

Activated aluminum for hydrogen generation from water

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Al-based alloys and mechanochemically activated aluminum powders were prepared in this study, and the regularities of their hydrolysis reaction with water were studied. Aluminum alloys were prepared by melting aluminum with additions of Ga–In–Sn eutectic (5 wt.%), bismuth (3 wt.%), antimony (3 wt.%), or zinc (3 wt.%). The temperature-dependent kinetics of their hydrolysis in a temperature range 25–70 °C was studied by using a volumetric technique. The most efficient activation of the hydrolysis process was achieved for the Al–Ga–In–Sn–Zn alloy, particularly at low temperatures (5 and 25° C). The addition of bismuth to the Al–Ga–In–Sn alloy significantly decreases the hydrolysis rate, whereas the addition of antimony has only a weak effect on the process, despite the fact that the standard electrode potentials of bismuth and antimony have rather close values.

Commercially available aluminum PA-4 and ASD-1 powders were mechanochemically activated by Ga–In–Sn or Ga–In–Sn–Zn eutectic alloys (5 wt.%) and graphite (1–3 wt.%) in a mixer type ball mill. Subsequently, they were pressed ($P = 4$ MPa) into the pellets, which were used to generate hydrogen from water via the hydrolysis process. X-ray diffraction study of the milled PA-4 powder revealed the presence of four phases, including aluminum, graphite, and two In–Sn intermetallic compounds (In_3Sn and $In_{1-x}Sn_x$, where $x \approx 0.04$). The quantitative analysis by EDX showed a uniform distribution of the activating additives over the pellet surface, while the graphite was partly aggregated. Studies on the hydrolysis kinetics when utilizing Al-based pellets demonstrated that the process readily proceeds at temperatures $\geq 5^\circ$ C. At the same time, the efficiency of hydrogen generation depends on the amount of the added graphite, particle size of aluminum powders, duration and medium of their mechanochemical treatment, and the hydrolysis temperature.

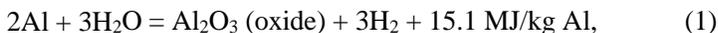
Keywords: Aluminum alloys, Activated aluminum powders, Hydrolysis, Hydrogen generation.

Introduction

During the past decades, hydrogen power industry, which is aimed on the use of hydrogen as an energy carrier and as a fuel, has been actively developing [1-3]. Particularly, the demand for fuel cells for various purposes, when electric current is generated as a result of the anodic oxidation of hydrogen and corresponding cathodic process, has been greatly increased. Broadening of the application scopes and increasing of the used amount of hydrogen call for improving technologies of its production, transportation and storage. Despite free hydrogen is not naturally available, it is however obtained from a variety of its compounds, first of all from water and hydrocarbons.

Among the known methods of hydrogen production, hydrolysis of so-called energy-storage substances (ESSs) [4] deserves special attention because the obtaining of hydrogen from water using ESSs can be carried out directly at the place of its use, which allows avoiding challenges associated with its accumulation, storage and transportation. The most efficient ESSs are binary and complex metal hydrides (MgH_2 , NaBH_4 , LiBH_4 etc.) and light metals (Al, Mg etc.) or their alloys.

Aluminum has a number of obvious advantages for use as an ESS, however, it must be activated in order to destroy the integrity of the protective oxide film on its surface. Depending on conditions, the unoxidized aluminum readily and rapidly reacts with water according to the following equations:



All these reactions are exothermic. The amount of hydrogen evolving from water is 1244 L H_2 /kg Al or equivalently 0.111 kg H_2 /kg Al.

Various mechanical, mechanochemical and chemical methods of activating aluminum are broadly utilized [5, 6]. In our studies, the alloys of aluminum with low-melting and electropositive metals, as well as pellets made from aluminum powders, mechanochemically activated by low-melting metals and graphite were prepared, and regularities of their hydrolysis were studied.

