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## ВЕСТНИК

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## **ELECTROCHEMICAL BEHAVIOR OF SILVER IN ACID SOLUTIONS OF POLARIZATION BY UNSYMMETRICAL CURRENT**

**Abstract.** In the scientific work, the effect of the magnitude of the current amplitude of the anodic and cathodic half-cycles on the current yield and the dissolution rate of silver during polarization by nonstationary currents in solutions of sulfuric and hydrochloric acids are considered. In this study, the current density in the cathode half-period was maintained at a constant value of 1000 A/sq.m, and in the anode half-cycle the current density varied from 0 to 1000 A/sq.m and vice versa. A special installation was used to convert the alternating current, which consists of an alternating current source, two diodes D1 and D2, one of which is connected in the transmission mode, and the other in the locking, two variable resistors R1 and R2, to control the magnitude of the cathode and anode half- R3 constant resistance, two ammeters A1 and A2, to control the current in the process of electrolysis in the cathodic and anodic half-cycle, electrolytic cell and oscillograph. The electrodes were silver and graphite plates. It has been established that in solutions of acids with the increase of size of amplitude of anodic semiperiod current output and speed of dissolution rise, and with the increase of size of cathode current there is a decline current output and speeds of dissolution of silver.

**Key words:** electrochemistry, electrolysis, not symmetric current, polarization, electrochemical dissolution, closeness of current.

Silver (from all metals) possesses the highest heat and electrical conduction and is widely used in electronics and electrical equipment. Alloyed by refractory metal, for example tungsten, silver is the ideal material for manufacture of high-voltage switches and electric interrupters. Silver contacts in sensor switches became as indispensable accessory of computer keypads, control panel of microwave ovens, call keys of elevators, etc. Electrical circuits in the microprocessor chips used in micro calculators, electrical instruments, automobiles, etc. are represented by conductors from alloys of silver and palladium.

Silver-oxide and galvanic cells (on the basis of silver oxide) have twice the high electrical capacity, than lead (acid) elements of the same size, therefore, all of them are more often used as in accumulators to aerospace technique and underwater fleet where is given pride of place to decreasing of mass of equipment, and in miniature batteries for watches and calculators [1, 2].

Metal silver serves for manufacture of high-quality optical mirrors by thermal evaporation. In the food industry, silver apparatus are used in which fruit juice and other drinks are prepared. It is known about the row of pharmaceutical preparations in medicine containing colloidal silver [3-5].

Silver alloys are widely applied to manufacture of coins, tooth seals, bridges and artificial limbs, tableware, in refrigerating chemical industry. Thus, processes of oxidation, restoration with an involvement of silver and its connections and also responses of its ionization in different water solutions is of a certain theoretical and practical interest.

Rapid development of the exact sciences in the modern world leads to origin of new methods of the research. Recently in electrochemical researches, special attention is paid to the processes proceeding with an electrode involvement by superimposed a. c. technique [6-12].

Use of the nonstationary mode of electrolyzing expands the possibilities of a research of the mechanism of the cathode and anode processes, opens essentially new opportunities of using them for the solution of different technological questions.

In the works [13-17] are provided this to polarization of a silver electrode by an industrial alternating current with a frequency of 50 Hz. It was set that in sulfate solution silver is dissolved with a high efficiency in case of low current densities, and in solution of hydrochloric acid the efficiency of dilution of silver makes only 10,4%.

It is necessary to mark that the detail researches carried out by us on a silver electrode and other researchers studying titanium, chrome, molybdenum, lead, etc. in case of polarization by an alternating current of industrial frequency, showed that the electrode processes proceeding with an electrode involvement by superimposed a. c. technique, sharply differ both on the mechanism, and according to the quantitative characteristics [18, 19]. In this regard we assumed that on results of the electrolyzing which is carried out under the influence of an alternating current, the considerable impact is exerted by change of the direction of currents, i.e. the electrode stays alternately in the cathode, in an anode half-cycle therefore it is possible that it undergoes certain structural changes. In order to make sure the researches of polarization by asymmetrical currents were carried out by us.

