

## NEW GENERATION OF ENERGY ACCUMULATING SUBSTANCES ON THE BASIS OF ACTIVATED ALUMINUM

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### ABSTRACT

*The study reported is focused on the increase of aluminum activity in its reaction with water through adding metals forming exfoliating systems or eutectics. Correlations between the composition of the alloy, the temperature and the rate of hydrogen evolution are established. A possibility of controlling the interaction of activated aluminum alloy with water is identified. It provides obtaining not only hydrogen at high rates but also hydroxides and oxides of aluminum of various compositions.*

*Keywords: energy accumulating substances, activated aluminum alloy, hydrogen.*

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### INTRODUCTION

The unique physical and chemical properties, as well as the almost unlimited resources give opportunity to use hydrogen as a source of energy in hydrogen energy systems. The environment safety is an important argument for introduction of hydrogen into the energy sector as only water vapor is discharged into the atmosphere when hydrogen is used. Furthermore, the use of hydrogen as a fuel excludes the possibility of greenhouse effect enhancement, harmful substances are not released (the automobile engine throws out 45 toxic substances, including carcinogens). There is also no danger of formation of stagnant zones of hydrogen as it easily escapes. The weight calorific value of hydrogen (28630 kcal kg<sup>-1</sup>) is 2.8 times higher than that of gasoline. The energy of ignition is 15 times less than that of the hydrocarbon fuel. The maximum velocity of propagation of the flame front is 8 times greater when compared with that of the hydrocarbons.

For wide application of hydrogen in power engineering, the problems of its effective production and highly effective use must be solved.

The fundamental physico-chemical and physico-

technical issues associated with the widespread introduction of hydrogen energy are largely determined by the need to develop new methods for efficient and environmentally safe production of hydrogen [1, 2].

In this regard, it seems promising to develop methods for obtaining hydrogen directly from water by its interaction with aluminum. The latter ranks first among the metals on the ground of its prevalence in nature. Its content in the earth's crust is 8.8 %. At the same time, it is known that a dense oxide film formed upon contact of aluminum with oxygen from the air creates diffusion limitations on the oxidation of aluminum even in boiling water. Working on this problem provides to solve a number of practical issues connected with the development of methods and conditions for aluminum activation by metals, especially in respect to its reaction with water.

The role of the activator metals' nature, the materials composition, the regimes of creating the necessary kind of non-equilibrium with the aim of obtaining hydrogen from water with high rates of emission is revealed. Based on the products of reaction, high-performance catalysts are advanced for the various chemical processes used. A number of technological methods for obtaining materials of a given concentration are developed. Thus, the

principle associated with the P.A. Rebinder's effect [3] is used for aluminum activation. It is based on the use of activators changing the specific surface energy. The strong activators include liquid metals and low-melting eutectics. Therefore, the following metals are used to activate aluminum: gallium, indium, tin, zinc, bismuth, lead, cadmium and antimony. The X-ray phase analysis applied verifies the eutectic character of the investigated alloys.

Under the influence of introduced metal-activators, the mechanical properties of the activated metals also change. The introduction of double and triple additives significantly reduces their strength. The sharp decrease of the mechanical properties is a consequence of the surface energy change realized through activator metals films formation. It is assumed that this proceeds following a mechanism of adsorptive degradation of strength [3, 4].

An increase of activator metals' percentage leads to milling of aluminum grain structure, an increase of the amount of the eutectics formed and their distribution in the bulk, an increase in the heterogeneity of alloys, while reducing strength. The established regularities correspond to the ideas of P.A. Rebinder's school on the change in state and properties of the solids' surface under the influence of metal-activators.

The aim of the present work is to study the kinetics and the interaction mechanism of activated aluminum alloys with water to obtain hydrogen from water of a different degree of mineralization.

## EXPERIMENTAL

### Materials

Activated aluminum alloy Rau-85 containing metals activators (gallium, indium, tin) in dispersed form of a size under 0.63 mm [4] was used.

Distilled water, sodium bicarbonate, sodium chloride, calcium chloride, magnesium chloride, HCl (35 %) were also provided.

### Methods

The experiments were carried out in a three-necked flask with a casing. The volume of the released gases was measured by a drum-type gas meter. The temperature of the water heating was measured by a thermometer with an accuracy of 0.1°C.

