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Studies on microstructure of activated aluminum and its hydrogen generation properties in aluminum/water reaction

A.V. Ilyukhina [a], [b], [*], O.V. Kravchenko [c], B.M. Bulychev [c]

[a] *Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya st. 13, bld. 2, Moscow, 125412, Russian Federation*
[b] *National University of Science and Technology (MISIS), Leninsky Prospect, 4, Moscow, 119049, Russian Federation*
[c] *Department of Chemistry, Moscow State University, Moscow, 119991, Russian Federation*

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ABSTRACT

Aluminum is a prospective material for hydrogen generation during metal/water reaction due to its high efficiency (1.24 l of H_2 from 1 g of Al), availability, low price, and safety. To realize its reactivity towards water at ambient conditions the metal activation is needed. The samples of aluminum activated by Ga-In alloy (70:30 wt%) at low-energy (LE) and high-energy (HE) treatment are considered. HE treatment (mechanochemical activation of aluminum in ball mill) allows to get high reactivity powders having H_2 generation rate in two orders of magnitude higher than for LE-activated aluminum. The values of activation energy for reactions of activated aluminum with water were calculated: $E_a = 55 \pm 5$ kJ/mol for LE-activated aluminum; $E_a = 35 \pm 5$ kJ/mol for HE-activated aluminum. The microstructure and composition of the samples of activated aluminum were determined by means of scanning electron microscope with energy dispersive X-ray spectrometer, differential scanning calorimeter and X-ray powder diffraction method. The depth profiles of the activated aluminum components have been measured by Auger electron spectroscopy. Possible mechanism of aluminum/activator interaction was proposed.

1. Introduction

The problem of developing new, high-efficiency hydrogen sources is a present-day challenge in study of hydrogen energy and its further progress. The application of hydrogen sources allows to avoid the H_2-storage and transportation stages and generate hydrogen “on demand” directly in the place of its use. Various approaches to solve this problem have been suggested, among which the reaction between water and metals (Al, Mg, etc.) under ambient conditions seems rather promising, particularly for microenergetics. The intensive development of proton exchange membrane fuel cells (PEMFC) [1–4] makes it possible the creation of power sources, including portable, having the source of hydrogen based on metal/water reaction.

Aluminum is considered as a prospective material for hydrogen generation from water due to its high efficiency (1.24 l of H_2 from 1 g of Al), availability, environmental safety of the reaction products, safety storage and transportation, and low price. Aluminum reacts with water producing hydrogen and hydroxides or oxides of Al according to the following reactions (1)–(3):

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2 + 16.3\ \mathrm{MJ/kg\ of\ Al} \quad (1)$$

$$2Al + 4H_2O = 2AlOOH + 3H_2 + 15.5\ \mathrm{MJ/kg\ of\ Al} \quad (2)$$

$$2Al + 3H_2O = Al_2O_3 + 3H_2 + 15.1\ \mathrm{MJ/kg\ of\ Al} \quad (3)$$

According to the data presented in Refs. [5], $Al(OH)_3$ is the most stable product at temperature of 20–280 °C (reaction (1)), while the reaction (2) prevails at 280–480 °C. Above 480 °C, Al_2O_3 is the most stable product (reaction (3)).

It is known, that aluminum does not react with water at ambient conditions (room temperature, atmospheric pressure) due to the formation of solid and dense oxide film on its surface. Therefore, various activation methods aimed to dissolve or remove the oxide film are used in order to carry out the aluminum/water reaction.

One of the old activation methods is use of mercury [6–9], but its application is restricted by the metal toxicity. One of the traditional methods is an oxidation of aluminum by alkaline solutions [10–16]. However, the high reaction rates are reached at

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[*] Corresponding author. Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya st. 13, bld. 2, Moscow, 125412, Russian Federation.

E-mail addresses: parmuzina@yandex.ru (A.V. Ilyukhina), krol@nextmail.ru (O.V. Kravchenko), bmbulychev@gmail.com (B.M. Bulychev).

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temperatures of 90–100 °C and in concentrated solutions (5 M NaOH) [12]. The hydrothermal oxidation of aluminum allows to rich the high reaction rate and 100% hydrogen yield [17,18]. However, this method is carried out at high temperatures (300–400 °C) and pressures (more than 200 atm), and requires a complex and expensive equipment.

The dispersion (grinding) of the metal is a usual way to increase its reactivity. This can be realized, for example, by mechanochemical treatment in a high-energy mill [19]. Such milling reduces the particles size of the metal and alters its structural, physical, and chemical properties [19–21]. Unfortunately, the activation of metal aluminum in this way (e.g., in a mill) have been unsuccessful because of the plasticity of aluminum. Therefore, the different additives such as NaCl [22–24], C [25,26], Bi [27], Bi-hydride or Bi-salt systems [28,29], etc. are used for grinding the aluminum in a mill. However, the reaction of Al-NaCl system with water is carried out at 55–70 °C having the maximum hydrogen generation rate of 70–100 ml/(g min) [22,23], and alloys with Bi having a higher reaction rate are toxic and expensive. The mixing of Al powder and different oxides powders (Al_2O_3, MgO, CuO, MoO_3, Bi_2O_3 or TiO_2 [30–34]) with further milling leads to formation of reactive Al. However, high values of H_2 yields and rates are reached at increased temperature (>50 °C), and the milling time can takes several hours.

To realize oxidation of aluminum at ambient conditions (atmospheric pressure, room temperature), one of the perspective activation methods is the doping of aluminum by the gallium-based alloys [35–42]. Besides gallium, such alloys may include indium, tin, and other metals.