Materials and Experimental procedures

Aluminum alloys with the additives of activating metals (eutectic Ga-In-Sn alloy, Bi, Sb, Zn) were prepared in a resistance electric furnace in an argon atmosphere with mechanical stirring. All used metals were of high purity (≥ 99.9 wt.%). The eutectic Ga-In-Sn alloy with mass fractions of the components of 67/22/11 % has a melting point of 10.7 ± 0.3 °C [7]. The regularities of hydrogen evolution during the interaction of the obtained alloys (1 g samples) with water were studied by periodically measuring the volume of hydrogen formed using a volumetric unit, which consisted of a thermostated reactor containing 100 mL of distilled water, an eudiometer and a connecting tube. The measured values of the volume of the released hydrogen gas were normalized to the normal conditions.

Mechanochemical activation of aluminum powders PA-4 (grain size ≤ 100 μm) and ASD-1 (grain size < 30 μm) by Ga-In-Sn or Ga-In-Sn-Zn eutectic alloys and graphite was performed in a SPEX SamplePrep 8000D[®] mixer ball mill (2 hardened steel vials, 2 steel balls in each vial, mass of one ball of 1 g, ball-to-mixture mass ratio of 1 : 1) in an argon atmosphere for 1, 2 or 4 hours. The melting point of eutectic Ga-In-Sn-Zn alloy with mass fractions of the components of 61/25/13/1 % is ≈ 3 °C [8].

X-ray diffraction patterns of activated Al powders were obtained using a powder X-ray diffractometer DRON-3.0 with Cu- K_{α} radiation. A full-profile refinement of lattice parameters was performed by the Rietveld method using the Fullprof software package [9, 10]. The surface morphology and composition of prepared pellets were studied using a Zeiss EVO 40XVP scanning electron microscope with an INCA Energy microanalysis system.

The obtained powders were compressed into the pellets ($P = 4$ MPa, $\varnothing = 1$ cm, $m = 0.2$ or 0.3 g) in a protective atmosphere of argon gas. The main elements of volumetric unit, used to control the volume of hydrogen released during the hydrolysis of aluminum, included a thermostated reactor with distilled water and a flowmeter SmartTrak[®] M100L.

Results and Discussion

Aluminum alloys, containing 3-10 wt.% of eutectic Ga-In-Sn alloy, started the hydrolysis reaction already at a temperature of 25 °C. The increase in the mass fraction of Ga-In-Sn eutectic in the aluminum alloy from 3 to 10 % led to a significant acceleration of the hydrolysis of aluminum (see Fig. 1). During the first minutes of the reaction, active cracking and grinding of the alloys took place, after which the hydrolysis of aluminum proceeded almost to the end, while its rates accelerated for the alloy samples containing a higher eutectic content. The metals of the activating eutectic did not participate in the hydrolysis reaction [11].

Therefore, doping aluminum by small amounts of Ga, In and Sn, forming the eutectic alloy, provides an efficient ESSs that can be widely used to release hydrogen from water under ambient conditions. However, hydrogen evolution rate varies greatly during the hydrolysis of aluminum based alloys, and the hydrolysis is accompanied by a significant heating of the reaction mixture when there is no external cooling.

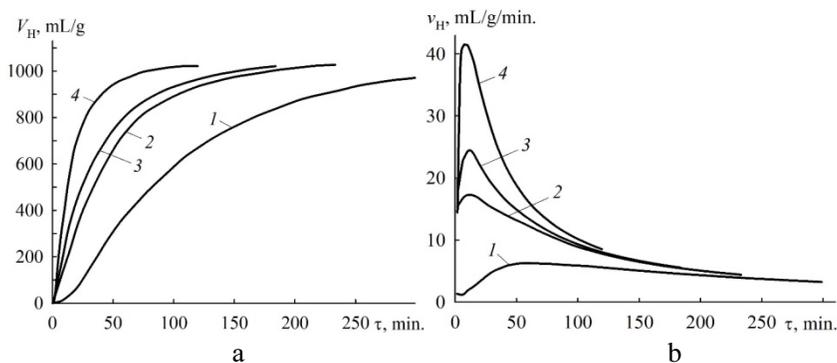


Fig. 1. Time dependencies of the volume of the evolved hydrogen (a) and average hydrogen evolution rate (b) during the hydrolysis at 25 °C of the aluminum alloys with mass fractions of eutectic Ga-In-Sn alloy (%): 3 (1); 5 (2); 7 (3); 10 (4)

