Nanoparticles formation and deposition in the trichel pulse corona

R H Amirov 1, A A Petrov 2,3, I S Samoylov 1
1 Department for Gas-Discharge Physics and Plasma Technologies, Joint Institute for High Temperatures of RAS, Izhorskaya 13 Bd 2, Moscow, 125412, Russia
2 Department of Physical Electronics, P.N.Lebedev Physical Institute of RAS, Leninskiy prospekt 53, Moscow, 119991, Russia
3 Moscow Institute of Physics and Technology, Institutskii per. 9, Dolgoprudyennyy, 141700, Russia

E-mail: amirovravil@yandex.ru

Abstract. Cathode erosion in the negative corona discharge has been studied in the point-to-plane electrode configuration with Cu cathodes in the Trichel pulse regime. Redeposition of erosion products has been found on the cathode surface in form of agglomerates of 10-nm nanoparticles. Nanocraters and nanoparticles formation in the negative corona discharge has been considered in frames of electro-explosive mechanism of cathode erosion. According to this mechanism the cathode erosion is performed as a consequence of elementary erosion events each of which is caused by a Trichel pulse. A 1-dimensional model of corona-produced nanoparticles dynamics in the gap was elaborated. According to results of the simulation, the redeposition is explained by charging of the nanoparticles due to positive ions adsorption and thermionic emission. The size, temperature and initial velocity of the aerosol nanoparticles have the decisive action on redeposition in the negative corona discharge.

1. Introduction
Negative corona discharge in the Trichel pulse mode [1] is a source of nanometer size aerosol particles which are produced as result of cathode erosion [2]. Nolan and Kuffel [2] proposed that aerosol particles in negative corona were produced due to condensation of cathode material vapors. To the same conclusion Borra [3] came. However, Nolan and O’Toole [4] noted that further work was required to elucidate the nature of the discharge nuclei at the moment of formation.

Cathode erosion in the negative corona discharge was first reported by Bennet [5]. However the mechanism of the cathode erosion in the negative corona is still unclear. The main hypotheses of the cathode erosion mechanism in the negative corona discharge are the next: sputtering by positive ions [6–8], chemical sputtering [7, 9], formation and destruction of dielectric layers [10], epton and electro-explosive processes [11–13]. Possibility of local heating and evaporation of cathode in corona was discussed by Goldman and Sigmond [7] and Borra [3].

The redeposition of erosion products on the cathode surface may occur [1] in the negative corona discharge. This process was explained by back diffusion [1, 14], divergent electric field action [15], trapping by vortex of electric wind [15, 16]. Redeposition of erosion products in the negative corona...
was reported in case of copper cathodes [11, 14], iron and aluminum cathodes [14], platinum cathodes [1]. However redeposition was not found in case aluminum cathodes [17] as well as in case of graphite cathodes [18]. Note that back diffusion and trapping by air vortexes predict the redeposition in case of any cathode material, but the action of the cathode material on the redeposition process seems to occur. So the other mechanisms of redeposition should be considered in the negative corona discharge.

The conclusion is that cathode erosion, nanoparticles formation, and redeposition process in the negative corona discharge should be considered in the context of a single model. The aim of this work is to explain these processes from the point of view of electro-explosive mechanism. For this purpose the cathode erosion in Trichel pulse corona was studied and a 1-dimensional model of erosion products transport in the gap was elaborated.

2. Experimental setup and procedure
Negative corona discharge has been studied in air in the point-to-plane electrode configuration in the Trichel pulse mode. Cathode pins were made of copper with tip diameter 10-100 mkm. Positive dc voltage on the range of 10 kV was supplied to the anode plane, which was an 8-cm diameter silicon disc. Cathode axis was perpendicular to the anode plane, the gap was 10 mm.

Discharge current was registered by S1-75 dial oscillograph with 300 MHz bandwidth which was connected across a 50-Ohm resistor between the cathode and the ground. Average discharge current was registered with use of M-906 dial ammeter; average current was 20-100 mkA. Relative humidity of air was in the range of 60-80 % and did not influence the regimes and typical erosion pictures observed.

Cathode surface during discharge was video-recorded with use of Canon w705i camcorder and MBS-9 binocular microscope with spatial resolution 1 mkm and exposition of a single picture 40 ms. The total time of discharge was 5-90 min so the cathodes became at least 30 mkm shorter due to erosion.

