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

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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):

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

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

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

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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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

[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).