The study of Al-Ga system [35] demonstrated the increase in hydrogen generation rate with temperature (from 25 to 85 °C) and gallium content (from 5 to 9 wt%). Al-6wt%Ga system can reach 285 l/(m^2 min) at 25 °C, but this value is difficult to compare with literature data as the authors [35] didn't indicate the specific surface area value. The excess of gallium in the Al-Ga alloys (50 or 72 wt%) leads to reaction rates increase, however the hydrogen yield is low (less than 10%) [36].

Use of Ga-based systems as activator (for example, Ga-In Refs. [37,38], Ga-In-Sn [36,39], Ga-In-Sn-Zn [40,41], etc.) instead of pure gallium leads to a higher reactivity of activated aluminum and high yield of hydrogen (more than 80%). At room temperature, Al-3wt%Ga-3wt%In system [37] demonstrates hydrogen generation rate of 100–120 ml/(g min). Activated aluminum 85 wt%Al-15 wt% Ga-In-Sn-Zn (60:25:10:5) reacts with water with maximum reaction rate of 185 ml/(g min) at temperature of 30 °C.

The early developed activation method [43,44] based on the low-energy (LE) treatment of aluminum pellets with gallium-based alloys allows to get the aluminum powders which react with water at ambient condition. The aluminum conversion in this reaction can reach 100%, but the average hydrogen generation rate does not exceed 10 ml/(g min). Such rate is not enough for the feeding of portable PEMFC.

Therefore, the new method for aluminum activation was developed [45,46]. The method is based on the additional mechanochemical treatment of the LE-activated aluminum powder in a planetary mill (high-energy (HE) treatment). This processing radically changes not only the microstructure of the metal, and also its physical and chemical properties. The hydrogen generation rate in the reaction between HE-activated aluminum and water increases by two orders of magnitude.

In spite of large number of publications concerned with the reactivity of activated aluminum (rate of hydrogen generation, yield of H_2, reaction kinetics) [47,48], there are a limited number of papers [36,39,49] focused on the microstructure of powders and alloys of activated aluminum, as well as the mechanism of interaction of activator and aluminum.

The purpose of this paper is the investigation of microstructure of aluminum activated by mechanochemical treatment with Ga-In alloy, having high reactivity properties, and the studying of mechanism of aluminum/activator interaction.

2. Materials and methods

The starting materials were aluminum pellets (analytical grade, 99.9 wt% Al) with average diameter of 10 mm, gallium (99.9999 wt % Ga), and indium (99.999 wt% In).

Activated aluminum was obtained via the following procedure:

(1) Activator (Ga-In alloy) was prepared by melting of gallium and indium at a ratio of Ga:In 70:30 wt% (79:21 at.%) in furnace at 160 °C, and then alloy was cooled to room temperature. After that a liquid two-phase system is formed, which consists of Ga-In eutectic (T_{melt} = 15.3 °C) and small amount of solid phase (further, Ga-In alloy).
(2) LE treatment: aluminum pellets were mixed with Ga-In alloy and then were crushed manually in a porcelain mortar in a dry nitrogen atmosphere. After such treatment the aluminum powder was formed. The amount of Ga-In alloy used in aluminum activation was 10 wt% (3.7 at.%).
(3) HE treatment: the powders obtained at the stage (2) were exposed to mechanochemical activation in a planetary mill AGO-2U (CJSC "NOVIC", RUSSIA) with steel balls 6 mm in diameter. The rotational speed of the grinding jars was 2220 rpm. The milling time was 3 min. The ball to powder mass ratio was 30:1.

The composition of activator (Ga-In (70:30) alloy, 10 wt%) was chosen according to our previous studies [43–45]. This composition demonstrates reliable and stable characteristics.

The hydrogen generation rate was determined volumetrically. An activated aluminum sample (~0,1 g) was placed into the water (150 ml) in the 300-ml glass reactor connected with the volume measuring system. The amount of hydrogen was measured by the amount of displaced water. The hydrogen released during the reaction was channeled to the water container driving the water out from the container to a measuring flask. The volume of water for reaction (150 ml) was taken in a large excess towards the reaction stoichiometry in order to avoid the temperature increase caused by the exothermic character of the reaction.

The amount of generated hydrogen was converted to the standard conditions (273 K, 1 atm) using the ideal gas equation. The hydrogen yield was determined as $\alpha = V/V_0$, where V is the current (experimental) volume of evolved hydrogen, converted to the standard conditions, and V_0 is the theoretical amount of generated hydrogen at standard conditions (1.244 l/g). The values of reaction rates and volume of generated hydrogen were referred to the weight of pure aluminum in the sample (90 wt%).

To determine the activation energy (E_a) the measurements of reaction rates were carried out at temperatures from 21 to 61 °C. To maintain a constant temperature the glass reactor was placed in thermostat.

The depth profiles of elements (aluminum, gallium, and indium) and their surface distribution were studied by Auger electron spectroscopy using a PHI-680 instrument (Physical Electronics)[1] with Ar^+ ion sputtering at a rate of 5 nm/min.

Surface microanalyses of activated aluminum powders were

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[1] The Auger electron spectroscopic studies were carried out at the Center of collective use "Materials Science and Metallurgy", National University of Science and Technology (MISIS).

carried out using a SUPRA 50 VP (LEO) scanning electron microscope (SEM) with energy dispersive X-ray (EDX) spectrometer INCA Energy+ (Oxford Instruments). Thermal analyses were performed on a DSC 204 differential scanning calorimeter. The specific surface area of powders was determined by the BET method on a Q-Surf M3 analyzer (Thermo Electron Corporation).

3. Results and discussion

3.1. Microstructure of activated aluminum

3.1.1. Composition of activated aluminum

At LE treatment of aluminum, the components of liquid Ga-In alloy penetrate into the metal bulk along grain boundaries, causing the embrittlement of the aluminum due to the destruction of grain bonds. This effect is the underlying principle of colloid chemistry, which is well-known as Rebinder's effect [38,41,50].