The introduction of the Bi or Sb additives (3 wt.%) into the alloy of aluminum with the Ga-In-Sn eutectic (5 wt.%) differently affected the course of the hydrolysis of aluminum. In the presence of bismuth in the aluminum based alloy, the rate of hydrolysis decreased significantly, while the presence of antimony did not significantly affect its course, although

the standard electrode potentials of bismuth and antimony have similar values (see Fig. 2). Obviously, the electrochemical properties of the Bi or Sb additives do not have a significant influence on the regularities of interaction of aluminum with water. The increase in temperature from 25 to 70 °C led to a significant increase in the rate of hydrolysis of aluminum for all investigated alloys [12].

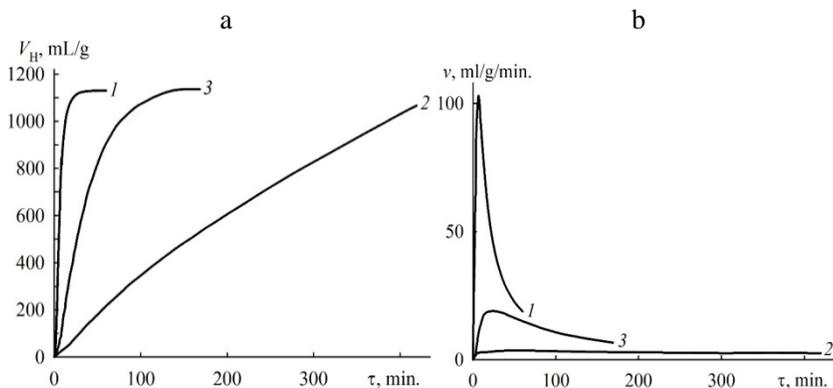


Fig. 2. Time dependencies of the volume of the evolved hydrogen (a) and average hydrogen evolution rate (b) during the hydrolysis at 55 °C of the aluminum alloys with 5 wt.% of eutectic Ga-In-Sn alloy (1) and 3 wt.% of Bi (2) or Sb (3)

It should be noted that during the hydrolysis of aluminum, doped with the Ga-In-Sn eutectic and bismuth, the generation of hydrogen occurred at almost constant rates for a long period of time, which is important to achieve a stable hydrogen supply to a fuel cell.

When zinc (3 wt.%) was used as an additional additive to the aluminum alloy with the Ga-In-Sn eutectic (5 wt.%), the rate of hydrogen evolution from water significantly increased, particularly at low hydrolysis temperatures (25 and 40 °C) (see Fig. 3) [13]. Thus, the change in the composition of the alloying additives to the aluminum-based alloys allows one to significantly change the regularities of aluminum hydrolysis and the productivity of hydrogen generation. According to the results of the X-ray diffraction phase analysis, the main component of the hydrolysis products of the investigated Al-based ESS is boehmite. In addition, the products

include bayerite and small amounts of alloying metals, which do not participate in the hydrolysis reaction [13].

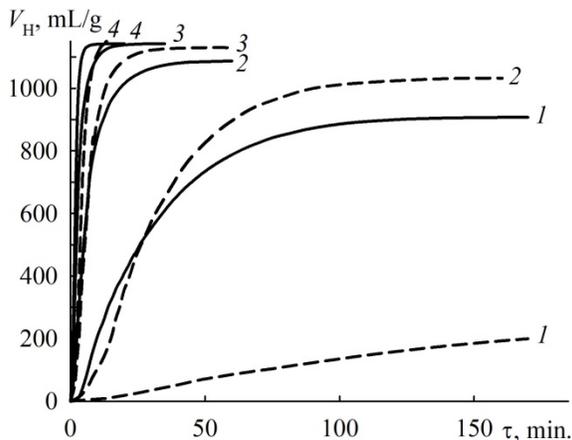


Fig. 3. Time dependencies of the volume of the evolved hydrogen during the hydrolysis of the aluminum alloys with 5 wt.% of eutectic Ga-In-Sn alloy (---) and 3 wt.% of Zn (—) at temperatures (°C): 25 (1); 40 (2); 55 (3); 70 (4)