The procedure was as follows: the tested water

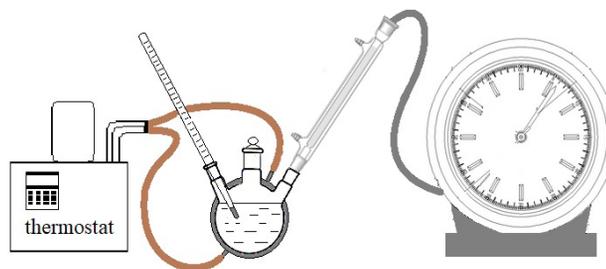


Fig. 1. The installation used to determine the rate of gas emission and the heat release.

(emitter of formation water) of the required mass was poured into the three-necked flask. The water temperature was set at 25°C and was further controlled by a thermostat. Rau-85 reagent was poured through the neck of the flask, then the system was hermetically closed. The thermostat was switched off. One of the necks of the flask was connected to the drum-type gas meter through a reflux condenser to prevent water vapor from entering the gas meter. The gas meter registered the volume of gas released during reaction.

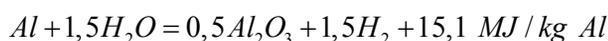
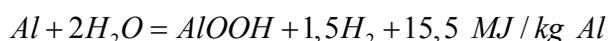
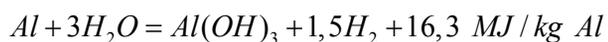
### Preparation of a formation water imitate

The salt composition simulating carbonate deposits referred to:  $\text{Ca}^+$  (1100 mg dm<sup>-3</sup>),  $\text{Mg}^{2+}$  (380 mg dm<sup>-3</sup>),  $\text{Na}^+$  (7500 mg dm<sup>-3</sup>),  $\text{HCO}_3^-$  (976 mg dm<sup>-3</sup>),  $\text{Cl}^-$  (14023 mg dm<sup>-3</sup>). Two solutions were prepared to obtain the imitate: A and B. Solution A contained  $\text{CaCl}_2$  (3046 mg dm<sup>-3</sup>), and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (3177 mg dm<sup>-3</sup>), while solution B –  $\text{NaCl}$  (18084 mg dm<sup>-3</sup>) and  $\text{NaHCO}_3$  (1344 mg dm<sup>-3</sup>).

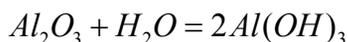
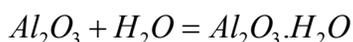
## RESULTS AND DISCUSSION

Aluminum activated by metals activators is an alternative source of energy providing hydrogen from water, its storage, as well as heat energy.

The interaction of aluminum with water is accompanied by release of hydrogen and heat. The composition of the solid product depends on the reagents ratio and the reaction temperature [6]:



Aluminium oxide hydration reaction can proceed in parallel with these reactions according to the equations:



It is noted [5] that the thermodynamic instability of activated aluminum to water makes it possible to obtain hydrogen at high rates as a reaction product. The intensity of the reaction depends on the structure of the alloy, the state of the grain boundaries, and the distribution of the additives between the body and the grain boundaries [8 - 9].

The reactivity of the alloy to water is determined by the conditions of its production. The most active one is an alloy prepared by quenching in liquid nitrogen. The introduction of activator metals to aluminum and quenching the alloys with high cooling rates promote the formation of a single-crystal structure of the metal and the increase of the number of micro-galvanic elements.

The processes leading to grains dispersion (quenching, additives increase) contribute to the activity.

The interaction of activated aluminum with water occurs on aluminum surface. It results in the production of hydrogen and a new phase of aluminum hydroxide. For the quantitative description of the reactivity of activated aluminum in respect to water, the Avrami-Erofeev equation is used.

The characteristic form of the topochemical reaction kinetic curve is shown in Fig. 2. However, the shape

of the curve is related to the character of the processes taking place. The induction period, which is characterized by initial changes in the system, is 1800 s, 600 s, 90 s and 30 s for Al-Ga; Al-In; Al-Ga-In; Al-Ga-In-Sn alloys, respectively.

