLLUTION DIAGNOSES)

First let us look at the current-voltage characteristic of corona-producing discharges (Fig. 1). At increasing voltage, there is, before corona onset, a region covering a very wide range of currents ($\approx 10^{-12}$ to $\approx 10^{-6}$ A) with a small variation range of voltages (only a few hundreds volts).

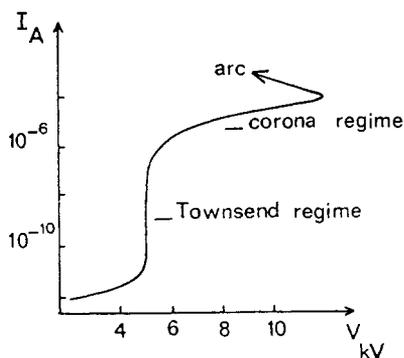


Fig.1. A typical current-voltage discharge characteristic of atmospheric glow discharges, showing in particular the Townsend and corona regimes.

This region corresponds to not self-sustained discharges, in the Townsend regime. Their very rapid increase in current makes them extremely unstable but, at the same time, gives them a remarkably high sensitivity to field/voltage variations and subsequently a great suitability for diagnoses on factors able to provide the necessary field/voltage enhancement. This will in particular be the case with charged particles drifting towards a surface just before hitting it, since the field generated forward by such particles in movement increases rapidly with the decrease of the distance x remaining to cross before reaching the surface. According to A.M. Chakrabarti and P.A. Chatterton calculations (ref. 3), the field increase should become apparent when the charged particles of radius R arrive at a distance $x \approx 4R$ from the surface, reaching a multiplication factor of ≈ 3 for $x = R$ and of ≈ 20 for $x = 0.1R$. By its influence on the primary ionization coefficient $\alpha(E)$, the field increase will locally promote ionization collisions of electrons with gas molecules and thus an increase of current, according to the relation :

$$M = \exp \left[\int_0^x \alpha(E + \Delta E) dx \right] \quad (1)$$

which gives the electron multiplication factor as a function of the coefficient α . The condition $x < 4R$ gives an upper limit for the process efficiency ; there is also a lower limit $x_{\min} \approx 0.5$ to $1 \mu\text{m}$, distance beyond which the field increase becomes inefficient for further ionization because of the too limited number of electron-molecule collisions possible in the remaining gap, but it should on the other hand become efficient for field emission of the surface.

The increase of current provided by Eq.(1) is used for the particles detection. The method has already been put into application for the detection of combustion particles in fire detectors, with devices of reduced size (a few centimeters for over-all dimensions). Figure 2 gives an illustration of its efficiency when submitted to standard fire tests (ref. 4).

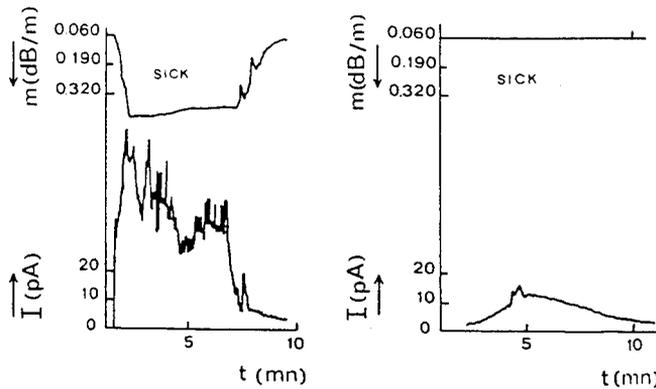


Fig.2. Comparative signals respectively observed with the discharge cell (lower curves) and an opacimeter (upper curves) during tests for the detection of combustion aerosols from normalized fires with heptane (at left) and alcohol (at right) (ref.4).

The principle could be applied to very many types of particles, beginning with all types of solid combustion particles and more generally with all kinds of aerosols, originally charged or not since it is always possible to charge them afterwards, for instance by corona means, for the detection needs. In the same category of applications should enter, with some improvements, the control of atmosphere cleanliness of special rooms, for instance for microelectronics processing. All gaseous particles ending, after reactions, with solid by-products also link to the same category.

