ATMOSPHERIC PRESSURE SECONDARY MICRODISCHARGE SYSTEM WITH VORTEX GAS FLOW

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This paper presents the results of investigation of the plasma-liquid system with the secondary discharge which supported by microdischarge in the vortex Ar flow. The plasma treated fluids were aqueous solutions of $AgNO_3$. Direct current atmospheric pressure microplasma system was presented. The microplasma discharge was powered by a DC supply. The plasma channel behavior was characterized by photo and video recording. The absorption spectra of the treated solutions of $AgNO_3 + C_6H_8O_7$, $AgNO_3 + C_6H_{12}O_6$ and $AgNO_3$ were presented at work.

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INTRODUCTION

Since the end of 19th century an active study of interaction between plasmas and liquids (solutions, in particular) were performed. Classic systems have the form of two electrode system, where one of the electrodes was immersed in liquid [1]. However, there is another approach when liquid plays a role of electrode in the secondary discharge. Thus, the main generator of discharge can serve different types of discharges.

Nowadays microdischarges of atmospheric pressure are one of the most promising types of discharges [2]. Microplasma is characterized by high current density and relatively low gas temperature that makes it handy for electrochemical applications of aqueous solutions.

Generation of plasma involving liquids becomes increasingly important in industrial applications [3]. Opened problems of water purification using plasma, the use of plasma treated liquids in the agroindustry, synthesis of nanosized particles, reforming of hydrocarbons etc remains until now.

Microplasma creates a unique environment for nanomaterial synthesis, which limits their agglomeration and allows formation of crystalline materials by selective heating [4]. The key advantages synthesis processes of nanomaterials based on micro-plasma is the fact that all chemical processes occur at a higher pressure and therefore the collision will be significantly strengthened, which can be favorable for the formation of particles [4]. The magnitude of the resulting particles is directly proportional to impact while being in the reaction chamber. Therefore, one method of reducing the size of the particles may be reducing the contact time of solution with the plasma. Another way is to reduce the size of the plasma zone. Also it should be kept in mind that the nanoparticles in the solution treated by plasma can take charge and create self-organized structures through interaction as a result of the Coulomb and Van der Waals forces.

The paper presents the results of studies of the plasma-liquid system with the secondary discharge, the supported microdischarge in the vortex Ar flow. The fluids treated by the plasma were aqueous solutions of $AgNO_3$. Microplasma generation takes place a constant current and at atmospheric pressure.

1. EXPERIMENTAL SETUP

Fig. 1 shows a schematic representation of the studied plasma-liquid systems with secondary discharge supported microdischarge.

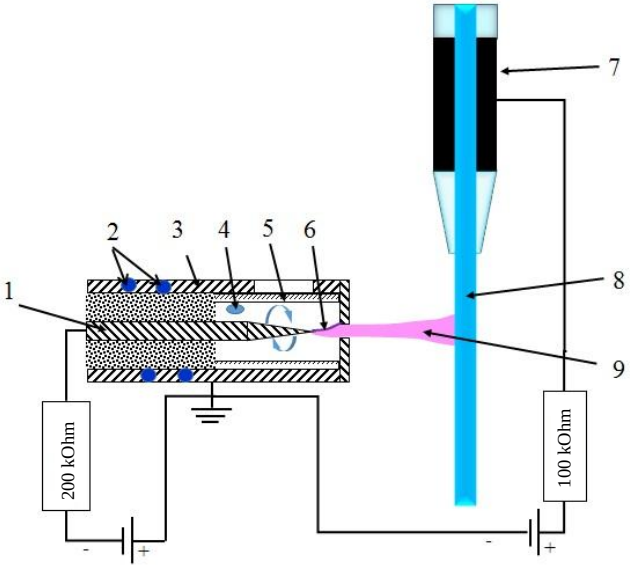

Fig. 1. Schematic representation of the studied plasma-liquid systems with secondary discharge supported microdischarge (1 – cathode of microdischarge; 2 – water cooling; 3 – anode of microdischarge; 4 – gas supply channel; 5 – quartz wall; 6 – the microdischarge; 7 – graphite tube that serves to transfer of potential on liquid; 8 – working liquid; 9 – secondary discharge)

