Research of the impact acidity of electrolytic cathode on the course of the plasma-electrolytic process

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Abstract. The object of research is a gas discharge with an electrolytic cathode, namely the influence of the nature of the cathode on the discharge. Is established that with decreasing the acidity of electrolytic cathode voltage of discharge ignition decreases. A mechanism is proposed to maintain the discharge at the gas-electrolyte interface.

1. Introduction

The classic methods of electrical treatment of steels, such as electrochemical, EDM, electro-thermal and electromechanical have drawbacks. Namely, a high consumption of electrical energy, big problems of disposing of the reaction products, the difficulty of obtaining the required surface profile at a given scale. In this regard, a strong demand existed develop and research new environmentally-friendly and cost-effective methods of electrical processing.

One of the new electro physical types of processing is the plasma-electrolytic method [1]. This method of processing is carried out by applying a voltage to electrodes in an electrolytic solution as a result of around one of the electrodes is initiated gas-vapor discharge [2]. The peculiarity of this discharge is that it burns between a solid and a liquid. Solid electrode can be both the anode and cathode. When discharge burning occurs at the cathode cleaning and polishing a workpiece, also under certain circumstances may be application of coatings [3]. When the anodic process on a metal having the property of forming during anodic polarization protective oxide layer with a high resistance is anodized with microarcs combustion, the process is called oxidation microarc [4]. On metals not having given properties observed erosion destruction of the metal and dissolution. The most similar in their impact on the work surface is a combined method of electroerosive and electrochemical machining [5]. In which the metal removal is occurs due to the anodic of dissolution and the electrical erosion. Anodic dissolution is the electrochemical oxidation of the metal in the electrolyte solution to form a soluble products and discharge of the liberated electrons to the external circuit. The difference between this combined method of processing from the anodic process of plasma-electrolytic processing is that erosion damage occurs due to the breakdown of the electrolyte and the formation of a discharge channel between the workpiece electrode (anode) and the tool electrode (cathode), and not due to burning gas discharge between the metal anode and electrolytic cathode. This is due to the fact that in the plasma-electrolytic processing interelectrode space is increased from 0.5 mm to tens of centimeters and is applied to the electrodes of more high voltage value (U>30 B). Despite such a broad application of the variety of discharge, remains an open question about the mechanism of maintenance of the discharge. The answer to this question is related with the mechanism of electron emission from

the cathode electrolyte - a liquid. The emission of electrons, of course, will depend on the type of electrolyte and the aim of this work was an experimental research of influence of acidity (hydrogen index) on the course of plasma-electrolytic process.

Of interest is the effect of the parameters of the solution to the ignition of the gas discharge with an electrolytic cathode. One of the important parameters of the electrolyte is its acidity, namely hydrogen index, pH - a measure of the activity of hydrogen ions in solution, and quantitatively expresses its acidity is calculated as the negative (taken with the opposite sign) decimal logarithm activity of hydrogen ions, expressed in moles per liter: $pH = - lg(H^+)$. Some minimal spread received reverse pH value - index of basicity of the solution, pOH, equal to the negative decimal logarithm of the concentration in the solution of ions OH^-: $pOH = - lg(OH^-)$ as in any aqueous solution at 25 °C $[H^+][OH^-] = 1,0 \times 10^{-14}$, it is clear that at this temperature: $pOH = 14 - pH$.

2. Experimental

To achieve this goal has been applied experimental setup which described in [5]. Was used pulsating current source obtained after full-wave rectification with smoothing capacitor filter and without it. Changing the shape of current and voltage at the time of discharge ignition was determined by the oscilloscope FLUKE 105 SCOPEMETER SERIES II, timebase varied from 5 ns to 60 s. The relative measurement error did not exceed 0.025%. Measurement of voltage and current discharge was carried out using two digital universal measuring devices MMH-930 and APPA 109 N relative measurement error is 0.8%. The measurement system was automated and included the analog input module measuring MBA8 and Digital Multimeter APPA 305 connected to the computer. To prevent changes in the size of the area of the anode wore dielectric protective case which leaves open only a well-defined part of the electrode. The electrodes used graphite anode and a copper cathode. $S_{anode}=316,25$ mm^2, $S_{cathode}=1802$ mm^2, $(S_{anode}/S_{cathode} =0,175)$. In this case, the discharge burns at the anode, which corresponds to the statement [5], where noted that plasma-electrolytic process takes place when $S_K > 5$ S_A.