3. CURRENT AMPLIFICATION PROCESS THROUGH PORES IN SURFACE LAYERS

On the contrary to the previous case where the initiation of not self-sustained Townsend discharges and the subsequent current increase (in the 10^{-12} - 10^{-6} A range) were the phenomenon used as a detection means, in the present case it is an increase of current of established corona discharges (in the 10^{-6} - 10^{-4} A range) which determines the detection signal. The amplification process concerned is well known from people acquainted with the functioning of electrostatic dust precipitators which may give rise to so-called back discharges. In this case, it is a disturbing phenomenon which occurs when the collecting electrode settled in the low field drift region of the electrode gap becomes covered with dust. In principle, no ionization is expected in this region, but electrical charges accumulating on the porous insulating layer formed by the dust produce a field high enough to develop microdischarges and consequently electron multiplication in the pores of the layer.

The phenomenon will present a threshold voltage monitored by the charges accumulating on the surface layer and be dependent on the mean diameter ϕ of the pores, on their mean length l and on the conductivity σ of their walls :

$$V_0 = f(\phi, l, \sigma)$$

It provides a tool for investigations on porous layers of low electrical conductivity on a conducting substrate as

may be formed by collected particles from the gas pollutants discussed in the previous section, but also as might constitute different kinds of plasma-deposited films on metallic surfaces. Diagnoses on the over-all porosity of layers will be achieved by current measurements with reference to values obtained without microdischarges. As an illustration, Fig. 3 shows the current enhancement produced by a simple paper sheet placed on the low field electrode of a negative air corona gap (ref. 5).

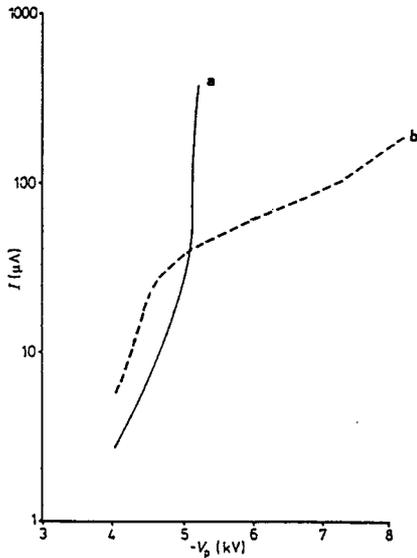


Fig.3. Current-voltage characteristics of a negative corona discharge with (curve a) and without (curve b) a porous layer, here a paper sheet, placed on the low-field electrode. One can see how microdischarges across the paper pores produce a significant current enhancement for voltages above ≈ 5 kV.

In fact, charges deposited on the surface layer behave here as a virtual electrode, providing an easy way for charging (or discharging) surfaces on which it should be less easy to set a metallic electrode in good contact. It is a solution sometimes used on insulating materials for surface and volume conductivity measurements (ref. 6).

4. CORONA-ASSISTED SURFACE POTENTIAL MEASUREMENTS FOR DIAGNOSES ON SURFACE LAYERS

We just saw a first set of applications based on the use of a corona plasma as a source of ions which develop electron multiplication phenomena in gaseous paths constituted by pores in a surface layer. But, as already mentioned, corona can be used in the same way as a tool for surface charging and discharging purposes and, in this case, it is more the electrical properties of the material itself which enter into play ; appropriate measurements can then be performed by surface potential measurements (which allow to follow potential variations of a surface B with respect to a stable reference surface A). Moreover, as we shall see later, not only the charged particles of the corona products can bring informations on the surface layers, but also neutrals and photons having got an internal energy sufficiently high to promote the displacement of electrons from the substrate to the surface. This will be for instance of special interest to study superficial layers of metallic surfaces in a gaseous environment at atmospheric pressure or around without appealing to more elaborated methods operating in vacuum, that may influence the surfaces to be studied.

But, first of all, of what are really made the superficial layers of a metallic surface in a gaseous environment ? Depending on the gas and on the impurities present in it, oxides, sulphides, salts, water molecules, OH groups polar and non polar organic pollutants, and indeed adsorbed gas molecules are to be found in more or less important amounts in the superficial layers forming an interface between the solid and the gas. These layers will influence the surface work function and, since the surface potential varies in the opposite way to the work function, it will be possible to have access to the surface work function variations by surface potential measurements. Let ΔV_s be the potential of a clean surface B with respect to a stable reference sample A, of gold for instance. We shall have :

$$\Delta V_s = \frac{1}{e} (\phi_A - \phi_B) \tag{2}$$

ϕ_A and ϕ_B being the respective work functions of the two samples A and B. If surface layers on B modify its work function by a positive or negative amount $\Delta\phi_B$, we shall find for ΔV_s a new value :