The source of self-discharge is based on micro-discharge and it is axisymmetric plasma generator. The peculiarity of the system is a vortex of gas supply in the interelectrode space. Power supply of discharge provides the output voltage of 7 kV (high voltage electrode – copper cathode). Working gas was supplied in the discharge chamber through the gas supply channel tangential to the inner cylindrical dielectric wall of the reaction chamber Ø15 mm (5). External grounded

copper electrode (3) had water cooling. The external grounded electrode microplasma jet was blown out through the axial hole. The discharge burning between copper electrodes, a cathode (1) and anode (3), which were located at a distance about 1 mm apart. Generated plasma was carried out by flow of working gas (Ar) from discharge gap through a hole in the anode (d = 2 mm) in open air space. The gas flow was G = 3 L / min.

The effect on the liquid in the system happened due to submitting additional potential difference between the liquid and the anode microdischarge (3). The potential was applied to the fluid through introduction in channel fluid supply graphite section (7), which acted as the secondary electrode contacting with liquid. The graphite material was chosen due to its chemical inertness. Furthermore, all fluid supply channel devoid of metal (to exclude chemical reactions between the liquid and the materials used in construction). The source voltage in the secondary discharge circuit is power supply (up to 7 kV, high-voltage electrode – the anode), of the secondary discharge current limited by ballast impedance (100 kOhm). The study of the system parameters was carried out at 18 mA primary discharge current and 15 mA secondary discharge current.

The discharge behavior of the system was studied by video and photo observations method. Also parameters of liquids after plasma treatment were investigated by absorption spectroscopy method. The absorption spectrum of processed solutions was recorded using CCD-based spectrometer Solar TII (S-150-2-3648 USB) (operating in the wavelength range 200…1080 nm).

2. RESULTS AND DISCUSSION

2.1. BEHAVIOR OF THE DISCHARGE IN SYSTEM

Atmospheric pressure barrier discharge plasma jet operated in Ar has a fairly large plasma area (plasma jet) [5]. But, as it was noted earlier, microdischarges that are similar to glow discharge in Ar at atmospheric pressure are less than 2…3 mm [6]. However, plasma region can be increased by secondary discharge generation supported by microdischarge (see Fig. 2). Photo and video recordings confirmed that the secondary discharge in argon looks like a set of individual fast moving in space channels (see Fig. 2,a). With decreasing of camera exposure time, it was determined that the system supports one channel, which quickly changes its position (see Fig. 2,b). Furthermore, the color varies along the discharge jet from white and blue in the source electrode area to purple at the surface of the liquid.

2.2. PROCESSING OF $AgNO_3$ SOLUTION TO OBTAIN SILVER NANOPARTICLES

In order to obtain silver nanoparticles from $AgNO_3$, solution had been collected and analyzed within a closed working fluid supply system (Fig. 3). The volume of fluid in the system was approximately 100 ml. To avoid overheating of the fluid, reactor construction had an envisaged passage of the solution through the tube with cooling capacity (H_2O and ice).