3. Results

For of experimental research by using smoothing capacitor filter were prepared 4 electrolytes: 5% aqueous solution of acid H_2SO_4 pH = 2; 5% aqueous salt solution Na_2SO_4 + 2% H_2SO_4 pH = 4; 5% aqueous Na_2CO_3 pH = 7; 5% aqueous alkaline solution NaOH pH = 11. The acidity of the solution changed in two ways: choice of type of electrolyte and changing the concentration of the electrolyte solution. Was investigated the dependence of the value of the ignition voltage of the discharge from the acidity of the solution. It was found that with increasing pH and decreasing ignition voltage of the discharge. This dependence is shown in Figure 1.
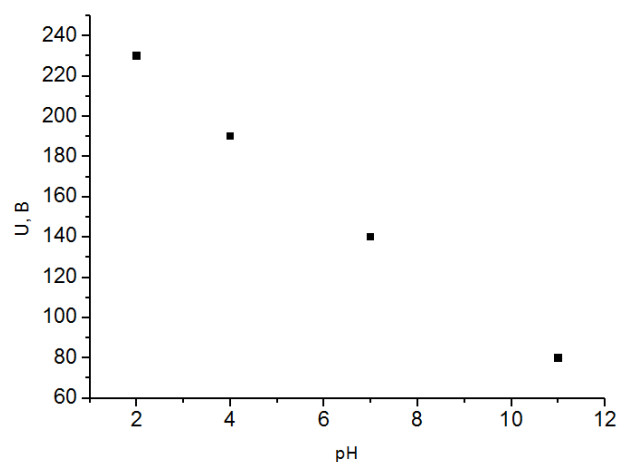

Figure1. The dependence of the ignition voltage of the discharge from pH.

As can be seen increasing the concentration of hydroxide-ions OH⁻ reduces the ignition voltage. This suggests that the necessary amount the charge carriers (electrons) is reached at lower voltages for solutions with a higher concentration of OH⁻. Thus it is possible to speak of hydroxide-ion plays an important role in maintaining the discharge. It was also revealed decrease pH with time discharge burning, which is observed in [6].

Experiments were conducted to determine the influence pH of solution (electrolytic cathode) on the current-voltage characteristics (CVC) of plasma-electrolytic process. In these experiments, we used the power supply without the smoothing capacitor filter. During the experiments, was fixed at which voltage rise to strong sound waves and discharge initiation.

Figure 2 shows the current-voltage characteristics of plasma-electrolytic process for various electrolytes. Current-voltage characteristics increase smoothly at the beginning and peaking are down. On a site where there is a linear increase in current on the voltage dominates the electrochemical processing. In the area of 65 - 120 V (depending on the type of electrolyte) begin to occur anode microdischarges and observed the formation of gas bubbles. With decreasing the current is observed increase in the intensity of the glow of plasma-electrolyte discharge for the salt solutions and bases. Established that the addition of low concentrations of alkaline or acid electrolyte hasn't a strong influence on the form the CVC, but adding more alkaline electrolyte the CVC maximum is shifted to lower voltages and drops from 112V to 70V.
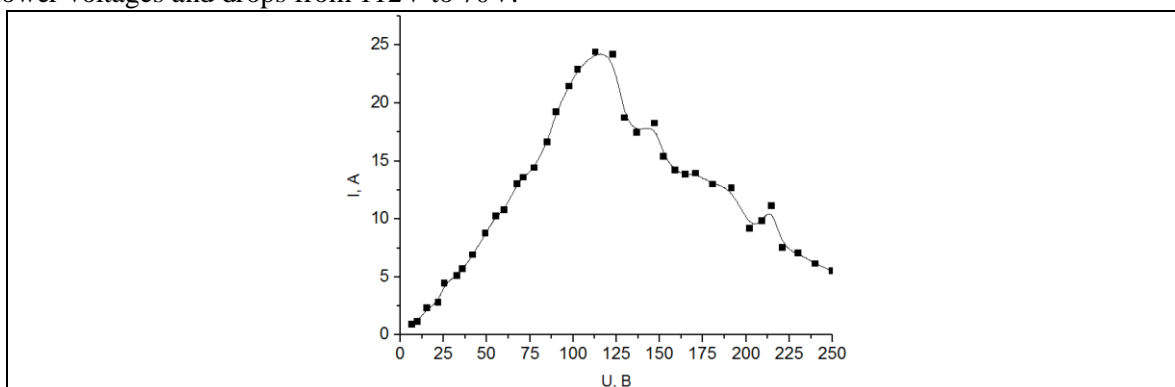