$$\Delta V'_s = \frac{1}{e} [\phi_A - (\phi_B + \Delta\phi_B)] \tag{3}$$

which gives

$$\Delta\phi_B = e(\Delta V_s - \Delta V'_s) \tag{4}$$

Physically, the potential variations are explained by the transport of electrons from materials of lower work

functions to materials of higher work functions. If now we have to do with superficial layers on B which possesses deep electron traps at their surface as provided by adsorbed gases, the growth of these layers will often be associated with an increasing negative potential for $\Delta V'_s - \Delta V_s$ and if we assume that the layers are thin and that the charge acquired is uniformly distributed at the external surface, it can be admitted that :

$$\Delta V'_s - \Delta V_s = \frac{\sigma x}{\epsilon} \tag{5}$$

where $\sigma = \frac{Ne}{S}$ is the surface charge density, which can be supposed constant for layers of increasing thickness x , and where ϵ is the permittivity of these layers. As an example, Fig. 4a curve represents the surface potential variations of tantalum samples covered with Ta_2O_5 layers of variable thickness as a function of this thickness. It shows the validity limit of Eq.(5) for a critical layer thickness x_c and the limited sensitivity of the method especially when the layers thickness increases. From the linear part of the curve corresponding to thickness $x < x_c$, one can get out the density number of deep electron traps on the surface. We find :

$$\frac{N}{S} = \frac{\epsilon}{e} \frac{\Delta(\Delta V'_s)}{\Delta x} \approx 2.4 \times 10^{11} \text{ cm}^{-2}$$

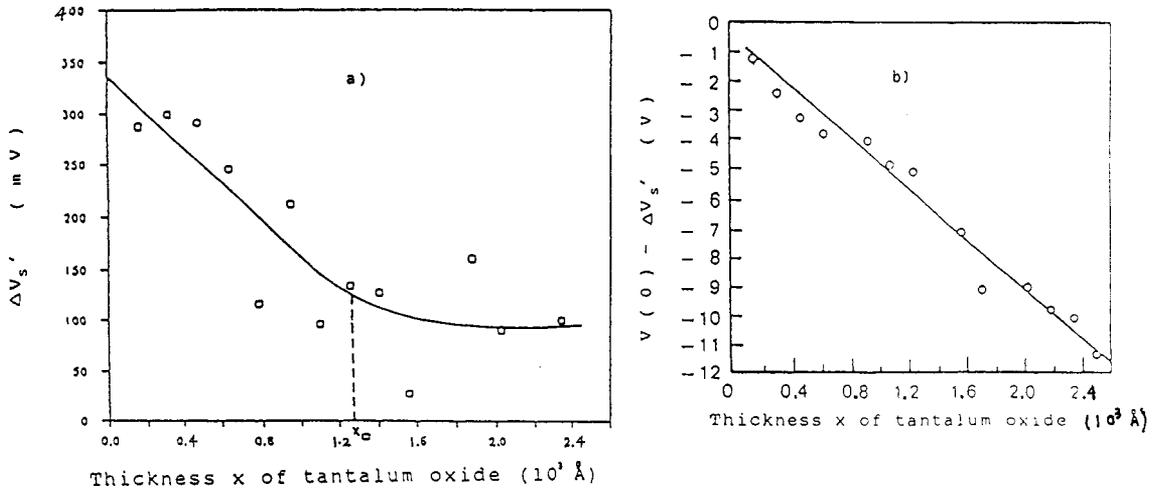


Fig.4. Surface potential variations of oxidized tantalum samples as a function of the thickness of their Ta_2O_5 oxides layers a) measurements without corona assistance b) corona-assisted measurements

Corona-assisted surface potential measurements can increase the sensitivity of the method, as soon as the discharge plasma is able to provide products of enough high internal energy to bring electrons from the substrate to the surface traps, and subsequently to increase the negative trapped charge.

Let us briefly look at the possible contribution of the different kinds of species produced by the discharge plasma. Figure 5 shows that the neutrals, photons included, bring a much larger contribution than ions.