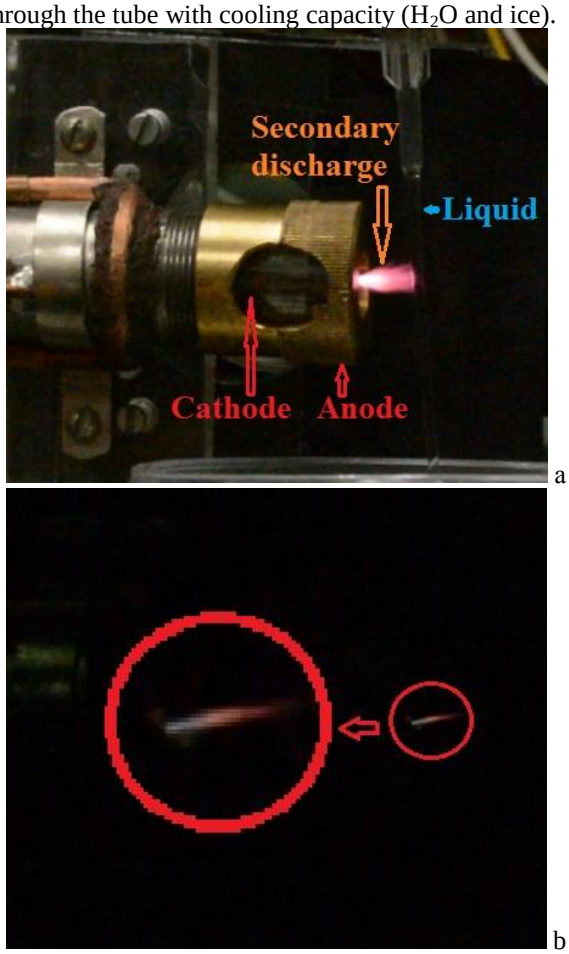

Fig. 2. Photos at of the secondary discharge at exposure time: a) – 33 ms and b) – 1 ms. Working gas – Ar, flow – 1 liter / min. The working liquid – citric acid solution

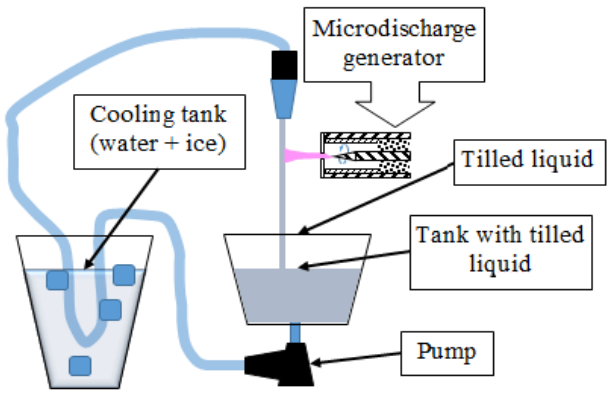

Fig. 3. Scheme of solution circulation

For the formation of silver nanoparticles three solutions in distilled water were studied:

№1 – $AgNO_3 + C_6H_8O_7$;
№2 – $AgNO_3 + C_6H_{12}O_6$;
№3 – $AgNO_3$.

Usually during plasma processing of $AgNO_3$ solution substances with a characteristic absorption spectrum in the visible range are not formed (the solution is transparent). Therefore, the citric acid ($C_6H_8O_7$) was added as chelator. In its turn, fructose can

produce a wide range of absorption spectra at thermal decomposition. In the third case − only silver nitrate solution processed to completely eliminate the possibility of exposure to products of decomposition chelators on absorption spectrum.

Treatment was carried out for 5 minutes with the following parameters:

• Self-microdischarges current – 18 mA;
• Voltage burning of selfdischarge – 2900 V;
• Current of secondary microdischarge – 15 mA;
• Voltage burning of the secondary discharge – 500 V in case of using solution № 1, 1100 V – solution № 2 and 1500 V – solution № 3.

The choice of the secondary discharge current was based on our previous studies with successful attempts to obtain nanoparticles of precious metals [7]. Note that the voltage in of the secondary discharge circuit includes the discharge voltage and also voltage that falls on the area near solution on the section between the discharge and graphite tube.

2.3. ANALYSIS OF PROCESSED LIQUID

A typical absorption spectrum of the colloidal silver nanoparticles solution from [7] presented in Fig. 4. As can be seen in the figure there is a characteristic maximum at 400 nm. In our work after 5 minutes of the secondary discharge burning can be observed significant color change of investigated liquid (Fig. 5). In cases of solutions № 1 and № 2 characteristic peaks weren't observed. Fig. 6 shows the absorption spectrum of the sample № 3. It can be seen that the results of sample № 3 are similar to results from work [7].