After LE treatment the Al powder is formed consisting of needle-like particles (Fig. 1) with average dimensions of 1 mm × 0.1 mm × 0.1 mm and a specific surface area of ~0.06 m^2/g, measured by BET-porosimetry. The surface of particles is non-uniformly, but entirely, covered with a liquid layer of Ga-In alloy, which can be observed visually and by SEM (Fig. 1).

According to microanalysis data (SEM and EDX) (Fig. 1b,c and Table 1), the surface of activated aluminum has areas with a gallium + indium content of 72–90 at.% and areas, where the total Ga + In content is not higher than 1.5–4 at.% (Fig. 1b,c and Table 1), that indicates the uneven distribution of Ga-In alloy on the aluminum surface. The atomic ratio of Ga to In (from 5.3:1 to 22:1) at different points of the aluminum surface is not correspond to the atomic ratio of the starting metals in Ga-In alloy (3.8:1), excepting the point 1 (Fig. 1b, Table 1) having a similar composition ratio. This indicates the compositional inhomogeneity of activating alloy. The same result was obtained by Wang et al. [40], showing that the Al-Ga-In-Sn alloy has a non-uniform distribution of components on the surface: the grain boundary phases are rich in In and Sn, and the Al grains contain Al and Ga elements. The presence of oxygen atoms is concerned with the partial oxidation of aluminum surface by air during its preparation for microstructure analysis.

X-ray powder diffraction data (not shown in this paper) for aluminum activated by Ga-In alloy at LE treatment demonstrate only reflections from aluminum, that indicates that Ga-In alloy on the aluminum surface is in a liquid state. The calculated average thickness of layer of Ga-In alloy on the aluminum particles is 1 μm, considering the average particle size of 1 mm × 0.1 mm × 0.1 mm and G-In alloy amount of 10 wt%.

The additional HE treatment of the aluminum powder in a planetary ball mill changes the shape and size of the aluminum particles (Fig. 2) and the chemical composition of their surface (Table 2). The average particle size of activated aluminum is 70–100 μm and a specific surface area is 0.1 m^2/g.

It is clear from the microanalysis (EDX) data (Table 2), that the surface of the mechanochemically activated aluminum powder is noticeably depleted in Ga-In alloy components compared to that prepared by LE treatment (Table 1 and Fig. 1). The gallium content is not higher than 4 at.% throughout the sample surface, and the indium content varies between very low <0.5 at.% (Fig. 2c, points 4,5, dark areas) and rather high 20–30 at.% (Fig. 2c, points 2,3, light inclusions). Aluminum remains the dominant element (~60–95 at.%). The oxygen content is reduced and does not exceed 9 at.%. These data indicate the redistribution of Ga-In alloy components on the surface and possible penetration of gallium, having a high rate of diffusion, both into the particle bulk at intergrain boundaries and into the aluminum grains. The penetration of Ga-In alloy components into Al grains does not take place under ordinary conditions because of the high activation energy of this process [50]. Indium is separated from gallium and is allocated to a separate phase on the surface of Al.

According to the X-ray diffraction data (not given here) the surface of mechanochemically activated aluminum contains only aluminum, indium, and an unidentified X-ray-amorphous phase. These data confirm the assumption about the redistribution of Ga-In alloy component and possible penetration of gallium inside the metal with its separation from In.

3.1.2. Composition of activator (Ga-In alloy)

The DSC data indicate that heating curve of aluminum activated at LE treatment (Fig. 3, curve 1) has a strong endothermic effect (with peak at 14 °C) associated with melting of liquid layer of Ga-In alloy on the surface of aluminum. While the heating curve of aluminum activated at HE treatment (Fig. 3, curve 2) indicates no thermal effects between −20 and 40 °C. It is likely due to the penetration of gallium into grain of aluminum there is no liquid phase on the mechanochemically activated aluminum surface. In case of uniform distribution of Ga-In alloy on the surface of particles with an average diameter of 100 μm, the layer of Ga-In alloy thickness would be ~0.3–0.4 μm and the film would be noticeable on the micrograph and endothermic effect would be at DSC, as in the case of the LE-activated aluminum powder.

The estimated composition of liquid layer on the surface of aluminum activated at LE treatment is Ga-In (70:30). However, the comparison of the DSC data for aluminum activated at LE treatment and for Ga-In (70:30) alloy (Fig. 3, curves 1 and 3, respectively) showed that for Ga-In alloy the endothermic effect has a peak at 24 °C and begins at 15–16 °C (Fig. 3, curve 3). For activated aluminum the endothermic effect has a peak at 14 °C and begins at 10–11 °C (Fig. 3, curve 1). These data correlate with a melting temperature $T = 15.3$ °C for Ga-In eutectic (78.6:21.4 wt%) [51].

It is possible, that the decrease in the melting temperature of activated aluminum in comparison with Ga-In alloy is caused by partial dissolution of aluminum in activator, and formation of a ternary (Ga-In-Al) liquid layer on the aluminum surface. This assumption is corroborated by our data obtained for the reaction between water and sample of Ga-In (70:30) alloy, which was in contact with aluminum for 1 month and then was separated from it. While the initial Ga-In alloy is practically nonreactive towards water, the Ga-In alloy that was in contact with aluminum reacts with water at room temperature: 16.5 g of the sample yields 68 ml of hydrogen in 15 h. Assuming that only aluminum is the component that is oxidized by water, we infer that Ga-In alloy contains 0.3 wt% of Al. However, this value is higher than the solubility of aluminum in gallium (0.16 wt%) [52]. The partial dissolution of Al in Ga-In-Sn alloy (less than 1 wt%) is also described in Ref. [36].

