Experimental study of atmospheric pressure surface discharge in helium

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Received 14 February 2001; accepted 15 May 2001

Abstract

The surface discharge generated at atmospheric pressure in helium was examined by monitoring the current and voltage at the discharge electrode. The discharge generated in helium behaves differently when compared to that generated in other gases (e.g. air). The single discharge duration and the time between consecutive discharges are longer because there is a different mechanism of discharge evolution. The metastable helium atoms play the most important role for discharge generation.Streamer-like and glow types of discharge were observed. The decay of helium metastables concentration determines the discharge regime. Hence, operation conditions have strong influence on the discharge regime. The introduction of gas flow removes metastable quenchers (gaseous products from dielectric and electrode surfaces) and transition to glow discharge is observed. Also covering the discharge electrode with thin dielectric foil to suppress Auger de-excitation of metastables at metal surface leads to generation of atmospheric pressure glow surface discharge. Properties of this discharge are comparable with properties of glow discharge at low pressure (e.g. the electron concentration). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Surface discharge; Metastable excited helium; Atmospheric pressure glow

1. Introduction

Plasma processes like e.g. the gas discharge treatments of polymer surfaces for improvement of wettability [1], adhesion [2,3], biocompatibility [4] or generation of ozone [5] are broadly accepted industrial techniques. The processes in a low temperature, low-pressure plasma allow a very strong modification of the surface properties. The disadvantage of low-pressure plasma is the need for an expensive vacuum system and low throughput capacity. Especially in the case of continuous processes for fibre, textile or foil modifications, a sophisticated air–vacuum–air transfer is necessary. The atmospheric pressure discharges as corona discharge [6], barrier discharge [7], spark or arc discharges avoid this disadvantage. But there are some other drawbacks of such discharges, e.g. weak modification, inhomogeneous treatment or limitation of size (thickness) and shape of treated material. Electrical discharges at near-atmospheric and higher pressure have a tendency to create plasma filaments, which are followed by a rapid formation of arc or spark. Also the type of the discharge and the discharge parameters such as discharge electrodes configuration, the type of energisation and gas depend critically on the form of material to be treated. This is why there is motivation for development of new atmospheric pressure plasma processes.

A discharge generated at a dielectric surface can generate highly active non-equilibrium plasma even at atmospheric pressure and room temperature. This type of discharge, called surface discharge, consists of a large number of mini nanosecond pulse streamers starting from the edge of the discharge electrode and developing in the vicinity of the dielectric surface. Streamers uniformly cover the dielectric surface. Devices based on surface discharge are used e.g. for generation of ozone [8], decomposition of gaseous pollutants [9,10], synthesis of ultrafine particles [11] or for treatment of nonwoven and woven textiles to achieve higher wettability or improved adhesion properties [12]. The streamer-like structure of the surface discharge enables homogeneous treatment of large-sized samples, but it causes small-scale treatment inhomogeneities. The localisation of treatment leads to the limitation of surface transformation, because a part of the surface can be degraded before the rest is sufficiently transformed.

Some features of the surface discharge are similar to the barrier (silent) discharge (e.g. filamentary structure). The surface discharge differs from the barrier discharge chiefly in that the streamers are parallel to electrodes and the dielectric
surface. In case of barrier discharge, they are perpendicular to electrodes and the dielectric barrier. The breakdown of gas at atmospheric pressure in the presence of dielectric barrier (barrier discharge) results in a large number of streamers or micro-discharges (filamentary discharges), which are very restricted in space (place of occurrence and size). Transition of the barrier discharge to the glow discharge (this discharge does not present a radial localisation, it means it is not a filamentary but a volume type of discharge) is known as atmospheric pressure glow discharge (APGD) [13–16]. Kanazawa et al. [17] showed that a stable and homogeneous discharge could be obtained, if some requirements are fulfilled (power supply frequency is higher than 1 kHz, insertion of a dielectric plate between metal electrodes and use of a helium dilution gas). APG discharges were shown to be of great interest for several applications including surface activation [18], ozone synthesis [19,20] or synthesis of polymer films [21]. It was shown by Okazaki et al. [13] that the measurement of the discharge current pulse shapes is a method of distinguishing between the atmospheric pressure glow discharge and the barrier discharge.

APG discharge with the same structure as that known for a low-pressure discharge could be obtained in helium. The aim of the present work is to investigate the transition of the surface discharge from the streamer (filamentary) type to the glow type at atmospheric pressure in helium using time resolved electrical measurements. Helium is very appropriate for this study because in case of barrier discharge it is easy to obtain both kinds of discharges in this gas.