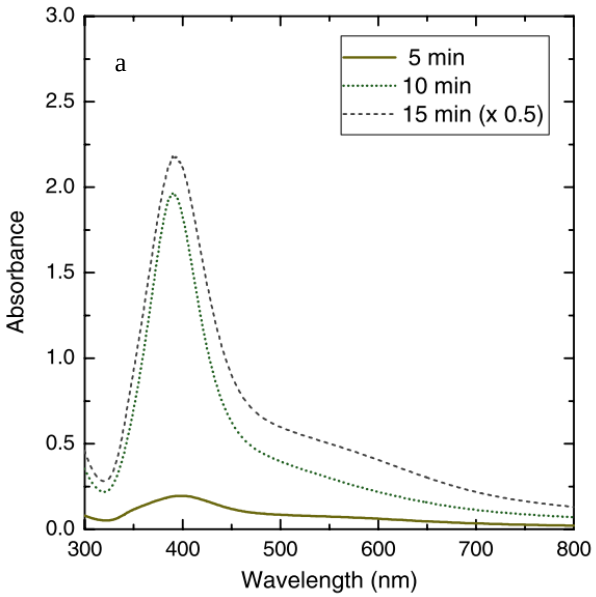

Fig .4. A typical absorption spectrum of colloidal solution $AgNO_3$ [4]

It should be noted that after one day after the treatment dark gray color precipitation observed in all samples. After repeated shaking of the solution - the degree of darkening was lower and eye visible particles are observed in the solution.

The experiment in an open system, when the solution passed through the area of contact with plasma was performed also the solution № 1 was chosen to be processed. We chose this solution because it changes the color the most after plasma. The absorption spectrum of the resulting solution is presented in Fig. 7. Expressed maximum in spectrum is absent. In this case, the darkening of solution can be connected to the fact that even after a single treatment, possible formation of sub-macroscopic sized metal. However this fact requires detailed study.

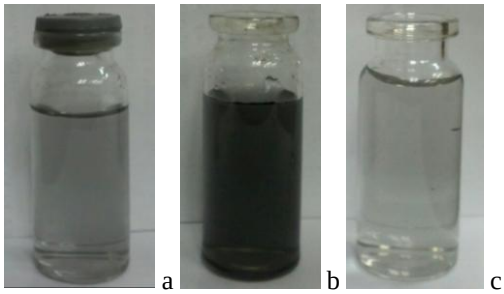

Fig. 5. Outward look of the solutions: a – 1; b – 2; c – 3 after the treatment

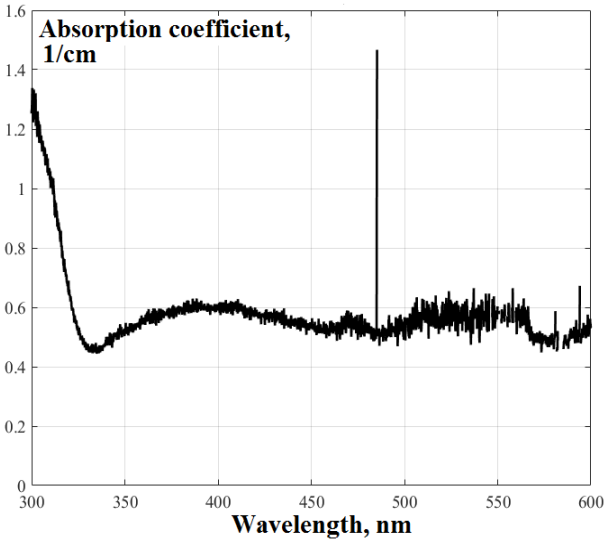

Fig .6. The absorption spectrum of the processed solution № 3 ($AgNO_3$) after 5 min processing