But, in all cases, all contributions will decrease as the layers thickness will increase (Fig. 6), giving their place, when ions are among the discharge particles provided to the surface, to another mechanism where the layers are

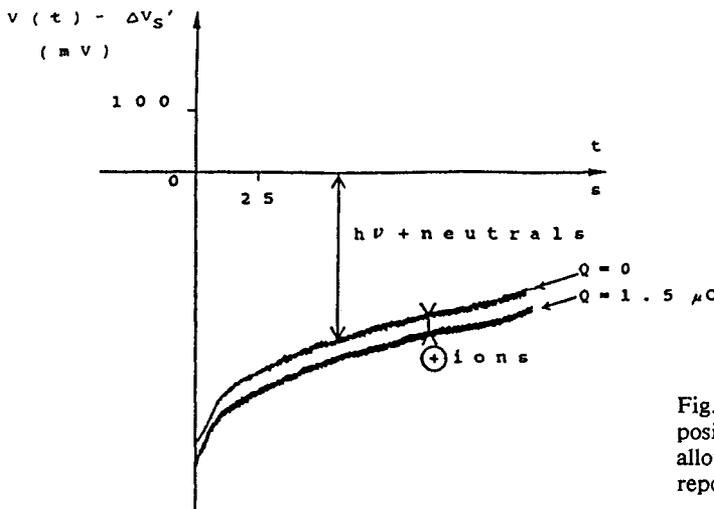


Fig.5. Surface potential signals induced by positive corona products on an aluminium alloy sample (just after mechanical repolishing).

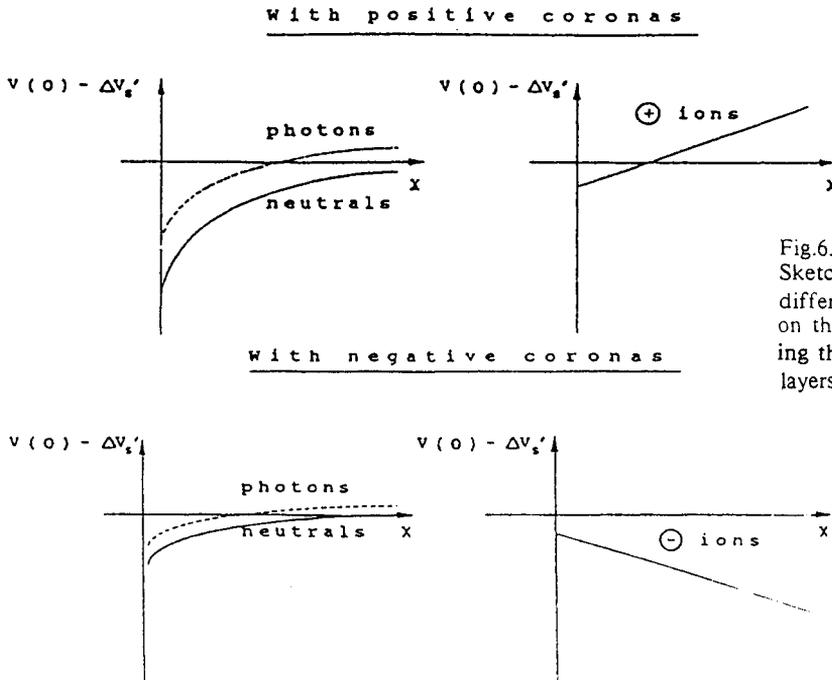


Fig.6. Sketch of relative effects of the different kinds of corona products on the surface potential for increasing thickness of surface "insulating" layers.

now supposed to behave as dielectric films with respect to the external charge $Q = \int idt$ brought to them by the discharge.

Modelling on this basis the surface potential decay after the supply of a charge Q , one can write :

$$V(t) - \Delta V_s' = V(0) e^{-t/\tau}$$

with $V(0) = \frac{Q}{C} = \frac{Qx}{\epsilon s}$, C representing the capacity of the superficial layers with the substrate playing as one capacitor plate and the charge over it as the second plate. The proportionality between $V(0)$ and x , as shown by Fig. 4b, will give access to the layers thickness and it will be possible to get informations on the layers nature by looking the decay constant :

$$\tau = RC = \rho \epsilon$$

where R represents the resistance of the layers working as an imperfect dielectrics and ρ its resistivity. A very high sensitivity can be obtained with such corona-assisted surface potential measurements which allows the observation of one single monolayer.

5. CONCLUSION

Corona-assisted diagnoses thus appear very sensitive, easy to use and relatively cheap. Adequate reproducibility is generally obtained but specific applications may need the use of compensating signals to become free from interfering effects.

The given survey is far from exhaustive. Effectively, a surprisingly wide variety of applications is potentially existent, see for instance the use of plasmas as virtual electrodes for the study and the evaluation of solid properties which can be linked to electrical properties. If we now turn to the exploitation of plasma induced gas phenomena, another wide diagnoses area opens.

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