2. Experimental set-up

The experimental arrangement used to study the surface discharge generated in helium at atmospheric pressure is sketched in Fig. 1. The discharge system consists of two electrodes separated by \(100 \times 100\) mm\(^2\) high-purity \(\text{Al}_2\text{O}_3\) ceramic plate. The thickness of alumina plate is 0.5 mm. The alumina plate has a discharge electrode on its upper surface and an induction electrode on its lower surface. The discharge electrode consists of 21 interconnected 1-mm-wide, 10-\(\mu\)m-thick and 80-mm-long strips with 3 mm strip-to-strip distance. The induction electrode is a square shaped \(90 \times 90\) mm\(^2\) and 10 \(\mu\)m thick deposited on alumina plate. Electrodes are made of tungsten. In some of our experiments, the upper side of the dielectric plate and discharge electrode is covered with 10-\(\mu\)m-thick PVC foil.

The discharge system is housed inside a glass chamber to allow containment of the process gas. Firstly, vacuum pumping is carried out in the vessel until a pressure of 10 Pa is reached. Then the process gas is introduced raising the pressure up to atmospheric pressure. A gas flow can be added maintaining the atmospheric pressure by slight pumping. The experiments are performed in helium (from Air Liquide) at atmospheric pressure.

A sinusoidal high voltage with a frequency of 2 kHz and peak-to-peak voltage 4 kV is applied between the discharge and induction electrodes. This produces a stable surface discharge starting from both edges of each strip electrode and covering uniformly the ceramic surface (Fig. 2).

The discharge voltage is measured with the high voltage probe (Tektronix P6015A), the discharge current is measured with the Rogowski coil (Pearson 4100) and they are visualised on a digital oscilloscope (LeCroy 9310AM). The typical voltage and current applied to the electrodes are shown in Fig. 3. The time distance between consequent single discharges \(\Delta t\) and the time of a single discharge current rise and decay \(\tau\) are measured from the current
Fig. 2. The atmospheric pressure surface discharge generated in helium.

The typical voltage and current waveforms of the surface discharge generated in helium.

Waveform (Fig. 4). Values of $\Delta t$ and $\tau$ represent mean value calculated from at least 5 single current peaks with amplitude $\Delta I$ higher than $\Delta I_{\text{max}}/e$, where $\Delta I_{\text{max}}$ is the height of the highest current peak during discharge period. Value of $\tau$ is the width of the current peak $\Delta I$ in $1/e$-part of amplitude.

3. Decay of APG Surface Discharge

It is known that helium metastable excited atoms are responsible for transition from the streamer-like discharge to the atmospheric pressure glow discharge because they maintain a production of electrons between two discharge pulses [16].

The streamer-like and glow discharges both produce nonequilibrium plasma, but the reason in each case is different. In case of streamer-like discharge, the lifetime of streamer is too short (few ns [22]) to transfer sufficient amount of energy from electrons to neutral particles. In APGD, the metastable excited atoms are the source of high-energy electrons. Each of the electrons emitted by the metastable–metastable collision loses its energy very fast (ns range) due to the elastic collisions. Consequently, the energetic equilibrium between such electrons and heavy particles is not possible, but due to high energy of these electrons and large energy accumulated in metastable atoms and gradually released in discharge volume, the glow discharge can be sustained. It was calculated that the density of the seed electrons, being greater than $10^6 \text{ cm}^{-3}$ is sufficient to produce the next breakdown under a low electrical field in helium at atmospheric pressure [23]. The density of metastables at the ignition depends strongly on their rate of creation during discharge and destruction during the time separating two consecutive discharges.

The decay of the metastable excited atom concentration $n_M$ can be calculated from the balance equation for metastable states [24]:

$$\frac{\partial n_M}{\partial t} = D\nabla^2 n_M - P$$  \hspace{1cm} (1)

where $D$ is the diffusion coefficient and $P$ is the volume loss term. At high pressure in the bulk plasma, the diffusion losses can be neglected compared to volume losses.

For high-pressure three main metastables loss processes should be taken into account [25]:

1. $\text{He}^2(2^1S) + \text{He} + \text{He} \rightarrow \text{He}_2(2^3\Sigma_u^+) + \text{He}$ 
   (three-body de-excitation)

2. $\text{He}^2(2^1S) + \text{He}^2(2^3S) \rightarrow \text{He}^+ + \text{He} + e$ 
   (binary metastable collision ionisation)

3. $\text{He}(2^3S) + e \rightarrow \text{He}^+ + 2e$ 
   (cumulative ionisation)
The third of these mechanisms can be disregarded when direct ionisation mechanisms are switched off. The second mechanism is not determining the duration of the APGD, because the destruction speed is decreasing with square of the metastables concentration [26]. Therefore, the destruction rate of metastables due to the mechanism 1 starts to be dominant and in a matter of facts is crucial for determination of the de-excitation time of metastables.