3.2. Reactivity properties and kinetics of activated aluminum

The reactivity properties of activated aluminum towards water are also changed significantly under mechanochemical treatment of aluminum. Fig. 4 shows the hydrogen generation rates and hydrogen yields for aluminum activated by Ga-In alloy at LE and HE treatment.

The sample of aluminum activated at LE treatment reacts with water at room temperature, and has a maximum hydrogen generation rate of 11 ml/(g min). The hydrogen yield is 97% in 400 min. The induction time is 1.5 min.

The sample of aluminum activated at HE treatment has a maximum hydrogen generation rate of 1280 ml/(g min). The hydrogen yield is 90% in 1 min after beginning of the reaction, and more than 95% in an hour.

As you can see, the hydrogen generation rate in the reaction

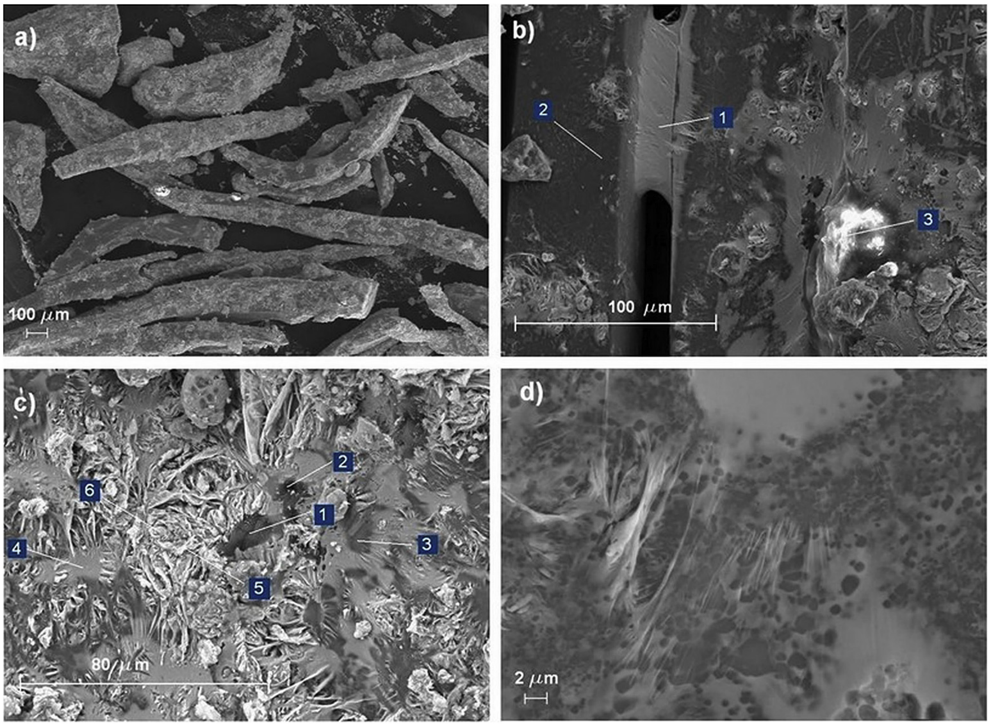

Fig. 1. Micrographs of activated aluminum powders prepared by LE treatment (magnification: (*a*) ×100, (*b*) ×1000, (*c*) ×2000, (*d*) ×5000).

Table 1
Composition of activated Al prepared by LE treatment (Fig. 1).

Spectrum	Element, at.%			
	Al	Ga	In	O
Data relating to Fig. 1b				
1	10.75	75.05	14.21	–
2	98.9	0.94	0.16	–
3	28.35	1.30	0.15	70.20
Data relating to Fig. 1c				
1	43.83	2.88	0.66	52.63
2	11.90	71.31	3.18	13.60
3	64.50	23.61	1.52	10.37
4	7.15	70.53	9.14	13.18
5	9.11	77.16	6.44	7.29
6	12.50	52.46	8.97	26.07

between water and mechanochemically (HE) activated aluminum is in two orders of magnitude higher than the hydrogen evolution rate for the LE-activated powders. This great acceleration of the reaction cannot be attributed to the increase in the specific surface area, which grows only by a factor of 2 upon HE activation, but it can be due to the formation of numerous defects on the aluminum surface.

After mechanochemical activation of Al (in ball mill) the ball-shaped particles are formed, and they most likely consist of agglomerates with smaller particles (Fig. 2a,b). We assume, that intensive milling causes the flattening of Al particles, and corresponding increase in the particle surface area. Simultaneously, the particles are disintegrated due to the Rebinder's effect and finer powder is formed. Further, the particles stick together into larger agglomerates, having non-uniform distribution of the activating metals in the bulk.

Once these agglomerates are brought into contact with water, they disintegrate into their constituent particles within a few seconds. This leads to increase in the activated aluminum surface area that is in contact with water and, accordingly, in a sharp increase in the aluminum oxidation rate.

It is known, that reaction rate increases with temperature. The temperature dependences for aluminum activated at LE and HE treatment are presented in Fig. 5. We can see, that maximum reaction rates increase essentially with temperature both for LE and HE-activated aluminum: from 11 to 95 ml/(g min) with temperature increase from 24 to 61 °C (LE treatment); from 1280 to 2600 ml/(g min) with temperature increase from 21 to 59 °C (HE treatment). The hydrogen yield is more than 90% for all investigated samples.

Using the temperature dependences the activation energy for reaction of activated aluminum with water was calculated. The obtained experimental data was described mathematically using the equation of Avrami-Erofeev (4):

$$\alpha = 1 - \exp[-(k\cdot\tau)n], \tag{4}$$

where α is the conversion degree; τ is the time, min; k is the reaction rate constant, min^{-1}; n is the reaction order. The rate constant of oxidation reaction was determined graphically by the plots in $[\ln(-\ln(1-\alpha))-\ln(\tau)]$ coordinates.