After treatment in discharge the cathodes were analysed with use of Jeol JSM-7001F and FEI Quanta 200 electron microscopes with spatial resolution ~ 1 nm. The X-rays componential analysis of the copper cathode surface with sensitivity 0.01 at.% has also been performed.

3. Results of experiment
Erosion was found in form of reduction of the cathode pin length with typical rate few mkm/min and in formation of micro and nanocraters on the tip. A copper cathode before and after treatment in the Trichel pulse corona is shown in the figure 1 – deleted and redeposited parts are well distinguished with use of optical microscope. Trichel pulse amplitude was 0.3 mA, the frequency of the Trichel pulses was 500 kHz at average current 60 mkA. A typical copper cathode tip after treatment is shown in the figure 2. The tip of the cathode is smooth as result of the discharge erosive action. Redeposited erosion material is observed in form of nanostructures on the side of the tip - figure 2. The edges of the redeposited structures are covered with 10-nm clusters which are forming the crystals probably due to field and temperature assistant surface drift – these clusters are well distinguished in the figure 3. According to results of X-ray analysis the redeposited structures consist of copper and oxygen in the proportion approximately 1:2. No traces of oxygen were detected on the smooth part of the tip.

Redeposition of erosion products has also been found in case of silver and platinum cathodes at atmospheric pressure. Redeposition on graphite cathodes was found at pressure lower than 200 torr.
4. Discussion

4.1 Nanocraters and nanoparticles formation

According to results of Asinovskii et al. [11] and Petrov et al. [18, 19] the cathode erosion mechanism in the negative corona discharge has the electro-explosive nature. This conclusion follows from the estimate of the integral of the specific action of a Trichel pulse for copper and graphite cathodes. According to the electro-explosive theory, the erosion process on the cathode is performed as a consequence of elementary erosion events. Each elementary erosion event is associated with a Trichel pulse and results in the formation of an elementary erosion crater on the cathode surface [19] – these 40-nm craters are shown in the figure 3.

The size of an elementary erosion volume was taken as relation of total erosion volume to total number of Trichel pulses during experiment. This value was calculated as $10^3$ nm$^3$. The current density $j$ on the cathode surface during a Trichel pulse was taken as relation of Trichel pulse amplitude to cross-section of an elementary erosion volume. It was estimated as $\sim 5 \cdot 10^8$ A cm$^{-2}$. Then the value of the integral of specific current action of a Trichel pulse:
\[ h = \int_{0}^{\tau} j^2 dt \sim 10^9 A^2 \cdot s/cm^4 \]  

(1)

where \( \tau = 10 \text{ ns} \) – FWHM of a Trichel pulse.

For graphite cathodes the integral of specific action of a Trichel pulse (1) was measured as \( 10^8 \text{ A}^2 \text{s cm}^{-4} \) [18]. Values of the integral of Trichel pulse specific action indicate that erosion in the Trichel pulse negative corona discharge is the most probably associated with the electro-explosive mechanism – the same values of the integral of specific current action are known from the experiments on the wire electrical explosion [20].

The mechanism of the cathode erosion in the negative corona discharge is described as follows. Local energy release is associated with the field emission on the micro-asperity on the cathode surface due to positive space charge of the cathode-directed ionization wave. These waves were experimentally registered by Ikuta and Kondo [21] and electric field strength in front of the head of this wave was calculated by Napartovich et al. [22] on the range of \( 10^6 \text{ V} \text{ cm}^{-1} \). This value may be increased in 10-1000 times due to micro-asperity geometry [23]. Pulsed electric field with magnitude up to \( 10^8 \text{ V} \text{ cm}^{-1} \) will result in field emission and local Joule heating of the bulk up to critical temperature \( 10^4 \text{ K} \) [24] in few nanoseconds – this causes the local electrical explosion and dispergation of the bulk. The size of aerosol particles which are presented in the figure 3 coincides with typical electron free path inside the cathode (10 nm) according to the hypothesis discussed by Lebedev and Savvatimskii [25], or critical size of nucleated particles (1-10 nm) according to theory presented by Tkachenko et al. [26].