The volume loss term \( P \), taking into account only the de-excitation due to the three body collisions with neutral particles accordingly to mechanism 1, is given by the expression:

\[
P = n_S n_M K_{M}^0
\]  

(2)

where \( K_{M}^0 = 2.5 \times 10^{-46} \text{ m}^6 \text{ s}^{-1} \) is quadratic destruction coefficient for \( ^2\text{S} \) metastable [27].

Now the balance of metastables can be written in simplified form as:

\[
\frac{\partial n_M}{\partial t} = -n_S n_M K_{M}^0
\]  

(3)

Solving this equation, the ratio of remaining metastable concentration after time \( t \) to the metastables concentration after switching off the heating mechanism \( n_M \) is given as:

\[
\frac{n_M}{n_{M_i}} = \exp\left(-\frac{t}{\tau_M}\right)
\]  

(4)

where \( \tau_M \) is the metastable decay constant given as:

\[
\tau_M = \frac{1}{n_N^2 K_{M}^0}
\]  

(5)

For neutral particle concentration \( n_N = p/(kT) = 2.4 \times 10^{25} \text{ m}^{-3} \) this time constant is 7 \( \mu \text{s} \) which is 3 orders of magnitude higher than the typical lifetime of streamer in a conventional barrier discharge [28].

The decay of metastable helium is faster, when contamination of the gas is present. The destruction mechanisms are in this case Penning collisions, i.e. ionisation [29]:

\[
\text{He}(^2\text{S}) + X \rightarrow \text{He} + X^+ + e
\]

An important destruction mechanism of metastable helium at conducting surface atoms (i.e. at the surface of the electrodes) is the Auger de-excitation [30].

4. Determination of discharge parameters

Models and formulas used for estimation of the time evolution of streamers in conventional surface discharges [31] are not suitable for helium APG surface discharge, which has properties much more similar to those of the low pressure positive glow discharge [23].

A characteristic feature of the APG surface discharge is the much longer duration time of the single breakdown event \( \tau \). Hence, the discharge has a relatively low resistivity, during such an event the charge stored in the ceramic capacitor between induction and discharge electrodes discharge not along a narrow streamer channel but over the large part of the ceramic surface (Fig. 5). Consequently, much longer time \( \Delta t \) is needed to charge this capacitor up before the next breakdown can occur. This explains the longer period \( \Delta t \) observed between the single breakdown events (Fig. 4).

The change of the electrical charge stored in ceramic capacitor can be estimated from the current flowing to the induction electrode according to the formula:

\[
\Delta Q = \int_{t_1}^{t_2} I(t) \, dt
\]

(6)

It is \( \Delta Q = 6.6 \times 10^{-9} \text{ C} \) for the example of the breakdown event depicted in Fig. 4, which represents typical current and voltage waveforms of discharge generated in helium (gas flow is introduced).

During the discharge of the ceramic capacitor through the APGD, the drop of voltage measured on the discharge electrode is \( \Delta V \). It corresponds to the difference between ignition voltage and sustaining voltage of the APGD. For the considered breakdown event in Fig. 4 it is \( \Delta V = 112 \text{ V} \). By knowing the charge and the voltage changes of the ceramic capacitor, its effective electrical capacity \( C_{\text{eff}} \) can be calculated:

\[
C_{\text{eff}} = \frac{\Delta Q}{\Delta V}
\]

(7)

and it is in our case 59 pF. For ceramic plate with a thickness of \( d = 0.5 \text{ mm} \) and dielectric constant \( \varepsilon = 6 \) this corresponds to the area of the effective capacitor \( A_{\text{eff}} \) given as:

\[
A_{\text{eff}} = \frac{C_{\text{eff}} d}{\varepsilon \varepsilon_0} = 5.6 \times 10^{-4} \text{ m}^2
\]

(8)

Assuming, that this area is a narrow strip with length \( w = 3.4 \text{ m} \) along the entire discharge electrode just at its edge, we obtain the width of this strip \( L = 0.17 \text{ mm} \) (Fig. 5). It is about three times less than the width of the region with high light emission intensity (Fig. 2). This discrepancy can be explained by the fact, that strong light emission can still be observed when the electron concentration drops by several orders of magnitude, but the largest part of current to the ceramic capacitor is flowing within the width, which is not less than \( 1/e \) part of the maximum electron concentration in the vicinity of the discharge electrode edge.

