Generation mechanism and spectral properties of an AC underwater discharge.

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Abstract: A mechanism of underwater AC discharge in capillary and its spectral characteristics are investigated. It is revealed that duration of emission of OH radicals and Hα is about 650-850 µs and Na atoms radiation is 250 µs. Physical process explaining delay of Na emission appearance in the spectrum of the discharge is suggested. It is well agreed with experimental data.

Keywords: OH radicals, underwater plasma, emission spectroscopy

1. Introduction

Plasma-solution systems attract the increasing attention of researchers from the technological point of view. For today the considerable quantity of the works devoted to application of underwater discharges for purification of water solutions from organic compounds (dyes, phenol, benzene, etc.) and sterilizations [1-3] has been published. Chemical influence of plasma on solutions is caused by presence in a zone of reactions of active particles generated under the plasma action. Main radicals and active particles, formed in the plasma- solution systems, are OH radicals (emission in the UV region 280-309 nm), O (779 nm) and H (486.1, 656.3). The basic second particles, registered directly in the solutions, are H2O2 and ozone. The majorities of plasma- solution systems are characterized by the high efficiency of organic compounds destruction with very low power consumption. Recently we have showed that the capillary AC discharge can ensure yield of H2O2 to 7.8 g/kWt*h at input power 8.3 W [4]. All underwater electrical discharges can be divided into two large groups, on the basis of the method of the generation of the plasma: the pulsed discharges and generated on the direct current or the currents of low frequency (to several kHz). The second group of plasma- solution systems includes the diaphragm, capillary discharges [5,6], micro-discharges on the valve metals [7], etc. From the physical point of view the mechanism of the excitation of the discharge in all types of DC or AC underwater plasma- solution systems has much in common. Gas-vapor bubble due to the Joule and the electrolysis is generated at the initial stage in the volume of electrolyte. Further the breakdown in the discharge gap with the formation of plasma has place. The qualitatively this process was described in a number of articles [5-6, 8]. Unfortunately, the detailed study of the physical processes taking place during generation of underwater discharges was not carried out up to now. The purpose of the presented work is to study physical processes in one of the forms of underwater discharges - the capillary discharge of alternating current, described by us earlier [9].

2. Method of experiments

Investigations of electrical and spectral properties of the discharge have been carried out on the set-up presented on fig.1.

![Fig.1 Set-up for investigations of the underwater discharge](image)

Two graphite electrodes (8) with the diameter of 7 mm are placed in the solution of electrolyte in the vessel (12) through the cover (9). The discharge is generated in the narrow channel in the dielectric tube (10). The current of the discharge were recorded by digital oscilloscope as a voltage drop across 110 Ohm resistance. The lateral and axial radiation of the discharge passed through the quartz window, soldered in the wall of reactor. The ne-
cessary emission wavelength is separated by monochromator (1) and is recorded by PMT. Two-stage amplifier (4) is used for amplification the signal obtained from PMT. An analysis of electrical circuit (capacity of filters, characteristic of PMT amplifier, the bandwidth of the oscilloscope) shows that the pass-band of the system for registration of emission is not worse than 5 MHz. Na₂SO₄ solutions with conductivity 500 and 4500 µS/cm were used as working solution for all experiments.

3. Results and discussions

I. Electrical characteristics of the discharge.

On fig. 2 typical current and voltage wave forms with time resolution 50 µs are shown.

![Fig. 2 Voltage, current waveform at solution conductivity 4 mS/cm.](image)

Area AB corresponds to formation of a gas-to-steam bubble. Further during of 1.5 ms grows of the bubble results to blocking the section of the current conducting channel. Respectively whole emf is applied to gap and bubble breakdown has place– area BC. Obviously, that mechanism of the bubble formation is a Joule heating of the solution. It was found from numerical simulation that time of solution heating (initial temperature 293 K, solution conductivity 500 µS/cm, applied voltage 4 kV, quartz capillary section is 0.5*10⁻⁶ m²) is 5.23 ms and decrease to 1.25 ms if initial solution temperature is 323 K as we observed in thermocouple measurement. In CD region during 1 ms the discharge development is accompanied by growth of a bubble due to heating of the gas. Part DE corresponds to the moment of destruction of the bubble. It is need to note that formed bubble does not block whole section of the capillary, otherwise we should observe falling to zero the current in the point B. Probably, for similar systems presence of a thin conductor layer on border of gas bubble-capillary is typical behavior. Our estimations show that at solution conductivity of 4 mS/cm and internal diameter of the capillary of 0.8 mm the electrolyte layer thickness should be of an order of 2.4*10⁻³ mm. Hereby, a thin conductor layer of a solution on a border gas bubble-wall of the capillary presents every time at the moment of discharge generation.

We can shown that in investigated plasma-solution system the breakdown starts by mechanism of Townsend [10] since value \( \alpha \) defining regime of the breakdown is about 4.6-6.9 (bubble diameter is 0.8 mm, \( \gamma \) emission is 10⁻⁷ and vapor pressure in bubble is 760 mmHg). This is considerably less than the value of \( \alpha \) required for the development of a streamer breakdown estimated as 18 [10]. If the applied voltage is 4 kV the field strength at the moment of breakdown can be estimated as \( E/N=2.10^8/760=2.6 \times 10^7 \) V/cm·Torr. With this field the drift velocity of the electrons in the vapors of water will be not less than \( 10^7 \cdot 10^8 \text{ cm/s} \) [10]. As it is known the time of the electron avalanches is defined by the drift velocity of electrons and the corresponding time of the breakdown will be much less than \( 10^{-7} \text{ s} \) as this is observed also in our experiments.