Lebedev and Savvatimskii [25], and Vorob’ev et al. [27] reported that 10-nm scale particles were produced in the process of wire electrical explosion due to dispergation of the wire. Explosive mechanisms of the cathode erosion in corona [11, 13] admit the aerosol formation due to direct dispergation of cathode bulky media without equilibrium vapor phase. So physics of cathode erosion in the negative corona may be similar to one in the processes of wire electrical explosion.

4.2 Nanoparticles redeposition model

A 1-dimensional model of the cathode erosion products dynamics in the negative corona discharge gap was elaborated. As was discussed in the previous section, the products of the cathode erosion in the negative corona discharge were 10-nm size aerosol particles. According to the electro-explosive hypotheses of the cathode erosion the initial velocity of these particles may be taken from the results of experiments on the wire electrical explosions up to \( 10^3 \text{ m sec}^{-1} \) [25, 28]. According to estimates of Lebedev and Savvatimskii [25], the initial temperature of particles in the process of wire electrical explosion was on the range of critical one (8900 for copper wires). It was proposed that the particles were uncharged in the moment of formation – otherwise the particles would be subjected to redeposition regardless the other initial parameters. The motion of a single aerosol particle in the gap may be described by the next equation:

\[ m \frac{dV}{dt} = F_{dr} + F_{el} \]  

(2)

in which \( m \) is the mass of the particle, \( V \) – velocity of the particle, \( F_{dr} \) – neutral drag force, \( F_{el} \) - electrical force. According to estimates the force of gravity and thermophoresis force and the force of electrical polarization are insufficient and may be neglected in the equation of motion of a 10-nm size particle.

The charging of an aerosol particle may be described by the equation:

\[ \frac{1}{S} \frac{dq}{dt} = j_{T} + j_{pl} \]  

(3)
Here $S$ is the surface of a particle, $j_T$ is the thermionic emission current density, and $j_{pl}$ is the current density of the charged species from the discharge media on the surface of the particle.

The thermionic current density on the aerosol particle surface depends drastically on the particle temperature. So the heat balance of the particle should be considered. Note that the heat redistribution inside a 10-nm size metal particle occurs in ~1 ns. The heat fluxes on the particle surface may be described by the equation:

$$mc \frac{dT}{dt} = P_{th} + P_{drag} + P_{rad}$$  \hspace{1cm} (4)

Here $c$ is the heat capacity of the particle material, $T$ is the particle temperature, $P_{th}$, $P_{drag}$, $P_{rad}$ is the total heat flux on the particle surface associated with thermionic cooling, interaction with the air molecules and radiation correspondently.

In the free-molecular regime the neutral drag force expression is [29]:

$$F_{dr} = \pi \rho \nu V r$$  \hspace{1cm} (5)

The Laplace electric field distribution in the point-to-plane gap on the gap axis may be given by the equation [9]:

$$E(x) = \frac{2U}{(r_c + x) \cdot \log \left( \frac{4h}{r_c} \right)}$$  \hspace{1cm} (6)

where $U$ is the gap voltage, $r_c$ is the curvature radius of the cathode, $x$ is the distance from the cathode surface, $h$ is the gap length. According to results of calculations of Napartovich et al. [22], the electric field distribution in the gap is highly disturbed only during the short 20-ns Trichel pulse active phase, and the rest time between pulses it is weakly disturbed. Hence the undisturbed approximation (6) may be used in the aerosol dynamics calculation.

Consider the charging of an aerosol particle by the charged species in the gap. Negative corona discharge flame in average consists of two unipolar zones–positive and negative one. The concentration of the positive ions in the region closer than 100 mkm to the cathode surface is on the range of $10^{12}-10^{13}$ cm$^{-3}$ [22, 30] during the active phase of a Trichel pulse. The positive ions concentration is negligibly small at the distance further than 100 mkm from the cathode surface. Then the charging of an aerosol particle by the attachment of the positive ions may be expressed by the equation [31]:

$$N = n_i \cdot \pi \cdot r^2 \cdot l$$  \hspace{1cm} (7)

where $N$ is the number of the unit charges on the particle, $n_i$ is the concentration of the positive ions in the unipolar positive zone near the cathode surface, $l$ is the path of the particle inside the unipolar charged zone. The approximation has been made that the cross section of the positive ions attachment was equal to the cut of an aerosol nanoparticle.