The values of reaction rate constant were used for activation energy calculation in accordance with the Arrhenius equation (5):

$$k = A\cdot\exp[-E_a/(RT)], \tag{5}$$

where A is a pre-exponential factor; E_a is the activation energy, kJ/mol; R is the universal gas constant ($R = 8.31$ kJ/(mol K)); T is the reaction temperature, K.

The activation energy of aluminum/water reaction for aluminum activated at different methods (LE and HE treatment) was calculated from the plots in $[\ln(k)-1/T]$ coordinates (Fig. 6).

The value of activation energy for reaction of LE-activated aluminum with water is 55 ± 5 kJ/mol, that is comparable to the $E_a = 53 \pm 4$ for 94Al-3.8Ga-1.5In-0.7Sn (in wt%) ingots [39] and

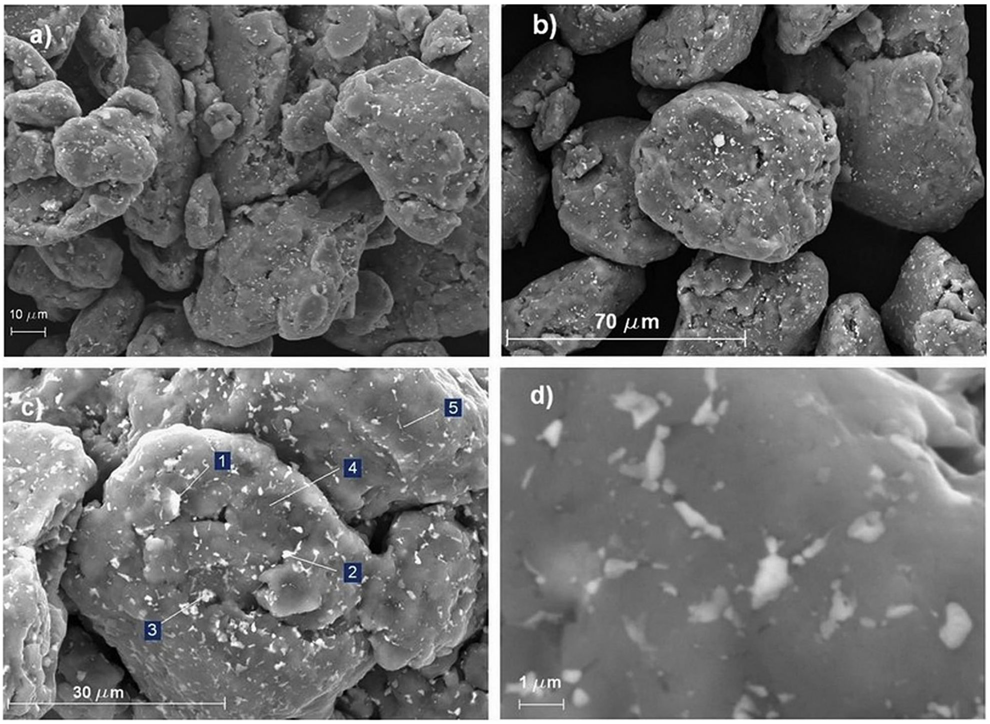

Fig. 2. Micrographs of activated aluminum powders prepared by HE treatment (magnification: (*a*) ×2000, (*b*) ×5000, (*c*) ×10000, (*d*) ×25000).

Table 2
Composition of activated Al prepared by HE treatment (Fig. 2c).

Spectrum	Element, at.%			
	Al	Ga	In	O
1	88.66	3.60	2.01	5.73
2	70.30	2.19	18.80	8.72
3	62.22	2.02	28.57	7.19
4	93.39	3.85	0.16	2.61
5	94.17	3.84	0.33	1.67

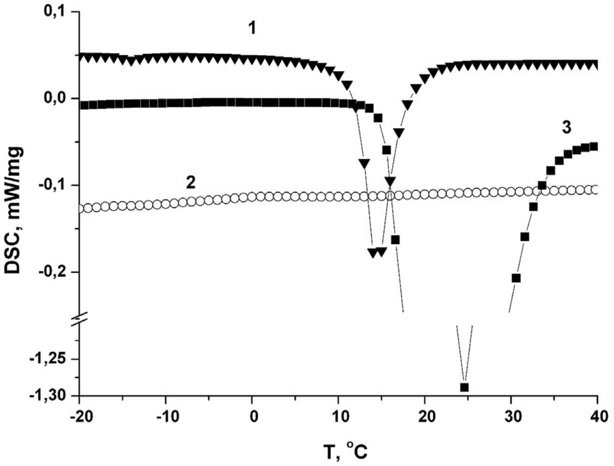

Fig. 3. DSC profiles for the aluminum samples prepared by (*1*) LE treatment and (*2*) HE treatment, and for (*3*) Ga-In (70:30) alloy.

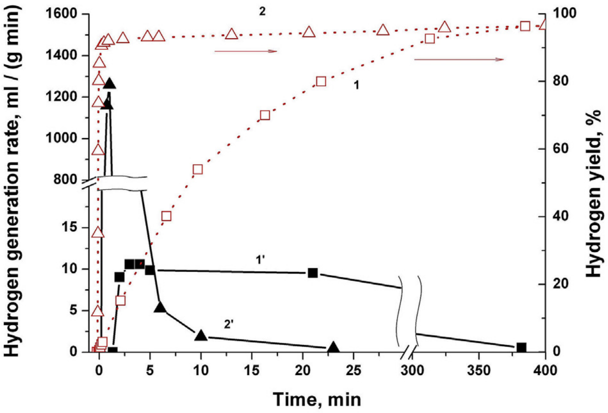

Fig. 4. Hydrogen yields (curves 1, 2) and hydrogen generation rates (curves 1′, 2′) in the reaction of LE-activated (curves 1 and 1′) and HE-activated (curves 2 and 2′) aluminum with water at room temperature (23 °C).

slightly higher than $E_a = 43.8$ kJ/mol for 50Al-34Ga-11In-5Sn (in wt %) alloy [36]. Probably, it may be explained by the higher amount of activator for the last sample (50 wt%). However, the value of activation energy for reaction of HE-activated aluminum with water is noticeably lower, $E_a = 35 \pm 5$ kJ/mol, that is caused by the high reactivity of Al towards water (Fig. 4).