An increase of the activator metals content in alloy leads to a reduction of the induction period. For the quaternary Al-Ga-In-Sn alloy containing 0.5 mass %, 1.0 mass %, 3.0 mass % and 5.0 mass % activator metals the induction period is 360 s, 250 s, 180 s, 30 s (Fig. 2b), correspondingly. The period of rapid increase of the rate of hydrogen evolution appears to be related to the formation and growth of a product nucleus in the reaction zone. This process involves the interaction of activated aluminum with water, followed by the formation of aluminum hydroxide's germs. The spots of complex eutectics isolation along the grain boundaries are nucleation centers of the new phase. The reaction rate starts to decrease after reaching a maximum. This is related to the aluminum hydroxide's germs growth leading to the formation of a continuous layer that gradually shifts deep into the reacting particles.

The investigation continues in this direction using the activated aluminum alloy Rau-85 as an oxidizer. It contains metals activators – gallium, indium, tin (5 mass %) in a dispersed form with a particles size under 0.63 mm. Aqueous solutions of sodium bicarbonate, chlorides of sodium, calcium and magnesium and mixtures thereof, with or without addition of HCl were prepared using

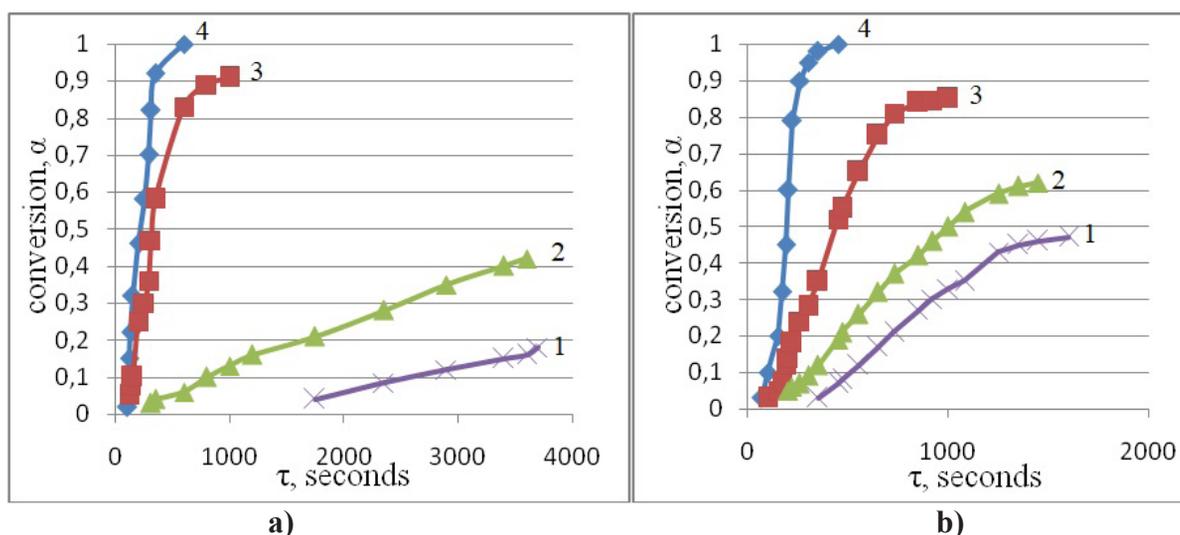


Fig. 2. Dependence of the conversion(α) of alloys interaction with water on time. a) 1 - Al-Ga; 2 - Al-Ga-In; 3 - Al-Ga-In; 4 - Al-Ga-In-Sn (5,0 mass % of metals activators); b) Al-Ga-In-Sn alloy containing metals activators (mass %): 1 - 0,5; 2 - 1,0; 3 - 3,0; 4 - 5,0;

Table 1. An ionic composition and properties of a formation water imitate

Model solution	Content of ions, mg·dm <sup>-3</sup>					$\rho$ , kg·m <sup>-3</sup>	pH	Eh, mV	Conductivity, mS·cm <sup>-1</sup>
	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>				
No. 1	760	14023	7500	1100	380	1009	7,81	-48	19,59

Table 2. Electrolytes solutions composition and total mineralization.