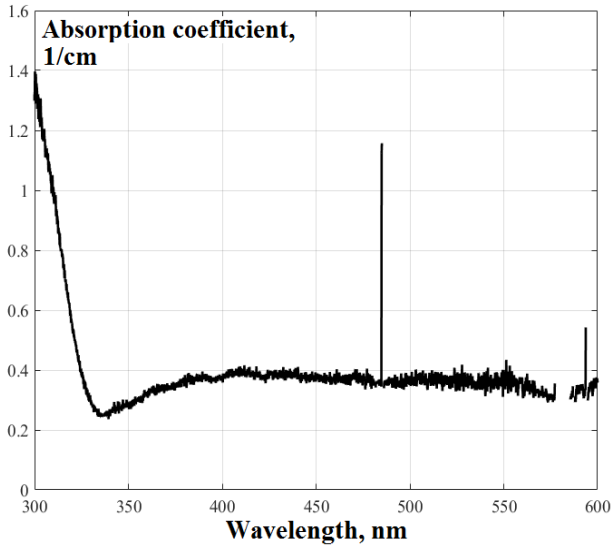

Fig. 7. The absorption spectrum of the processed solution № 1 ($AgNO_3$ + $C_6H_8O_7$) after one cycle of treatment

CONCLUSIONS

- It was observed darkening of all tested solutions after secondary discharge plasma treatment Since the common component for all solutions was silver nitrate observed darkening of working liquids can be connected with formation of silver nano-sized particles.
- The presence of organic chelators (fructose, citric acid) in solution intensifies the process of precipitation.
- In all test solutions formation of sediment were observed. But only in the case of a pure solution of silver nitrate characteristic peak in the area of plasmon resonance of silver nanoparticles was observed. It's absents in other two cases may be related to particle coagulation process and the formation of macro-clusters.
- Gradual lighting of the solution indicates that the particles are able to partially dissolve.

The deposition process of silver from nitrate in aqueous solution was observed to be intense, but for some reason it leads to the formation of macro-particles with subsequent deposition. It can be caused by a coagulation process or overgrowth of particles due to high formation rate. On the other hand, formations of microparticles can be utilized for applications related to water purification from heavy metals.

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ВТОРИЧНЫЙ РАЗРЯД, ПОДДЕРЖИВАЕМЫЙ МИКРОРАЗРЯДОМ В ВИХРЕВОМ ПОТОКЕ ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ

Д.К. Гамазин, В.Я. Черняк, О.В. Соломенко, О.В. Присяжная, Е.В. Мартыш, А.К. Трофимчук, А.В. Легенчук, В.В. Лендьел

Представлены результаты исследования плазменно-жидкостной системы с вторичним разрядом, который поддерживается микроразрядом в вихревом потоке Ar. Обрабатываемыми плазмой жидкостями были водные растворы $AgNO_3$. Представленна система постоянного тока при атмосферном давлении. Фото и видео технологии были использованы для исследования плазменного канала. Представлены спектры поглощения обработанных растворов $AgNO_3 + C_6H_8O_7$, $AgNO_3 + C_6H_{12}O_6$ и $AgNO_3$.

ВТОРИННИЙ РОЗРЯД, ЩО ПІДТРИМУЄТЬСЯ МІКРОРОЗРЯДОМ У ВИХРОВОМУ ПОТОЦІ ПРИ АТМОСФЕРНОМУ ТИСКУ

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Представлено результати дослідження плазмово-рідинної системи із вторинним розрядом, що підтримується мікророзрядом у вихровому потоці Ar. Оброблюваними плазмою рідинами були водяні розчини $AgNO_3$. Представлена система постійного струму при атмосферному тиску. Фото і відео технології були використані для дослідження плазмового каналу. Представлені спектри поглинання оброблених розчинів $AgNO_3 + C_6H_8O_7$, $AgNO_3 + C_6H_{12}O_6$ та $AgNO_3$.