The hydrolysis of aluminum is a heterogeneous reaction, and its rate depends on the interface area between the reagents. Therefore, an obvious way to achieve a high rate of hydrogen generation is by using the pre-activated fine powders of aluminum. Analysis of the published reference data shows that the kinetics of interaction of the activated aluminum powders with water depends on the activation method, the amount and composition of the activating substances used, size and morphology of the powders and the temperature of the process, further to the amount of the reagents, in particular, water. In our studies, aluminum powders PA-4 and ASD-1 were mechanochemically activated by the eutectic Ga-In-Sn or Ga-In-Sn-Zn alloys (5 wt.%) and graphite (1-3 wt.%), then compressed into the pellets. X-ray phase analysis of the non-pressed activated PA-4 powder showed presence of the phases of aluminum and graphite as well as intermetallic compounds of indium and tin (In_3Sn and $\text{In}_{1-x}\text{Sn}_x$ ($x \approx 0.04$)). SEM micrographs of the pellet surface showed the well developed interfaces between the compressed aluminum grains. According to the

energy dispersive X-ray analysis, the distribution of activating elements in the pellet surface was very uniform, but the graphite was partially aggregated [14].

The kinetics studies of the hydrolysis of activated aluminum powders used in the form of the pellets showed that the use of graphite as an additional activating additive led to an increase in the rate of the hydrolysis for more than an order of magnitude (see Fig. 4).

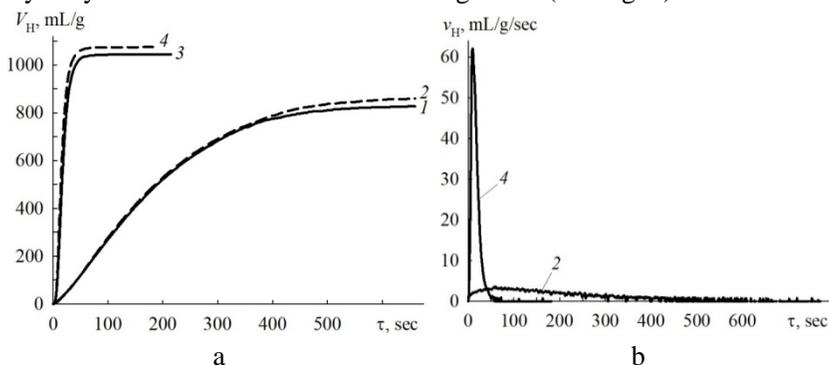


Fig. 4. Time dependencies of the volume of the evolved hydrogen (a) and average hydrogen evolution rate (b) during the hydrolysis of the pellets from PA-4 powder activated during 4 h with following additives:

Ga-In-Sn (5 wt.%) (1, 2); Ga-In-Sn (5 wt.%) + graphite (3 wt.%) (3, 4);
hydrolysis temperature 25 °C, $m_{\text{pellet}} = 0.2$ (1, 3) and 0.3 g (2, 4)

Based on the data presented in Fig. 4a, the values of the hydrogen yield were calculated as related to the theoretically limiting volumes of the evolved hydrogen. The reached values of the hydrogen yield were: 70 % (1); 73 % (2); 91 % (3); 94 % (4) (see Fig 4a). From Fig. 6a it is also clear that an increase in the weight of the pellets from 0.2 g to 0.3 g led to a slight increase in the hydrolysis rate and hydrogen yield.

The difference in the values of the melting point of eutectic alloys Ga-In-Sn and Ga-In-Sn-Zn is about 8 °C, but the replacement of one alloy with another one during the mechanochemical activation of aluminum powders together with graphite did not lead to a considerable change in the rate of the hydrolysis of aluminum from activated and compressed powders

as well as the hydrogen yield. Apparently, the amounts of the used eutectic alloys (5 wt.%) were too small to identify the effect of the difference in their melting points on the regularities of the hydrolysis of aluminum from the prepared pellets [14].

The influence of the amount of graphite in the prepared pellets and the temperature of their hydrolysis on the rate of hydrogen evolution can be estimated from the dependencies shown in Fig. 5. It is seen that the evolution of hydrogen during the active stage of aluminum hydrolysis from pellets of PA-4 powder mechanochemically activated by Ga-In-Sn eutectic is accelerated with an increase in the amount of graphite and temperature.