Charging of the nanoparticles by the negative ions may be described by the same equation (7); the negative ions are distributed in the gap with the maximum concentration approximately $10^{12}$ cm$^{-3}$ in the region between 100 and 200 mkm from the cathode surface. In the region further than 200 mkm from the cathode surface the concentration of the negative ions is sufficiently lower because of its repulsion spreading.

Electrons are formed in the gap due to secondary processes on the cathode surface and because of the impact ionization of the gas during the Trichel pulse active phase. The duration of the active phase is on the range of 10 ns [22]. The concentration of electrons during the active phase is on the range of $10^{13}$ cm$^{-3}$ with average electron energy 10 eV; these electrons are mostly localized in the region between 50 and 150 mkm from the cathode surface. After the active phase is gone the electrons concentration diminishes drastically in 10 ns because of the electron attachment to the oxygen molecules [32]. The charge of an aerosol particle received due to attachment of electrons may be found from the equation [33]:

$$...$$
\[ N = n_e \cdot \pi \cdot r^2 \cdot V_e \cdot \tau \]  \hspace{1cm} (8)

in which \( n_e \) is the electrons concentration, \( V_e \) is the electrons velocity, \( \tau \) is the duration of the active phase of a Trichel pulse. The probability to get an elementary negative charge during the active phase of a Trichel pulse is on the range \( 10^{-1} - 10^{-2} \) for a 10-nm particle. So the aerosol particle should stay in the active region of the discharge during 10-100 mks to get an elementary charge due to electrons attachment.

The ionization threshold of a metal particle is on the range of 5 eV with maximum at 15 eV. According to Smirnov [31] the probability of electrons attachment exceeds the probability of the impact ionization of a particle in the negative glow region of the negative corona discharge flame.

The thermionic current density \( j_p \) on the aerosol particle surface may be expressed by equation:

\[ j_p = A T^2 e^{\frac{\varphi}{kT}} \]  \hspace{1cm} (9)

where \( A=120 \text{ A cm}^{-2} \text{Coul}^{-2} \), \( \varphi \) is the work function of the particle material, \( k=1.38 \cdot 10^{-23} \text{ J K}^{-1} \) is the Boltzmann constant. The work function depends on the particle radius and charge in the following approximation:

\[ \varphi \simeq \varphi_0 + \frac{q}{4\pi \varepsilon_0 r} \]  \hspace{1cm} (10)

where \( \varphi_0 \) is the work function of the particle with no charge. According to the estimates the external field \( E \) does not influence the aerosol material work function in the conditions concerned.

Consider the heat balance of a particle. The thermionic cooling may be specified in the next way:

\[ P_{th} = I \cdot \varphi + 2I \frac{kT}{e} \]  \hspace{1cm} (11)

where \( I \) is the thermionic current on the particle surface; it may be found from the equation (9).

The heat flux associated with the interaction between the aerosol particle and the gas molecules may be found from the diffuse reflection model of the particle cooling in the free-molecular regime [29]:

\[ P_{\text{deg}} = \frac{2m_p n}{\sqrt{\pi}} S \left( \frac{2kT_e}{m_o} \right)^\frac{3}{2} \left( \frac{T}{T_e} \right) I_1(\sigma) - I_2(\sigma) \]  \hspace{1cm} (12)

Here \( S \) is the particle cross section. Parameters \( I_1(\sigma) \) and \( I_2(\sigma) \) may be found from the next equations:

\[ I_1(\sigma) = \exp(-\sigma^2) + \left( \sigma + \frac{1}{2} \right) \sqrt{\pi} \cdot \text{erf} \sigma \]  \hspace{1cm} (13)

\[ I_2(\sigma) = \frac{1}{2} \left( \sigma^2 + \frac{5}{2} \right) \exp(-\sigma^2) + \frac{1}{2} \left( \sigma^2 + 3\sigma + \frac{3}{4\sigma} \right) \sqrt{\pi} \cdot \text{erf} \sigma \]  \hspace{1cm} (14)

in which \( \text{erf} \) is error function,

\[ \sigma = \sqrt{\frac{m_p V^2}{2kT}} \]  \hspace{1cm} (15)

According to the equation (12), the heat flux on the particle surface may be either positive or negative depending on the relation between the particle temperature, ambient temperature and particle velocity.
Different approaches to a nm-particle radiation description exist [34]. In any case the radiation power of a particle and evanescent cooling are sufficiently lower than the neutral drag heat flux in the conditions of the task concerned at least at temperatures smaller than 5000 K.

