ХІМІЧНІ ТЕХНОЛОГІЇ

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INFLUENCE OF TEMPERATURE ON THE RATE OF RELEASE OF HYDROGEN THROUGH THE INTERACTION OF AK7 ALLOY WITH ALKALINE-CHLORIDE SOLUTION

The dissolution rates of the test alloy and the evolution of hydrogen depend on the activity of the components of the test solution, which can be increased by changing the concentrations of sodium hydroxide and halide activators, changing the surface roughness of the samples, applying additional mixing and temperature control.

This work is devoted to determining the effect of the temperature of the test solution on the rate of hydrogen evolution by the interaction of the aluminum casting alloy brand AK7 with an alkaline-chloride medium. The influence of the temperature factor was investigated in the intervals (293 ÷ 323) K in a solution of sodium hydroxide with a concentration of 2.5 mol /dm^3 with impurities of sodium chloride with a concentration of 0.1 mol /dm^3.

The results of the research proved the activating effect of the temperature factor on the dissolution rate of the AK7 alloy and, as a consequence, the rate of hydrogen evolution. When the temperature rises to 323 K during the interaction of the alloy AK7 with an alkaline-chloride solution, there is a rapid increase in the rate of hydrogen evolution by an order of magnitude compared to room temperature and equal to 1.25 m^3 per 1 m^2 per 1 hour. This behavior is due to the activity of the components of the test solution, which with increasing temperature acts on the surface of the aluminum alloy accelerating the process of its dissolution and the rate of hydrogen evolution reaches such large values.

The value of activation energy H for the temperature rang (303 ÷ 323) K, which varies from 9 to 14 kJ/mol, is calculated, which indicates the diffusion nature of the rate of interaction of the aluminum alloy brand AK7 with alkaline-chloride solution.

Using the software package MS Exel 2016, regression polynomial relations were determined, which characterize the behavior of the dissolution rates of the sample and the indicators of the synthesized hydrogen from changes in temperature in the alkaline-chloride solution.

Key words: *hydrogen, AK7 alloy, the dissolution rate of the alloy, alkaline-chloride solutions, temperature, hydrogen evolution rate, halides, chemical dissolution.*

Introduction. The modern energy sector needs development, which consists in the use of environmentally friendly energy sources, which play an important role in hydrogen production. Industrial synthesis of hydrogen is an integral part of its use, because it is almost not found in nature in pure form and must be extracted from other compounds by various chemical and electrochemical methods.

To date, a large number of works on the synthesis of hydrogen, mainly for its use as an environmentally safe and alternative source of heat [1]. Its largest volumes are obtained by high-temperature conversion of coal and natural gas [1-3]. However, the cost of this hydrogen increases significantly compared to natural gas due to the need for additional purification operations. Electrochemical methods for producing hydrogen and methods of depolarizing destructive dissolution of metals are used to a lesser extent due to significant energy costs. The cost of this hydrogen increases 5-8 times compared to natural gas. Despite the high economic costs, hydrogen production by thermoelectric depolarizing cycles and electrolysis is constantly improved due to the high degree of purity of the obtained hydrogen [4]. To reduce energy and economic costs, a new method of hydrogen synthesis has been proposed - the method of biocatalytic systems [5]. However, its implementation takes a long time.

Modern methods of hydrogen production are characterized by the high cost of the final product due to additional purification operations, unsatisfactory economic consequences, utilization of by-products of the reaction, which inhibits the development of the hydrogen industry.

Alternative methods of hydrogen synthesis are chemical-thermal cycles by which hydrogen is obtained by the interaction of some metals with solutions, where they dissolve with the release of hydrogen. One of the most promising in this regard is the release of hydrogen by dissolving aluminum or its alloys in alkaline solutions. Given the large volumes of aluminum production, its use in the form of alloys, production waste and lack of products can actually reduce the cost of synthesized hydrogen by dissolving these alloys in alkaline solutions [7].