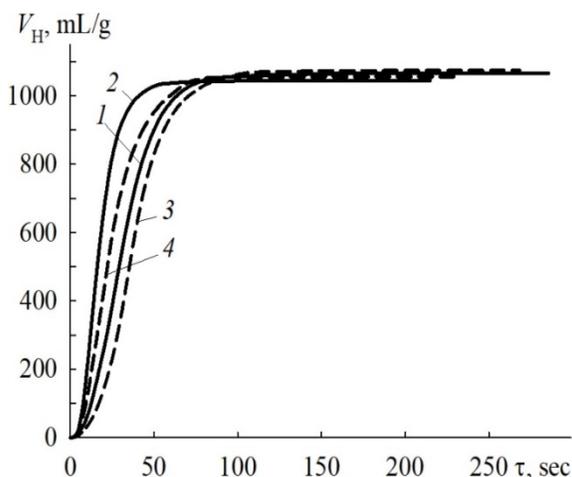


Fig. 5. Time dependencies of the volume of the evolved hydrogen during the hydrolysis of the pellets from PA-4 activated for 4 h using Ga-In-Sn eutectic alloy (5 wt.%) with 3 (1, 2) and 1 wt.% of graphite (3, 4); hydrolysis temperature 5°C (1, 3) and 25°C (2, 4), $m_{\text{pellet}} = 0.2 \text{ g}$

It should be noted that PA-4, activated and compressed as described above, actively reacts with water already at a temperature of 5 °C. The effect of the grain size of the aluminum powders on the performance of the hydrogen evolution during hydrolysis of the pellets prepared from the both powders, which were mechanochemically activated by 5 wt.% of Ga-In-Sn-Zn eutectic and 3 wt.% of graphite, is shown in Fig. 6. It can be seen

that replacing a coarser PA-4 powder with a finer ASD-1 powder led to the higher rate of the hydrogen evolution and hydrogen yield.

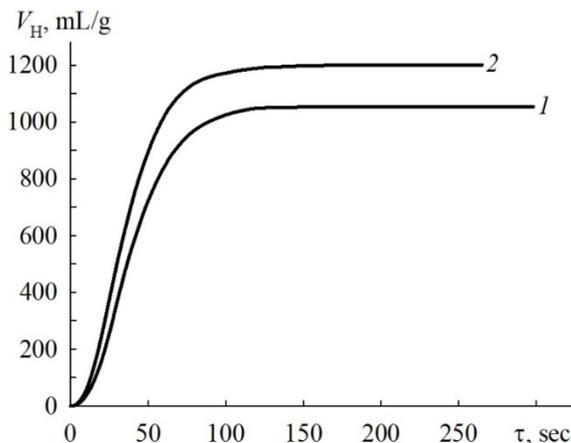


Fig. 6. Time dependencies of the volume of the evolved hydrogen during the hydrolysis of the pellets from PA-4 (1) and ASD-1 (2) powders activated by Ga–In–Sn–Zn (5 wt.%) + graphite (3 wt.%) during 4 h; hydrolysis temperature 5°C , $m_{\text{pellet}} = 0,3\text{ g}$

Our studies have shown that the duration of mechanochemical activation of aluminum powders also affects their activity in the hydrolysis process. As it follows from the Fig. 7, increasing the duration of the treatment of the ASD-1 powder together with 5 wt.% of Ga–In–Sn eutectic and 3 wt.% of graphite in the mill from 1 to 4 hours resulted in a significant increase in the rate of the hydrolysis of the aluminum from the prepared pellets and the hydrogen yield [14].

A medium, in which the powders were treated, also influenced their activity during hydrolysis. According to Fig. 8, the rate of hydrogen evolution and its yield during hydrolysis of PA-4 powder mechanochemically activated by Ga–In–Sn–Zn eutectic (5 wt.%) and graphite (3 wt.%) in air were lower, than during the hydrolysis of the same powder activated in an argon atmosphere.