3.3. Mechanism of aluminum/activator interaction

Contact of activator (Ga-In alloy) with aluminum (LE treatment) leads to penetration of Ga-In alloy into the metal along grain boundaries and aluminum embrittlement under the action of Rebinder's effect. At the same time, the wholeness of oxide film on aluminum surface is destroyed. As shown in Section 3.1, the resulting powders of LE-activated aluminum are covered with a liquid layer of Ga-In alloy, which contains some aluminum (0.3 wt %).

We suppose that the interaction of LE-activated aluminum with

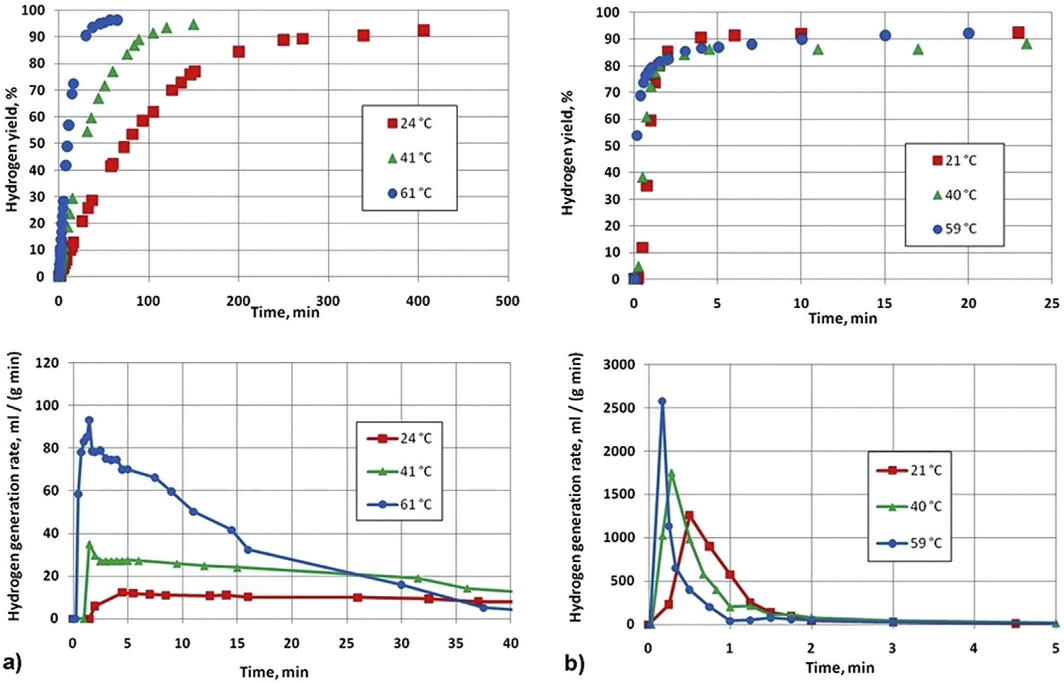

Fig. 5. Hydrogen yields and hydrogen generation rates for (*a*) LE-activated and (*b*) HE-activated aluminum at different temperatures (from 21 to 61 °C).

water is carried out as follows: aluminum dissolved in liquid layer of Ga-In alloy reacts with water forming Al hydroxide and hydrogen. Based on the fact that aluminum conversion can reach 100%, the formed hydroxide layer is porous and discontinuous, or may separates from metal exposing the surface. Then aluminum from bulk diffuses through the liquid layer to the reaction sites and reacts with water.

According to the data presented in Section 3.1, HE treatment of aluminum leads to redistribution of Ga-In alloy components on the surface, separation of indium from gallium and possible penetration of Ga into the aluminum grains. However, some unidentified layer covers the activated aluminum surface preventing the formation of uncovered areas that is confirmed by almost complete oxidation reaction (Fig. 4) and by the preservation of HE-activated aluminum reactivity during its prolonged storage in air (up to two month at room temperature, and 70% relative air humidity) [45]. Such layer has no liquid properties unlike the LE-activated aluminum.

To study the composition of this layer, the distribution of Ga-In alloy components in depth of HE-activated aluminum was investigated using Auger spectroscopy. The profile of sample components distribution is presented in Fig. 7. We can see the increase in aluminum concentration up to 91 at.% during the etching of aluminum surface in 30 min. The gallium concentration initially increases to 12 at.% and then gradually decreases. The maximum indium concentration of ~10 at.% is observed at a depth of ~20 nm (4 min after the beginning of etching). This indicates that indium is locally distributed in aluminum. The presence of oxygen and carbon can be explained by their adsorption on the surface of material during its preparation. Subsequent etching results in a decrease (or disappearance) of these elements.

The element distribution maps of the etched surface (randomly selected area) (Fig. 8a) show that aluminum is present almost everywhere on this surface (red points in Fig. 8b). The amount of gallium is small (white and pink points in Fig. 8c), and at a depth of ~150 nm it is fairly uniformly distributed throughout the surface, including the aluminum grains. Indium (light blue areas in Fig. 8d) is concentrated in certain places, primarily in cracks and pits. It should be noted that areas with indium has no gallium (Fig. 8c,d). These observations are in qualitative agreement with the above conclusion (Section 3.1.1) that Ga-In alloy components are redistributed under the action of HE milling, and In separates from Ga.