Electrolyte composition	NaHCO <sub>3</sub> , mg·l <sup>-1</sup>	NaCl, mg·l <sup>-1</sup>	CaCl <sub>2</sub> , mg·l <sup>-1</sup>	MgCl <sub>2</sub> ·6H <sub>2</sub> O, mg·l <sup>-1</sup>	Total mineralization, mg·l <sup>-1</sup>
Solution No. 1 (formation water simulation)	1344	18084	3046	3177	25651
Solution No. 2	2688	-	-	-	2688
Solution No. 3	2688	36168	-	-	38856
Solution No. 4	5376	-	-	-	5376
Solution No. 5	5376	72336	-	-	77712

distilled water.

The ionic composition of the produced imitate of formation water, its physical and chemical properties are shown in Table 1. The data listed there shows that the model solution No. 1 is slightly alkaline with a pH value of 7.81 and a density of 1009 kg m<sup>-3</sup>. This water sample is highly mineralized. Its oxidation-reduction potential value is -48 mV, which corresponds to the conditions of the reduction environment (from +200 mV to -300 mV) [10].

The electrolyte solutions compositions and their total mineralization values are summarized in Table 2.

To evaluate the oxidation efficiency of the activated aluminum alloys in aqueous solutions of salts with hydrochloric acid addition the hydrogen yield and the amount of the released heat by the reaction are calculated using the equation:

$$Q = m \cdot \Delta t \cdot 4,186$$

where  $m$  is the mass of the formation water imitate used in the experiment, while  $\Delta t$  is the time gap between two subsequent readings of the gas meter and the thermometer.

The rate of hydrogen emission is calculated on the ground of the formula (ml g<sup>-1</sup> min<sup>-1</sup>):

$$W_H = \frac{V}{m \Delta \tau}$$

where  $V$  is the volume of the emitted hydrogen,  $m$  is the weight of Rau-85, while  $\Delta t$  is the time gap between two subsequent readings of the gas meter and the thermometer.

Fig. 3(a) shows the evolution curves of hydrogen (gases) obtained by oxidation of the activated aluminum alloy by model saline solutions of sodium bicarbonate (curves 1 and 5), sodium bicarbonate with sodium chloride (curve 2) and sodium bicarbonate with sodium, calcium and magnesium chlorides (curve 4) in a hydrochloric acid medium at a room temperature. The weight of Rau-85 reagent amounts to 1g. The weight of the water-salt solution is 234 g (the mass of water is much larger than that of the water required by the reaction stoichiometry), the addition of HCl (35 %) refers to 39 g.

Based on the data in Fig. 3, it can be concluded that the reactivity of the alloy in respect to water can be controlled by introducing appropriate additives to water, varying the amount thereof, and also by varying the temperature of the test and the conditions for the alloy heat treatment.

It is found that the rate of hydrogen evolution during oxidation of activated aluminum Rau-85 in distilled water is higher than that in the formation water imitate. The reaction takes place without an induction period, while in the formation water imitate the induction period is 15 min - 20 min. The rate of oxidation of activated