Analysis of recent research and publications. In [8] it is shown that when reacting with alkaline solutions, aluminum and its alloys show thermodynamic instability, which is associated with the destructive process of the metal. When aluminum interacts with alkali solutions, aluminate and complex hydroxide ions $[Al(OH)_4]$ are formed: at pH>11 the dissolution reaction proceeds by a destructive mechanism with hydrogen depolarization [2, 9-12]. Reactions of ionization of aluminum proceed gradually, they include stages of interaction of an oxide film with hydroxide and dissolution of metal on the following reactions:

$$Al_2O_3+2NaOH \rightarrow 2NaAlO_2+H_2O \quad (1)$$

$$Al+OH^- \rightarrow AlOH_{адс}+e^- \quad (2)$$

$$AlOH_{адс}+2OH^- \rightarrow AlOOH+H_2O+2e^- \quad (3)$$

$$AlOOH+OH^-+H_2O \rightarrow [Al(OH)_4]^- \quad (4)$$

$$H_2O+e \rightarrow H_{адс}+OH^- \quad (5)$$

$$H_{адс}+H_2O+e \rightarrow H_2+OH^- \quad (6)$$

The final product of reactions (1-6) is $Al_2O_3{\cdot}H_2O$, which can still be used in the production of aluminum, but in [14-17] as an experimental alloy selected brand AK7, which includes other impurities that affect the stationary potential alloy, namely the shift to the positive region due to the action of potentials and impurities at a given pH.

The rate of interaction of the aluminum alloy brand AK7 with alkaline solutions is slowed down due to the presence of impurities in the alloy. It contains 6-8% silicon, as well as impurities of copper, iron, manganese and zinc, which do not exceed 1.5%. When the AK7 alloy interacts with alkaline solutions, all these impurities form insoluble surface oxides of these metals [14]. Such compounds are localized on the surface of the alloy in the form of a porous and hydrated film, which changes the composition and, depending on the composition of the solution, the surface roughness of the sample diffuses from its surface.

In [15-19] the results of the rate of hydrogen evolution by the interaction of the alloy AK7 with the classes of surface purity from ∇3 to ∇7 in alkaline-halide solutions; the influence of fluoride and chloride ions on hydrogen synthesis was determined. The research results show that the most effective is the simultaneous use of chloride and fluoride activators with concentrations of 0.09 ÷ 0.11 mol/dm^3 and 0.19 ÷ 0.21 mol/dm^3, respectively, in a solution of 2.4 ÷ 2.6 mol/dm^3 NaOH. Simultaneous action of NaCl and NaF accelerators allows promising use in hydrogen production, as the obtained data on the specific dissolution rates of AK7 alloy are 10 times higher than the absence of impurities and are characterized by the following values: ΔP=2321,43 g and V_{H_2}=1126,4·10^3 in terms of 1 m^2 for 1 hour. The choice of the purity class of the sample surface is substantiated. The technologically selected surface roughness is recommended for which ∇5, for which ΔP=1000 g/m^2·h, and V_{H_2}=830 cm^3/h.

However, in works there are no researches of such indicator as change of temperature of solution. It can be assumed that by regulating the temperature, the components of the solution will accelerate the diffusion of the reaction products (metal oxides are formed from impurities) from the aluminum surface, increasing the rate of hydrogen evolution.

The aim of the work is to study the effect of temperature on the rate of hydrogen evolution in an alkaline-chloride solution containing 2.5 mol/dm^3 NaOH + 0.1 mol/dm^3 NaCl.

Results and discussions. The effect of temperature on the dissolution rate of the alloy AK7 is determined by the temperature dependence of the rate constant of this reaction in diffusion or kinetic control according to the exponential law of Arrhenius:

$$K(\Delta m)=Ae^{-Q/RT}, \quad (7)$$

where $K(\Delta m)$ – the rate of change of the alloy mass, g / cm^2 · h;; A – constant, which is equal to Δm at $1/T$=0; Q – activation energy; R=1,987 cal/mol (8.31 J / mol).