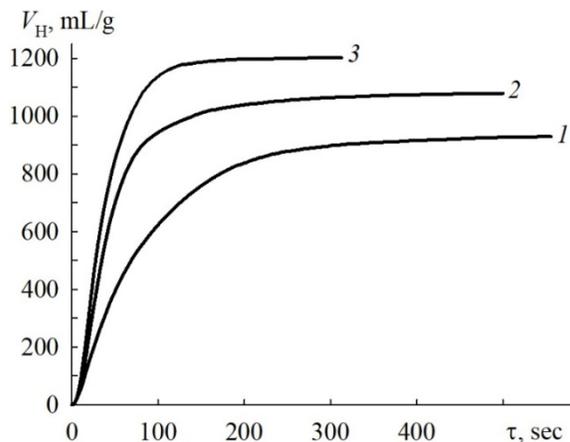


Fig. 7. Time dependencies of the volume of the evolved hydrogen during the hydrolysis of the pellets from ASD-1 activated by Ga–In–Sn (5 wt.%) + graphite (3 wt.%) during 1 (1), 2 (2), and 4 h (3); hydrolysis temperature 5 °C, $m_{\text{pellet}} = 0.2$ g

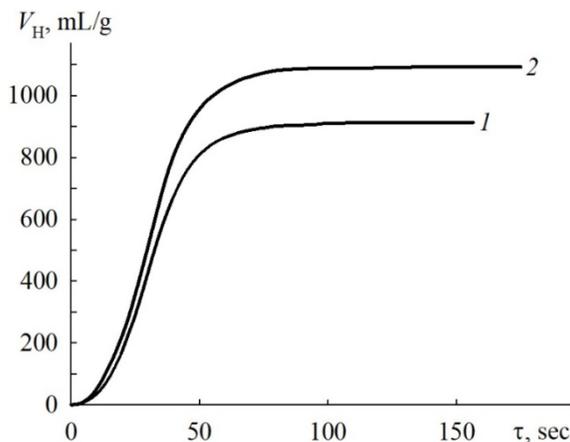


Fig. 8. Time dependencies of the volume of the evolved hydrogen during the hydrolysis of the pellets from PA-4 activated by Ga–In–Sn–Zn (5 wt.%) + graphite (3 wt.%) during 4 h in air (1) and in argon (2); hydrolysis temperature 5 °C, $m_{\text{pellet}} = 0.2$ g

Thus, hydrogen evolution during the hydrolysis of the pellets prepared from the aluminum powders mechanochemically activated by low-melting metals and graphite depends on many parameters. It is important that such materials actively release hydrogen from water at temperatures of ≥ 5 °C and can be used in autonomous hydrogen generators of hydrolysis type for various purposes.

Conclusions

The activation of aluminum by the alloying with small quantities of the Ga–In–Sn eutectic alloy, bismuth, antimony, or zinc dramatically improves the performance of the individual Al metal used for generating gaseous hydrogen as a result of the hydrolysis process at temperatures of ≥ 25 °C. The variations in the qualitative and quantitative composition of the alloying additives to the aluminum-based alloys allows to significantly change the regularities of aluminum hydrolysis and the productivity of hydrogen generation.

Mechanical grinding of PA-4 and ASD-1 aluminum powders with additions of Ga-In-Sn or Ga-In-Sn-Zn eutectic alloys and graphite, followed by pressing the obtained activated powders into pellets, makes it possible to obtain materials capable of intensively evolving hydrogen from water at temperatures down to 5 °C. The hydrolysis of the aluminum powders, treated in such a way, occurs quickly and almost completely. The performance of aluminum pellets during their hydrolysis and hydrogen generation becomes significantly more efficient with increasing graphite content in the pellets and duration of the mechanochemical treatment of the powders in argon atmosphere as well as with decreasing grain size of the aluminum powders and increasing the hydrolysis temperature.

The investigated Al-based ESSs are promising for use in hydrolysis-type hydrogen generators of various performance parameters and purposes without an additional heating of the reaction mixture. Taking into account the peculiarities of the hydrolysis of such ESSs, it is possible to use aluminum alloys in hydrogen generators as disposable cartridges, for example, when charging batteries of mobile electronic devices, while dosing of the pellets made from activated aluminum powders can provide

long-term operation of autonomous current sources based on fuel cells and hydrogen generators of hydrolysis type.

Acknowledgment

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