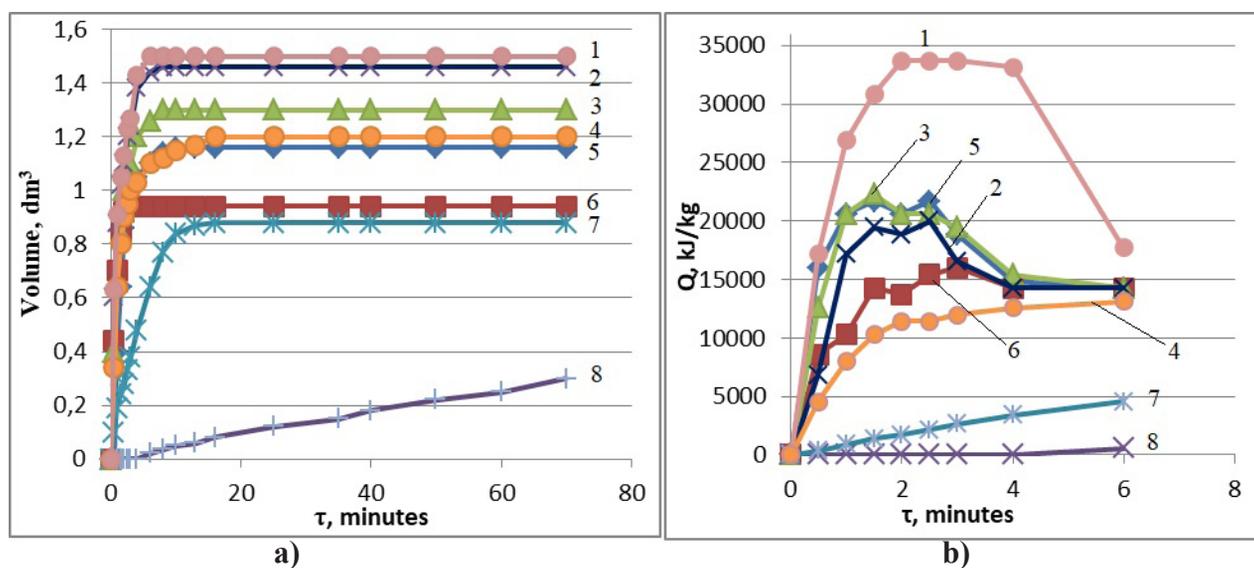


Fig. 3. Dependence of the evolved gases amount (a) and the heat of reaction (b) during the oxidation of activated aluminum alloy Rau-85 by electrolyte solutions. 1 - solution no. 5 with HCl; 2 - solution no. 4 with HCl; 3 - solution no. 3 with HCl; 4 - distilled water with HCl; 5 - solution no. 1 with HCl; 6 - solution no. 2 with HCl; 7- distilled water without HCl; 8 - solution no. 1 without HCl.

aluminum by solutions of electrolytes with additions of hydrochloric acid increases with the transition from a multicomponent solution to a one-component solution of  $\text{NaHCO}_3$ . The greatest yield of gases (1.51 liters per 1 gram alloy) is obtained within 8 min in case of using solution No. 5 containing 5376 mg.  $\text{l}^{-1}\text{NaHCO}_3$  (curve 1). The volume of the released gases is much larger than the theoretically calculated volume of hydrogen (1.24  $\text{m}^3$  of hydrogen is stoichiometrically estimated per kg of Al). The obtained results indicate that during the exothermic reaction, the aqueous solution of the salt is heated to 60°C. At this temperature sodium hydrogen carbonate decomposes into sodium carbonate, carbon dioxide and water.

The experiments show that a large number of active centers appear on activated aluminum surface in hydrochloric acid medium. Besides, the reaction begins immediately over the entire surface. The reaction proceeds without an induction period.

Hydrochloric acid is a strong electrolyte. Apparently, the electrolytic dissociation in its medium shifts toward the formation of hydrated ions, hydroxonium ion,  $\text{H}_3\text{O}^+$ , and  $\text{OH}^-$  (irreversible stage). The hydroxo-

nium ion,  $\text{H}_3\text{O}^+$ , is an active oxidizer. It is established that in distilled water with addition of HCl (5 %), the interaction with the activated aluminum alloy proceeds with a noticeable increase of the hydrogen yield and heat release. The latter in the acidized formation water imitate is 6 times higher than that obtained in an acid absence. The rate of hydrogen evolution during the reaction of the activated aluminum alloy Rau-85 with acidized imitate of formation water reaches 1100  $\text{ml g}^{-1}\text{min}^{-1}$ , and it proceeds within 6 min, while in the acid absence, the maximum rate of hydrogen evolution is only 20  $\text{ml/g min}$ . When formation water pH decreases with the addition of hydrochloric acid to values below zero, the volumetric yield of hydrogen increases and reaches up to 99 % of theoretical one, while the heat reaches a value of 33712  $\text{kJ kg}^{-1}$ .

## CONCLUSIONS

Thus, the study of the kinetics and mechanism of activated aluminum alloys interaction with water shows that the reactivity of the alloy in respect to water can be controlled by introducing appropriate additives to

water, changing the degree of their mineralization and pH, varying the temperature of the experiment and the conditions of the alloy preparation.

The rate of hydrogen evolution during the oxidation of activated aluminum Rau-85 in distilled water is higher than that in a formation water imitate.

The transition from a multicomponent to a single component salt solution containing hydrochloric acid increases the rate of oxidation of activated aluminum.

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