The system of equations (2-4) was numerically solved in a 1-dimensional nonuniform mesh. Two different types of the system behavior have been revealed – the case of the cold clusters with no thermionic emission and the case of the hot clusters when thermionic emission was active.

In the first case the particle motion may be adequately solved analytically. Position of the particle in time may be approached by the equation:

\[
x(t) = \frac{V_0}{\pi \cdot r^2 n m V_T} \left[1 - \exp(-4\pi \cdot r^2 n m V_T t)\right]
\]

in which \(V_0\) is initial velocity of aerosol particle. In the figure 5 the first line is the trajectory of a 10-nm size copper particle with initial velocity 500 m s\(^{-1}\). This particle remains in the region of the positive unipolar region during the Trichel pulses development. Approximately in 0.1 ms it will get a unit positive charge due to ion attachment and will return on the cathode surface. The second line is the path of a 10-nm size copper particle with initial velocity 1100 m s\(^{-1}\). This particle passes the positive space charge zone in few nanoseconds and enters the region of the negative volumetric charge. As result this particle will get a negative charge and will move away from the cathode surface. So the action of the cathode material on redeposition process may be explained by difference of initial velocities of the aerosol particles in case of different cathode materials. Elimination may also be assisted by trapping of a particle by electric wind.

![Figure 5](image1.png)

**Figure 5.** Dynamics of a 10-nm size copper particle in time: 1 – redeposition is observed at initial velocity 500 m s\(^{-1}\); 2 – no redeposition at initial velocity 1100 m s\(^{-1}\).

![Figure 6](image2.png)

**Figure 6.** Dynamics of a copper cluster with initial velocity 1000 m s\(^{-1}\) with initial temperature 4800 K: 1 – \(r = 3\) nm; 2 – \(r = 4\) nm; 3 – \(r = 5\) nm; 4 – \(r = 6\) nm. In case of 3 and 4 the thermionic charging is responsible for redeposition in 1 mks.

The second type of system behavior takes place when aerosol particles are hot enough initially to get charge due to thermionic emission. In the figure 6 the path of a copper particle with initial velocity 1100 m s\(^{-1}\) is shown. Initial temperature of a particle was 5000 K. In this case the particle will get a unit positive charge in the first 10 ns of its way. As result approximately in 1 mks it will be deposited on the cathode surface. So the action of cathode material on the redeposition process may be explained by difference of initial temperatures of the particles in case of different electrode materials. Change of the particle radius may also influence the redeposition effect, as follows from the figure 6.

So the conclusion is that the redeposition is explained by charging of a particle by positive ions and due to thermionic emission. The proposed model of redeposition is in agreement with the electro-explosive mechanism of the aerosol particle formation.
5. Conclusions
Formation and redeposition of nanoparticles has been studied in the Trichel pulse negative corona discharge. According to results of topographical analysis the redeposited structures on the side of a copper cathode consist of 10-nm size nanoparticles. So the material transport in the negative corona is associated with the flux of nanoparticles.

Nanoparticles formation and cathode erosion in the negative corona discharge was explained by electrical explosions on the cathode surface. The nanometer-size aerosol particles are formed due to dispergation of the cathode bulky media. Values of the integral of specific action of a Trichel pulse confirm the electro-explosive mechanism of cathode erosion and aerosol formation in negative corona discharge.

A 1-dimensional model of the aerosol particles dynamics was proposed. According to results of the simulation, the redeposition is explained by charging of the aerosol particles due to positive ions adsorption and thermionic emission. Redeposition depends drastically on the size, temperature and initial velocity of the aerosol particles.

Acknowledgements
The work has been made under partial financial support of the Ministry of Education and Science of Russian Federation with use of the equipment of the centre of the collective use of Moscow institute of physics and technology (contract № 16.552.11.7022); the authors would like to thank Evgenii Korostylev, Pavel Starikov and Andrei Baturin for microanalysis of electrodes. The work has been made with partial financial support of the Russian Basic Research Foundation, grant № 12-08-01223 “Research of the cathode erosion mechanism in the negative corona discharge”.