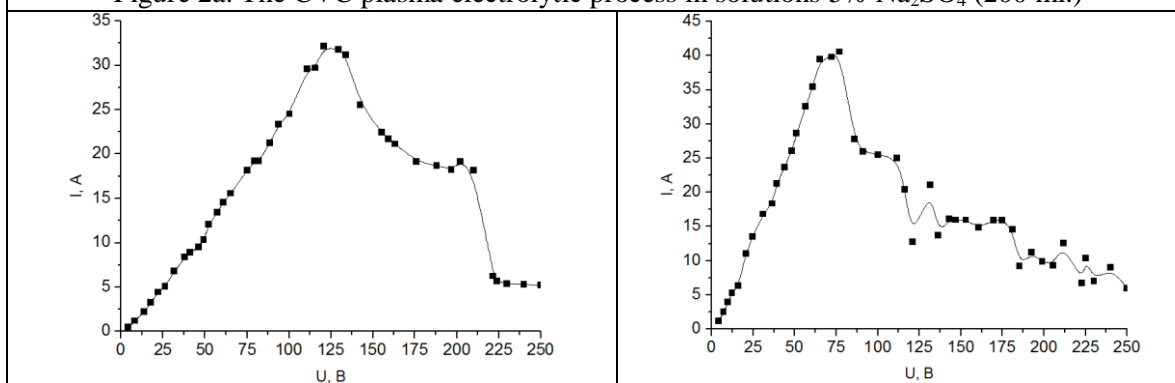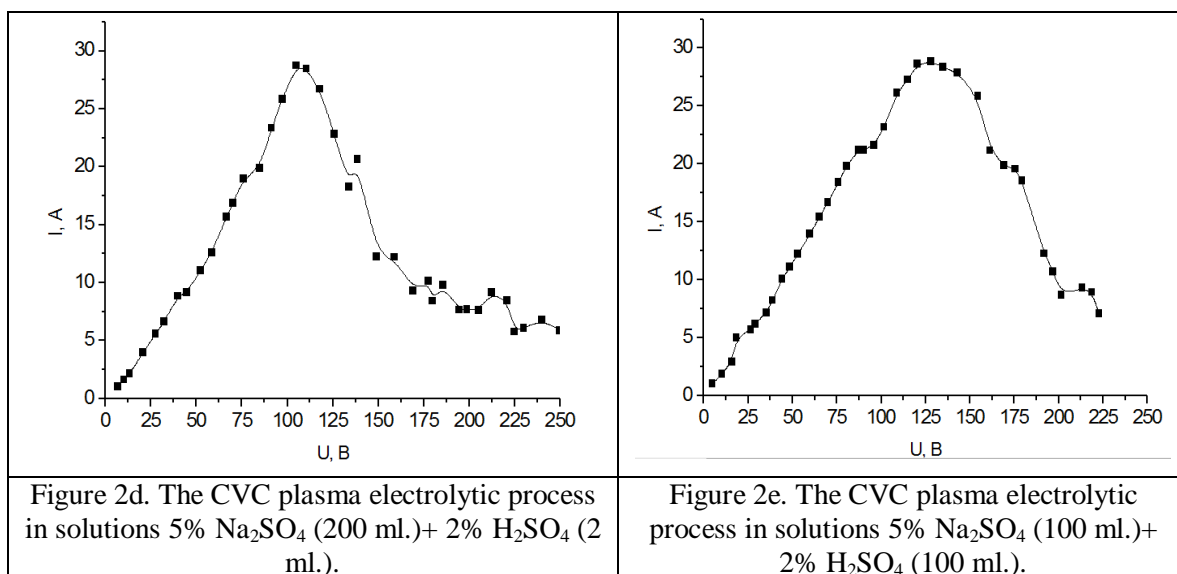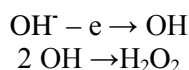Figure 2a. The CVC plasma electrolytic process in solutions 5% Na_2SO_4 (200 ml.)

Figure 2b. The CVC plasma electrolytic process in solutions 5% Na_2SO_4 (200 ml.)+ 5% NaOH (2 ml.)

Figure 2c. The CVC plasma electrolytic process in solutions 5% Na_2SO_4 (100 ml.)+ 5% NaOH (100 ml.).

| Figure 2d. The CVC plasma electrolytic process in solutions 5% Na_2SO_4 (200 ml.)+ 2% H_2SO_4 (2 ml.). | Figure 2e. The CVC plasma electrolytic process in solutions 5% Na_2SO_4 (100 ml.)+ 2% H_2SO_4 (100 ml.). |

In the case of adding an acidic electrolyte opposite picture is observed and the maximum the CVC shifting from 112 to 130 V. The first CVC describe the plasma-electrolytic process in a neutral environment. Found that sound waves observed at ~ 75 V and glow occurs ~ 90-95 V. For environment 5% Na_2SO_4 (200 ml.) + 5% NaOH (2 ml.) with indicator pH = 10 as sound waves observed at ~ 75 V, glow ~ 90-95 V. But for the 5% Na_2SO_4 (100 ml.) + 5% NaOH (100 ml.) with indicator pH = 12 with sound vibrations ~ 41 V, glow ~ 65 V. For 5% Na_2SO_4 (200 ml.) + 2% H_2SO_4 (2 ml.) and 5% Na_2SO_4 (100 ml.) + 2% H_2SO_4 (100 ml.) sound vibrations at ~ 85 V, glow ~ 120 V. Thus, with the pH change of the solution occurs CVC maximum displacement.

As can be seen, hydroxide- ion plays an important role in maintaining the plasma discharge. And it can be assumed that the discharge will be to certain the limiting reduce of concentration OH^-. Also in [7] was founded that when the discharge was is observed super Faraday formation of hydrogen peroxide H_2O_2. Hence we can assume the following mechanism for the maintenance discharge at the gas-electrolyte:

$$OH^- - e \rightarrow OH$$
$$2\ OH \rightarrow H_2O_2$$

Acknowledgments

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