The purpose of this work was the study of electrochemical behavior of silver in case of polarization by asymmetrical current. Change of a ratio of values of amplitudes of anode and cathode half-cycles of an alternating current gives the chance to set dependence of efficiency of dilution of silver from a share of current of one of half-cycles by constant value of values of current of other half-cycle.

The experiments of polarization by asymmetrical and pulse currents in 0,5 M solutions of sulfuric and hydrochloric acids were carried out for a study of influence of values of anode and cathode half-cycles on dilution of silver. For transforming of an alternating current the special installation offered in the work was used [20].

The experiments were made in the 50 ml electrolyser without division of electrode spaces. Silver and graphite plates were served as electrodes. The efficiency of dilution of metal was calculated on an anode half-cycle of an alternating current on change of weight of a silver electrode.

Then the influence of a ratio of values of amplitudes of currents of anode and cathode half-cycles of an industrial alternating current with a frequency of 50 Hz was probed by us.

The influence of value of amplitude of current of an anode half-cycle on efficiency and the speed of dilution of silver is considered in case of polarization by nonstationary currents in solutions of sulfuric and hydrochloric acids. In this research the value of a current density in the cathode half-cycle was maintained constant, equal 1000 A/sq.m, and the current density in an anode half-cycle was changed in the range from 0 to 1000 A/sq.m. With increase in value of amplitude of an anode half-cycle the efficiency of dilution of silver begins to increase in sulfate solution and in case of ratio  $i_a/i_k = 0,6$  reaches 2,2%. In case of further increase in value of current of an anode half-cycle the efficiency and the speed of dilution of silver are decreased, and in case of a symmetric alternating current the efficiency will be equal to 0,4% (figure 1). From this discussion, it is explained by increase in a share of response of formation of oxygen.

With increase in value of amplitude of an anode half-cycle the efficiency on dilution of silver grows in solution of hydrochloric acid and in case of ratio  $i_a/i_k = 1$  reaches 3% (figure 2). As we would expect, with increase in value of amplitude of an anode half-cycle the efficiency and the speed of dilution are increased to values, i.e. to a ratio of values of anode and cathode half-cycles to equal unit, i.e. responding to a symmetric alternating current.

The study results of ratios influence of magnitude relation of amplitude of the cathode and anode half-cycle currents on the efficiency and speed of dilution of silver in case of polarization by nonstationary alternating currents in solutions of sulfuric and hydrochloric acids were presented respectively in figures 3 and 4.

The current density in the cathode half-cycle was changed from 0 to 1000 A/sq.m, supporting the current density in an anode half-cycle, being equal to 1000 A/sq.m.

At the same time the efficiency of metal dilution, with increasing in a current density in the cathode half-cycle, is gradually decreased. If in case of an anode pulse current, the efficiency of dilution was equaled to 26%, then upon step-by-step transition to a symmetric alternating current, i.e. in case of  $i_k/i_a = 1$  is decreased, reaching 0.4% in solution of sulfuric acid.

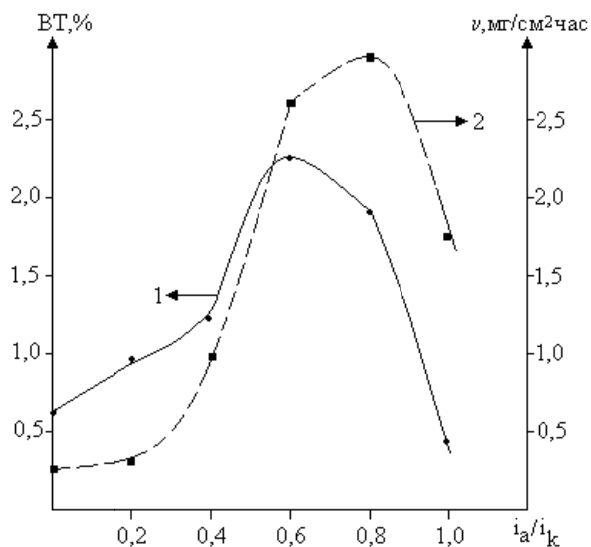


Figure 1 – Influence of correlations of sizes of amplitudes anodic and cathode semiperiods ( $i_a/i_k$ ) on CO of dissolution of silver in a 0.5 M solution of sulphuric acid:  
 $i_k=1000$  A/sq.m,  $\tau=0.25$  hour,  $t=25$  °C