References
[1] Loeb L B 1965 Electrical Coronas. Their Basic Physical Mechanisms. Berkeley, CA: Univ. California Press, p 694
[2] Nolan P J and Kuffel E 1957 Geofisica Pura e Applicata. 36 201
[3] Borra J P 2006 Journal Physics D: Applied Physics. 39 19
[4] Nolan P J and O'Toole C P J 1959 Pure and Applied Geophysics. 42 117
[5] Bennet G W H 1940 Physical Review. 58 992
[6] Buchet G and Goldman A 1970 1st International Conference on Gas Discharges, IEE Conf. Publ. 459–462
[7] Goldman M and Sigmond R S 1982 IEEE Transactions on Electrical Insulation. EI-17 90
[8] Weissler G L and Schindler M 1952 Journal of Applied Physics. 23 844
[9] Sigmond R S 1978 Corona Discharges. In: Meek, J.M. and Craggs, J.D. (Ed.) Electrical Breakdown of Gases, Wiley: London, chapt. 4, p. 319–384
[10] Korge H, Laan M and Paris P 1993 Journal Physics D: Applied Physics. 26 231
[11] Asinovskii E I, Petrov A A and Samoylov I S 2008 Technical Physics. 53 279
[12] Laan M, Paris P and Repan V 1997 J. Phys. France. 4 259
[13] Mesyats G A 1995 Physics-Uspekhi. 38 567
[14] Giao T N and Jordan J B 1970 Journal of Applied Physics. 41 3991
[15] Laan M and Mirme A (2000). Aerosol and corona discharges. In: Veldhuizen, E.M. (Ed.) Electrical discharges for environmental purposes: fundamental and applications, Nova Science Publisher Inc. Ch. 8, p. 193–220
[16] Sigmond R S, Goldman A and Goldman M 1992 Proceedings 10th International Conference on Gas Discharges and their Applications, Swansea, UK, p. 330–333
[17] Amirov R H, Petrov A A and Samoylov I S 2009 International Journal of Plasma Environmental Science and Technology. 3 35
[18] Petrov A A, Amirov R H, Asinovskii E I and Samoylov I S 2009 Journal of Plasma Fusion Research Series. 8 780
[19] Petrov A A, Amirov R H and Samoylov I S 2009 IEEE – Transactions on Plasma Sciences. 37 1146
[20] Kotov Yu A 2003 Journal of Nanoparticle Research. 5 539
[21] Ikuta N and Kondo K 1976 IEE Conf. Publ. 143 227
[22] Napartovich A P, Akishev Y S, Deryugin A A, Kochetov I V, Pan’kin M V and Trushkin N I 1997 Journal of Physics D: Applied Physics. 30 2726
[23] Rees T and Paillol J 1997 Journal of Physics D: Applied Physics. 30 3115
[24] Mesyats G A 2000 Cathode phenomena in a vacuum discharge: the breakdown, the spark and the arc. Moscow: Nauka, 400
[25] Lebedev S V and Savvatimskii A I 1984 Soviet Physics Uspekhi. 27 749
[26] Tkachenko S I, Vorob'ev V S and Malyschenko S P 2004 Journal of Physics D: Applied Physics 37 495
[27] Vorob’ev V S, Malyschenko S P, Tkachenko S I, and Fortov V E 2002 Journal of Experimental and Theoretical Physics Letters 75 373
[28] Nazarenko O 2007 Proc. of European congress of chemical engineering (ECCE-6), Copenhagen, 16
[29] Williams M M R 1973 Journal of Physics D: Applied Physics. 6 744
[30] Chyhin V I and Karpyak S Y 2007 Condensed Matter Physics. 10 209
[31] Smirnov B M 2000 Physics-Uspekhi. 43 453
[32] Nasser E 1971 Fundamentals of Gaseous Ionization and Plasma Electronics. New York: Wiley-Interscience, 442
[33] Reist P C 1984 Introduction to aerosol science. Macmillan, New York
[34] Dedkov G V and Kyasov A A 2007 Technical Physics Letters. 33 305