The logarithm of formula (7) allows to obtain a linear equation of the dependence of the rate of interaction of the aluminum alloy with an alkali chloride solution from $1/T$:

$$\lg K=\lg A-(H/2{,}303T), \quad (8)$$

where H – effective activation energy, which is determined from experimental data.

According to M.P. Juka [20], the activation energy of the destructive process is due to the kinetic nature, which includes the formation of new compounds in the aluminum alloy due to its significant values not exceeding 15÷ 20 kJ/g · mol, or purely diffusion processes occurring on the surface of the reactive alloy diffusion nature of the solution, reaction products in the form of aluminum oxide compounds and hydrogen evolution.

The logarithmic interpretation of the dependence of the dissolution rate of the aluminum alloy AK7 in alkaline-chloride solution on the effect of temperature is shown in Fig. 1. The obtained interpretation allows us to estimate the activation energy of the dissolution of the alloy and the mechanism of hydrogen evolution, which is associated with the interaction of the destructive medium (solution) with the aluminum alloy.

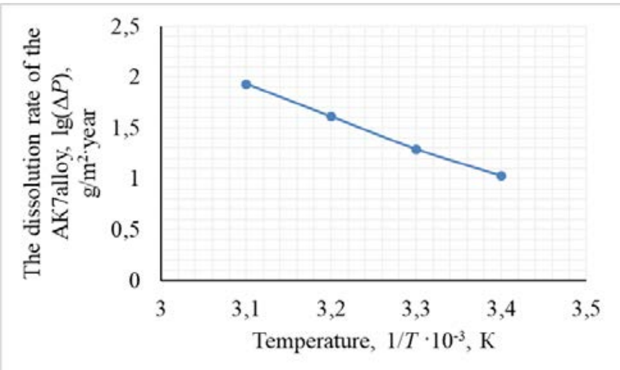

Fig. 1. Logarithmic interpretation of the dependence of the dissolution rate of the AK7 alloy in the temperature range (293÷323) K

The calculation of the activation energy according to Figs. 1 for the temperature range (303÷323) K varies from 9 to 14 kJ/mol, which indicates the diffusion nature of the rate of interaction of the alloy AK7 with an alkali-chloride solution.

Fig. 2 shows the dependence of the rate of hydrogen evolution during the interaction of the alloy AK7 with an alkaline-chloride solution of NaOH 2.5 mol/dm^3 + NaCl 0.1 mol/dm^3 in the temperature range (293÷323) K for one hour.

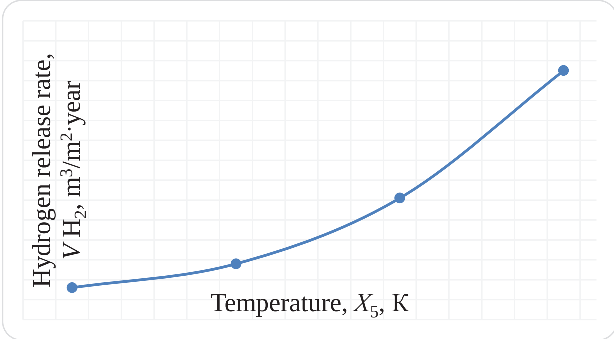

Fig. 2. The rate of evolution of hydrogen in alkaline-chloride solution at temperatures (293÷323) K

Fig. 2 indicates that with increasing temperature, the rate of hydrogen evolution increases markedly: at temperatures (293÷303) K the rate of hydrogen evolution is 0.16-0.28 m^3/m^2 · h, and with its increase to (313 ÷ 323) K the rate of hydrogen evolution increases to 0.61-1.25 m^3 / m^2 · h, which is several times higher than the alkaline solution, in which activator impurities are absent.

The behavior of the specific dissolution rate of the aluminum alloy is similar to the rate of hydrogen evolution: with increasing temperature from 293 K to 323 K, the dissolution rate of AK7 increases reaching values from 10.71 g / m^2 · h (at T = 293 K) to 85.57 g / m^2 · h (at T = 323 K).