We found out that the distribution of elements on the sample's surface after etching varies with time. In 5 min after etching the composition of activated aluminum surface is: Al (60.7 at.%), In (25.4 at.%) and Ga (13.9 at.%). Further etching during 10 min leads to increase in Al (up to 89 at.%) and decrease in Ga (to 8 at.%) and In (to 3 at.%). However, after some time, the composition of activated aluminum surface also changes significantly (Fig. 9). The gallium and indium concentrations increase with time, indicating the high mobility of Ga-In alloy components and their tendency to some "averaging" of the surface layer composition.

Thus, the surface of HE-activated aluminum is always covered with a three-component metal layer (Ga-In-Al) possessing unique properties. On the one hand, this film adheres strongly to the

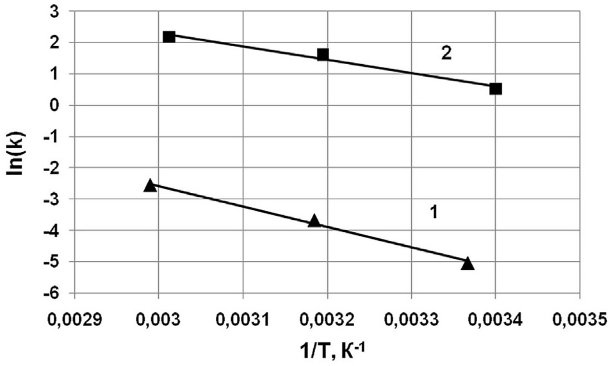

Fig. 6. Arrhenius plots for the reaction with water of (*1*) LE-activated and (*2*) HE-activated aluminum.

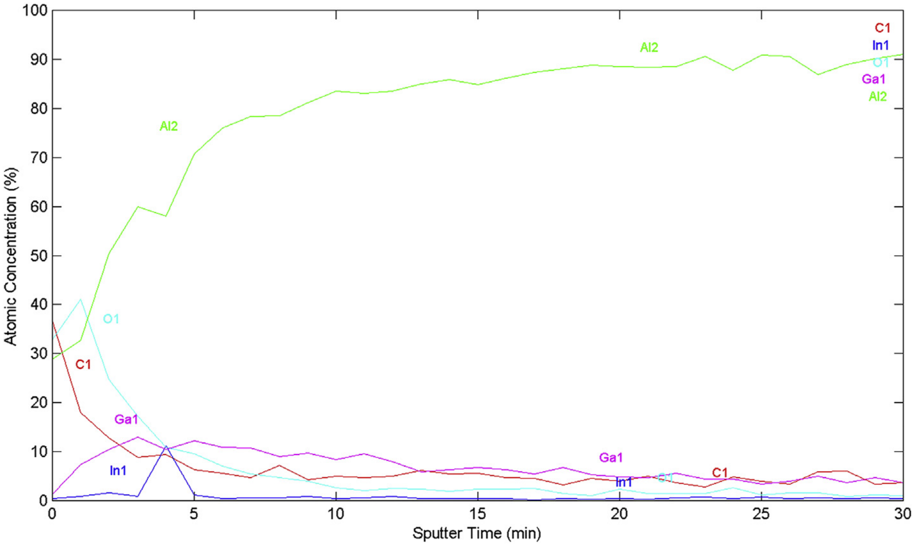

Fig. 7. Distribution profile of the HE-activated aluminum components in depth of the sample.

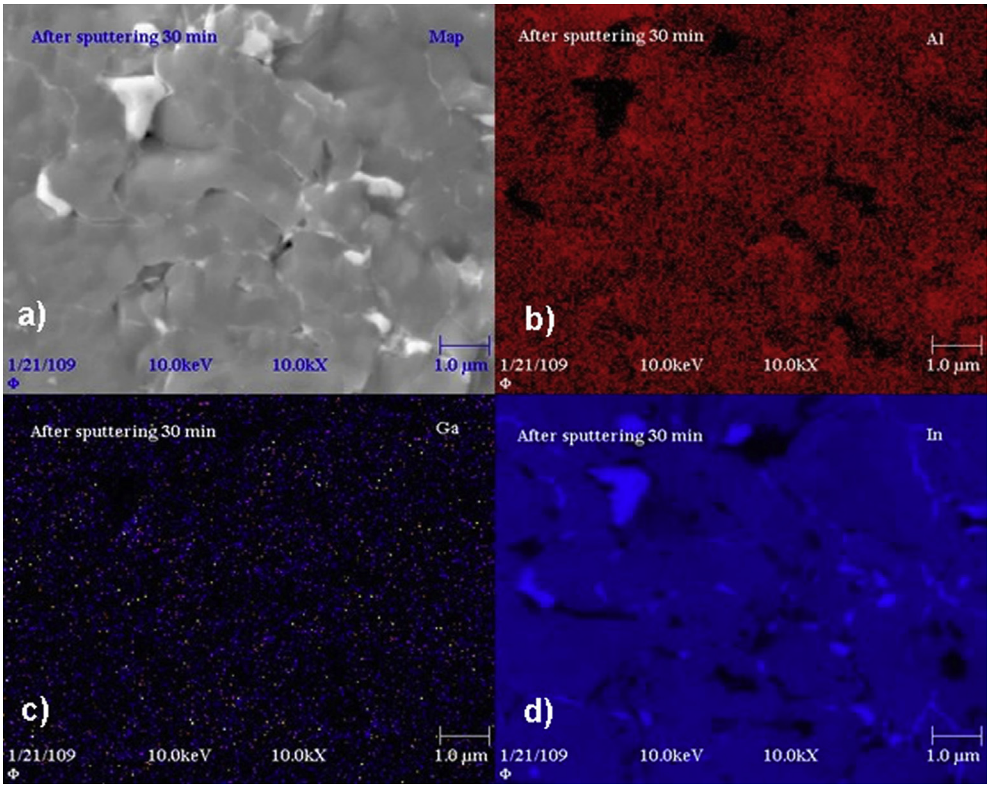

Fig. 8. (*a*) Activated aluminum surface obtained by 30-min-long etching and its (*b*) aluminum, (*c*) gallium, and (*d*) indium distribution maps.