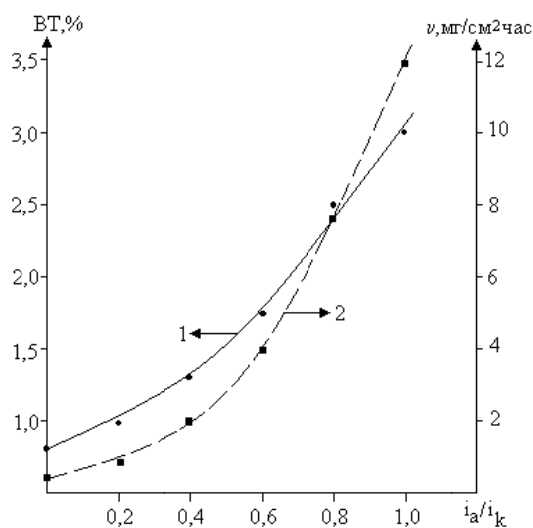


Figure 2 – Influence of correlations of sizes of amplitudes anodic and cathode semiperiods ( $i_a/i_k$ ) on CO of dissolution of silver in a 0.5 M solution of hydrochloric acid:  
 $i_k=1000$  A/sq.m,  $\tau=0.25$  hour,  $t=25$  °C

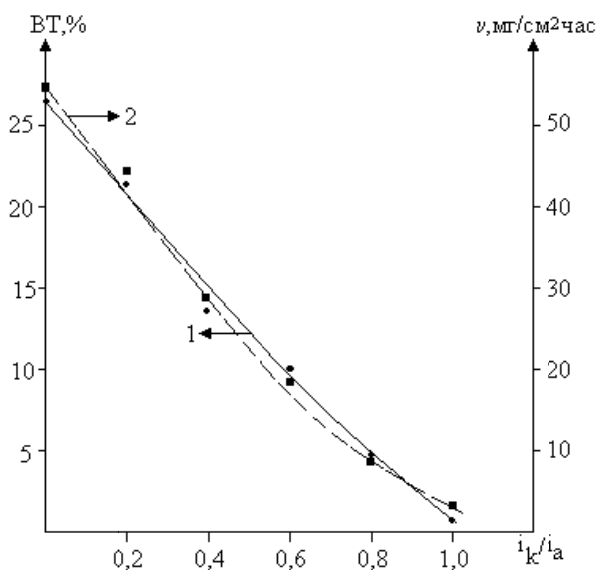


Figure 3 – Influence of correlations of sizes of amplitudes cathode and anodic semiperiods ( $i_k/i_a$ ) on CO of dissolution of silver in a 0.5 M solution of sulphuric acid:  
 $i_k=1000$  A/sq.m,  $\tau=0.25$  hour,  $t=25$  °C

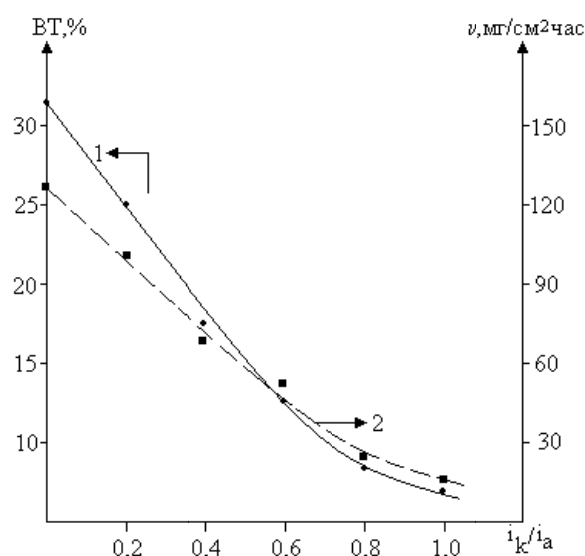


Figure 4 – Influence of correlations of sizes of amplitudes anodic and cathode semiperiods ( $i_k/i_a$ ) on CO of dissolution of silver in a 0.5 M solution of hydrochloric acid:  
 $i_k=1000$  A/sq.m,  $\tau=0.25$  hour,  $t=25$  °C

The similar course of curve dependence the efficiency –  $i_k/i_a$  clearly is shown in solution salt acids. Here it is also possible to control the lowering of the efficiency and speed of dilution of silver with increase in value of the cathode current. That seemed to be connected to the fact that with increase in value of current in the cathode half-cycle the speed of the reverse restoration of the formed ions, oxides, sulfates or chlorides of silver in an anode half-cycle is increased.