The results of studies of chemical dissolution of AK7 alloy in alkaline-chloride solution correspond to polynomial functions and are interpreted by the following equations:

– hydrogen release rate:

$$V_{H_2} = 0{,}0013X_5^2 - 0{,}7648X_5 + 112{,}65, \quad (9)$$

– the dissolution rate of the alloy AK7:

$$\Delta P = 0{,}09X_5^2 - 52{,}962X_5 + 7804{,}7, \quad (10)$$

where X_5 – temperature, K.

The obtained equations (9), (10) determine the change in the specific indicators of the rate of hydrogen evolution in accordance with Figs. 2, and the dissolution rate of the AK7 alloy, which is affected by the reaction rate of the interaction of aluminum with OH^- and Cl^- ions. In addition, with increasing temperature, the intensity of diffusion of the reaction products of the aluminum alloy with the solution also increases.

Conclusions. The results of these studies indicate a rapid increase in the rate of hydrogen evolution with increasing temperature of the alkali chloride solution. In a solution of 2.5 mol/dm^3 NaOH + 0.1 mol/dm^3 NaCl at temperatures (303 ÷ 313) K, the index V_{H_2} becomes larger than the temperature of 293 K. This behavior is due to the formation of significant activity of the components of the solution, which with increasing temperature act on the surface of the reacting alloy, accelerating the process of its dissolution.

Prospects for further research are characterized by the substantiation of technological parameters of hydrogen production by the interaction of aluminum alloy brand AK7 with alkali-halide solutions.

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ВПЛИВ ТЕМПЕРАТУРИ НА ШВИДКІСТЬ ВИДІЛЕННЯ ВОДНЮ ШЛЯХОМ ВЗАЄМОДІЇ СПЛАВУ АК7 ІЗ ЛУЖНО-ХЛОРИДНИМ РОЗЧИНОМ

Швидкість реакції розчинення дослідного сплаву і виділення водню залежить від активності компонентів дослідного розчину, яку можна збільшити, змінюючи концентрацію гідроксиду натрію і домішок галогенідних активаторів, шорсткість поверхні зразків, а також застосовуючи додаткове перемішування і регулювання температури.

Цю роботу присвячено визначенню впливу температури дослідного розчину на швидкість виділення водню шляхом взаємодії алюмінієвого ливарного сплаву марки АК7 із лужно-хлоридним середовищем. Вплив температурного фактору досліджено в інтервалах (293÷323) К у розчині гідроксиду натрію за концентрації 2,5 моль/дм^3 *із домішками хлориду натрію концентрацією 0,1 моль/дм*^{3}*.*

Наведені результати досліджень довели активуючу дію температурного фактору на швидкість розчинення сплаву АК7 і, як наслідок, швидкість виділення водню. За підвищення температури до 323 К під час взаємодії сплаву АК7 із лужно-хлоридним розчином відмічено стрімке зростання швидкості виділення водню на порядок порівняно із кімнатною температурою, яке дорівнює 1,25 м^3*, перераховане на 1 м*^{2} *за 1 годину. Така поведінка дослідного розчину зумовлена активністю його компонентів, яка за збільшення температури діє на поверхню алюмінієвого сплаву, прискорюючи процес його розчинення, тому швидкість виділення водню досягає великих значень.*

Представлено розрахунок величини енергії активації Н для інтервалу температур (303÷323) К, який змінюється від 9 до 14 кДж/моль, що вказує на дифузійну природу швидкості взаємодії алюмінієвого сплаву марки АК7 із лужно-хлоридним розчином.

За допомогою програмного пакету MS Exel 2016 визначено регресійні поліноміальні співвідношення, що характеризують поведінку швидкостей розчинення зразку, і показники синтезованого водню залежно від зміни температури у лужно-хлоридному розчині.

Ключові слова: *водень, сплав АК7, швидкість розчинення сплаву, лужно-хлоридні розчини, температура, швидкість виділення водню, галогеніди, хімічне розчинення.*