aluminum monolith and has no properties of a liquid (according to the DSC-data); on the other hand, it prevents the formation of a dense aluminum oxide film and is sufficiently permeable for water, making possible the reaction between water and aluminum.

4. Conclusions

The microstructure of aluminum activated by Ga-In alloy at LE and HE treatment was investigated by means of SEM, EDX, XRD and DSC analyses. It was demonstrated that surface of LE-activated aluminum is covered with a thin liquid layer of Ga-In alloy, which contains aluminum (0.3 wt%) – Ga-In-Al layer. The composition of HE-activated aluminum is changed through the action of mechanochemical treatment: the surface is depleted of gallium due to its possible penetration into the aluminum grains. In addition, In is separated from Ga and is allocated to a separate phase. The layer of Ga-In alloy on the surface of HE-activated aluminum has no properties of a liquid.

It was demonstrated that activation of aluminum at HE treatment essentially increases the reactivity of metal towards water.

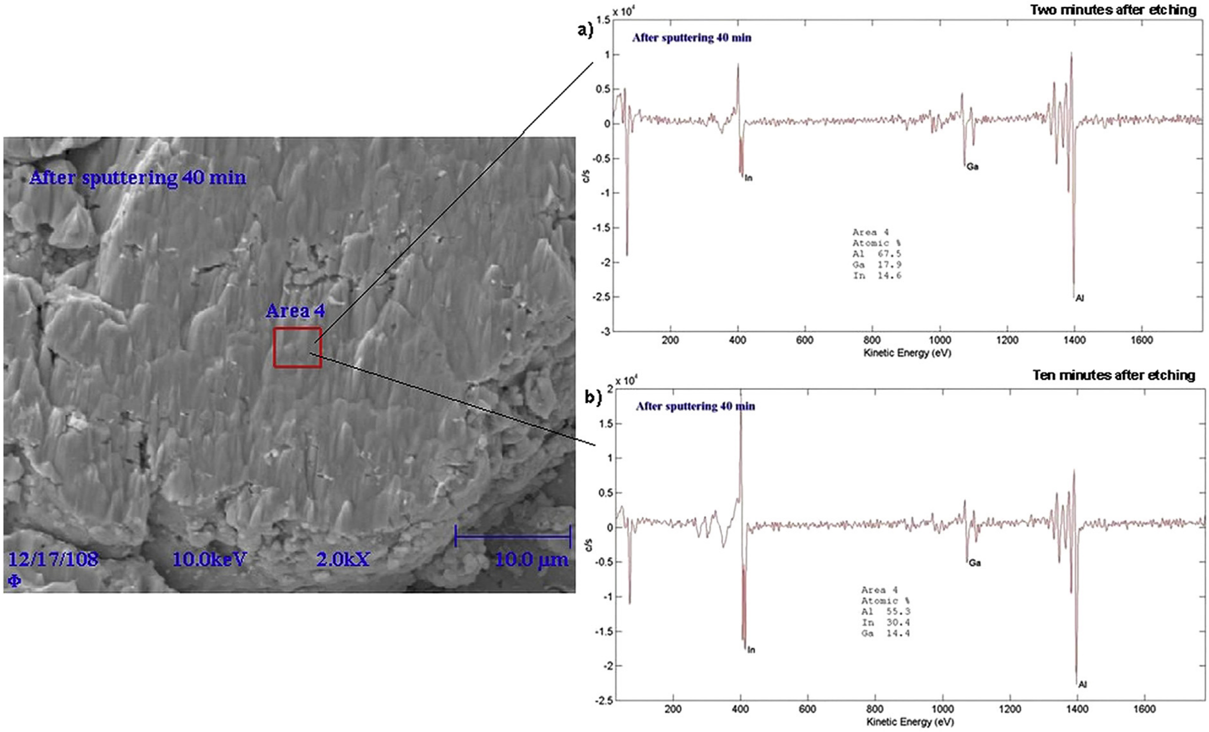

Fig. 9. Micrograph of etched HE-activated aluminum surface with its composition in (*a*) two and (*b*) ten minutes after etching.

Maximum hydrogen generation rate at room temperature for LE-activated aluminum is 11 ml/(g min), for HE-activated aluminum – 1280 ml/(g min). Such difference can be explained by the formation of numerous defects on the aluminum surface and creation of aluminum particle agglomerates with high specific surface.

The temperature dependences of reactivity of aluminum activated at LE and HE treatment towards water were defined. The temperature increase leads to significant increase in hydrogen generation rates, especially for HE-activated aluminum. The values of activation energy for reactions of activated aluminum with water were calculated: $E_a = 55 \pm 5$ kJ/mol for LE-activated aluminum; $E_a = 35 \pm 5$ kJ/mol for HE-activated aluminum.

Investigation of HE-activated aluminum in depth showed the high mobility of Ga-In alloy components and their different distribution in the aluminum bulk and on the aluminum surface. Gallium penetrates readily into the sample bulk and even inside the aluminum grains, while indium concentrates mainly on the surface of the aluminum particles, and in cracks.

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