Thus, the electrochemical oxidation of silver in case of polarization by asymmetrical and pulse currents was explored by us for the first time and it was defined that the magnitude relation of amplitude of the cathode and anode half-cycles has a great impact to the efficiency and silver dilution speed.



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**ҚЫШҚЫЛ ЕРІТІНДІЛЕРІНДЕ СИММЕТРИЯЛЫ ЕМЕС  
ТОКПЕН ПОЛЯРИЗАЦИЯЛАҒАНДА КҮМІСТІҢ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІ**

**Аннотация.** Ғылыми жұмыста стационарлы емес токпен поляризациялағанда күкірт және тұз қышқылдарының ерітінділерінде анодты және катодты жартылай периодтарындағы ток амплитудасының шамасының күмістің еруінің ток бойынша шығымына және еру жылдамдығына әсері қарастырылды. Бұл зерттеуде катодты жартылай периодта ток тығыздығының шамасы тұрақты  $1000 \text{ A/m}^2$ , ал анодты жартылай

периодта ток тығыздығы 0-ден 1000 А/м<sup>2</sup> аралығында өзгертіліп тұрды. Айнымалы тоқты түрлендіру үшін арнайы қондырғы пайдаланылды, ол айнымалы ток көзінен, екі диодтардан Д1 және Д2, катодты және анодты жартылай периодтардағы токтың мәнін реттеу үшін екі айнымалы резисторлар R1 және R2, R3 тұрақты кедергі, анодты және катодты жартылай периодтардағы ток күшін бақылау үшін екі амперметр А1 және А2, электролиттік ұяшықтан және осциллографтан тұрады. Электродтар ретінде күміс және графит пластинкалары қолданылды.

Қышкыл ерітінділерінде анодты жартылай периодтың шамасының артуымен күмістің еру жылдамдығы және ток бойынша шығымы жоғарылайды, катодты жартылай периодтың шамасы артуымен күмістің еруінің ТШ және еру жылдамдығы төмендейтіні анықталды.

**Түйін сөздер:** электрохимия, электролиз, симметриялы емес ток, поляризация, электрохимиялық еру, ток тығыздығы.

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### ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ СЕРЕБРА В КИСЛЫХ РАСТВОРАХ ПРИ ПОЛЯРИЗАЦИИ НЕСИММЕТРИЧНЫМ ТОКОМ

**Аннотация.** В научной работе рассмотрены влияние величины амплитуды тока анодного и катодного полупериодов на выход по току и скорость растворения серебра при поляризации нестационарными токами в растворах серной и соляной кислот. В данном исследовании величина плотности тока в катодном полупериоде поддерживалась постоянной, равная 1000 А/м<sup>2</sup>, а в анодном полупериоде плотность тока менялась в интервале от 0 до 1000 А/м<sup>2</sup> и наоборот. Для преобразования переменного тока использовалась специальная установка, которая состоит из источника переменного тока, двух диодов Д<sub>1</sub> и Д<sub>2</sub>, один из которых подключен в пропускающем режиме, а другой - в запирающем, двух переменных резисторов R<sub>1</sub> и R<sub>2</sub>, для регулирования величины токов катодного и анодного полупериодов, R<sub>3</sub> постоянное сопротивление, два амперметра А<sub>1</sub> и А<sub>2</sub>, для контролирования силы тока в процессе электролиза в катодном и анодном полупериоде, электролитической ячейки и осциллографа. Электродами служили серебряная и графитовая пластинки. Установлено, что в растворах кислот с увеличением величины амплитуды анодного полупериода ВТ и скорость растворения повышается, а с увеличением величины катодного тока наблюдается снижение ВТ и скорости растворения серебра.

**Ключевые слова:** электрохимия, электролиз, несимметричный ток, поляризация, электрохимическое растворение, плотность тока.

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