Fig. 5. The equivalent electrical circuit for the discharge.
From the time diagram in Fig. 4 we can also estimate the APGD resistance accordingly to formula:

\[ R = \frac{\Delta V}{\Delta t} \]  

(9)

In this case \( R = 18.7 \, \text{k}\Omega \). Assuming, that the height of the APGD is determined by the height of the discharge electrode \( h = 10 \, \mu\text{m} \), the resistivity of the discharge can be obtained:

\[ \rho = \frac{Rwh}{L} \]  

(10)

We can calculate the electron concentration using the resistivity of 3.8 k\Omega m (Eq. (10)) from formula:

\[ \rho = \frac{m_e v_m}{e^2 n_e} \]  

(11)

The frequency for electron–neutral particle momentum transfer collisions \( v_m \) is given by:

\[ v_m = n_N \sigma_m v_e \]  

(12)

For a typical cross section \( \sigma_m = 10^{-19} \, \text{m}^2 \) [32] (for momentum transfer at electron temperature 3 eV), neutral particle concentration \( n_N = \rho/(kT) = 2.4 \times 10^{25} \, \text{m}^{-3} \) (at gas temperature 300 K) and thermal velocity of electrons:

\[ v_e = \sqrt{\frac{8kT_e}{m_e}} = 1.2 \times 10^6 \, \text{m s}^{-1} \]  

(13)

the collision frequency is \( v_m = 2.8 \times 10^{12} \, \text{s}^{-1} \). The electron concentration calculated from Eq. (11) is \( n_e = 2.6 \times 10^{10} \, \text{cm}^{-3} \). This value is comparable with value typical for low pressure, high density glow discharges.

5. Influence of operation conditions

The current waveform of streamer-like discharge is shown in Fig. 6a in the case of no gas flow and with electrodes non-covered with dielectric foil. The time constant of single discharge \( \tau \) is 0.24 \( \mu \text{s} \) — much shorter than in case of pure helium without impurities i.e. metastable quenchers (see the value calculated in previous paragraph). The time between two single discharges is only 1.7 \( \mu \text{s} \), which is a simple consequence of the short duration time of the single discharge (see Eq. (6)). As only small charge is taken from the ceramic capacitor because of the limited size and short

![Graphs](image-url)

Fig. 6. Time evolution of the current flowing during cathodic half-period of the surface discharge excitation cycle: (a) with electrode system non-covered with dielectric foil without gas flow; (b) with electrode system non-covered with dielectric foil with gas flow; (c) with electrode system covered with dielectric foil without gas flow; (d) with electrode system covered with dielectric foil with gas flow.
duration of streamers, much shorter time is needed to compensate it for achieving again the breakdown voltage.

When introducing the gas flow, the gaseous products are removed from the dielectric and electrode surfaces and the time constant \( \tau \) increases to 0.89 \( \mu \text{s} \) (Fig. 6b). From the calculation in the previous paragraph the transition to APGD can be observed. In this case, much larger charge is taken from the ceramic capacitor (see Eq. (6)), because discharge is not developing in streamers. Hence, the time between two consecutive discharges is much longer than in previous case.

Fig. 6c illustrates that the influence of metallic surface is even stronger than volume impurities. The introduction of a dielectric coating to the metallic surfaces leads to extension of the single discharge time up to 2 \( \mu \text{s} \).

Also in this case the introduction of a gas flow causes an increase of \( \tau \) to 4.9 \( \mu \text{s} \) (Fig. 6d), which is already very close to the estimated theoretical value of metastable helium atom lifetime (7 \( \mu \text{s} \) from Eq. (5)).

6. Conclusions

The main conclusion of this work is that there is a possible transition of atmospheric pressure surface discharge generated in helium from streamer-like to glow type. Transition to glow discharge is possible when enough energy is stored in the gas between two consecutive discharges. The main species controlling the breakdown mechanism are the seed electrons and the metastable atoms. The higher the density of metastables when discharge is ignited the easier it is to obtain glow type of discharge. Their density at the ignition depends strongly on their rate of creation during discharge and destruction during the time separating two consecutive discharges.

The metastables are created during discharge. However, there is also a production of gaseous product from the electrode and the dielectric surfaces. These impurities interact with helium metastable atoms in Penning collision and increase their destruction rate. This effect can give rise to high destruction of metastables and consequently to transition from the glow type to the streamer-like discharge. The relation between the discharge regime and the presence of impurities in process gas discussed in [18] is in good agreement with our experiments. Without any gas flow, amount of metastable quenchers increases and transition to glow type was not possible in our experiments.

Another mechanism, which substantially accelerates the destruction of metastables, is Auger de-excitation in the vicinity of metal surfaces (e.g. electrode surface). This mechanism can be reduced by covering the electrode system with thin dielectric foil.

So the metastable state quenchers mainly control the transition from streamer-like to glow type of discharge. The destruction of metastable helium can be suppressed by:

- using gas flow to remove the gasified products from the foil out from the discharge zone to suppress Penning collisions
- covering the discharge electrode with dielectric foil to suppress Auger de-excitation of metastables.

Acknowledgements

The authors wish to thank Akihiro Etoh for arranging the experimental set-up and technical support.

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