II. Spectral characteristics of the discharge.

As it was shown by the large number of researchers the underwater discharges are characterized by the generation of different active particles, including OH radicals, H, O atoms, etc. The spectrum of discharges is fairly complicated and it contains the broad band in the region of 280-330 nm corresponding to the emission of OH radicals \( \Lambda^3 \Sigma^+(\nu=0) \rightarrow X^3 \Pi(\nu=0, \nu=1) \), hydrogen lines \( H\alpha \) and \( H\beta \) on 656.3 nm and 486.1 nm, \( Na^7 \) lines on 589 and 589.6 nm and also line of oxygen in the regions of 779 and 845 nm. In this work detailed investigations of discharge emission: \( Na^+ \) (589, 589.6 nm), line \( H\alpha \) and OH radicals (309 nm) by time resolved technique has been carried out.

On fig.3 the temporary dependences of the discharge current and lateral radiation of OH radicals during one discharge pulse are shown.

![Fig.3 The emission of the discharge (OH radicals, 309 nm) and current waveform. Current is inverted.](image)
tween pulses is about 0.5-1 ms. The duration of individual pulses of OH radicals emission is 650-800 µs. The emission of OH radicals reaches the maximum value during 3-8 µs from the moment of the breakdown. After 5-7 µs the radicals emission begins to decrease exponentially as it shown on fig. 4.

The dynamic radiation characteristics of discharge corresponding to line Hα (656.3 nm) manifest all regularities analogous described above for OH radicals. Duration of the emission impulse is of the order of 750 µs. The comparison of the current waveforms and the discharge emission shows that the maximum of the current of the discharge practically coincides maximum of the emission.

It is possible to see from data presented of fig.5,6 that the duration of the emission of Na is considerably shorter than the same value for OH radicals and Hα. On average duration of individual impulse of sodium atoms emission is about 100-250 µs. The shape of pulses is complex, at the initial moment of the breakdown of discharge gap (moment of a sharp increase of current) the peak on emission waveform is not observed in contrast to the data for OH radicals and Hα. An appearance of the emission of Na line has delay from the moment of the breakdown and reaches the maximum of intensity after 25 µs from the moment of the breakdown.

Summarize presented data it is possible to emphasize a number of the features of the generation of the underwater AC discharge. First of all 2 peaks of emission of OH radicals, Na and Hα are observed during each half-period of the applied voltage. The duration of impulses of OH radicals emission as well Hα emission are about 650-800 µs. The emission of Na atoms in the discharge is characterized by shorter pulses with duration of 250 µs. On the waveforms of the emission of OH radicals and Hα it is possible to separate the initial period of fast increase of the signal during 5-6 µs. Further the emission exponentially decreases. The comparison of the current waveform and Na atoms intensity shows that the maximum of the discharge current does not coincide maximum of emission. This delay time $\tau_{Na}$ is 25 µs. At the initial moment after breakdown the absence of the emission of alkali metal during first 4-7 µs is observed contrary to OH radicals and Hα lines.

One of the possible explanations of this delay of occurrence of Na lines in the discharge spectrum can be made on the basis of a hypothesis offered in works [11, 12] for glow discharge between metal electrode and water surface. Authors supposed that components of solution are sputtered from liquid surface by means of ions impact as big neutral clusters containing neutral ionic pair (cation-anion). Characteristic time of metal radiation will be defined by time of clusters transport in a gas phase. This transfer of components in a zone of the discharge from a solution is defined only by linear speed of gas-vapor stream from area of a cathode spot. Such process initiated by ions impact has been investigated recently [11,12]. On the basis of this data for the discharge burning at a current 50 mA and gas temperature in the bubble 1600 K (rotational temperature of OH radicals [9]) and diameter of the bubble of 0.8 mm we can estimate linear speed of a stream of molecules into gas phase. This value is about 844 cm/s. Respectively a delay time of appearance of Na atoms radiation in the spectrum has to be 90 µs that close
to experimental results 25 µs. Difference between estimated and experimental delay time can be explained by understated value of the transfer coefficient of the molecules of water under the experimental conditions and considerably higher than 1600 K temperature of heavy particles in gas phase after breakdown.

4. Conclusions
Detailed investigation of the electro physical properties of the underwater discharge is carried out. It is revealed that during formation of plasma a thin layer of electrolyte with thickness of 2 µm between gas-vapor bubble and wall of capillary is in existence. The processes of the breakdown in the gap formed by Joule heating of the solution is realized by the Townsend mechanism. It is revealed that the process of the appearance of the radiating particles (OH radicals, H and Na atoms) in the discharge zone is different. Duration of the emission of OH radicals and hydrogen atoms at half-period of applied voltage is about 650-850 µs, while time of the emission of Na atoms is considerably shorter - 250 µs. The 25 µs delay of the appearance of resonance radiation of sodium emission relative to the moment of breakdown is found. For the emission hydroxyl radicals and H atoms this effect does not observe. The model of plasma- solution interaction explaining the observed effect is proposed.

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References