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Generation of hydrogen by aluminium oxidation in aqueous solutions at low temperatures

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ABSTRACT

Hydrogen forming by aluminium oxidation with liquid water of water solutions at low temperatures is complicated by the following reasons. Firstly, on an aluminium surface a film of oxide is formed effectively preventing further oxidation. Secondly, the rate of aluminium oxidation considerably decreases as the temperature of the system decreases.

However, in this study the methods are given which enable one to overcome the above difficulties.

The experiments on the oxidation of powdered activated aluminium in different water solutions have been carried out. The data obtained have been used to plot a number of curves characterizing hydrogen flow rates depending on the solution composition and the temperature of the process (the original weight of the powder was 0.25 g, solution volume - 300 ml, measuring time - 180 min). At −40 °C for KOH solution the yield of hydrogen was 50 ml, for $CaCl_2$ – about 5 ml, and for $ZnCl_2$ – approximately 2 ml. At −10 °C H_2 yield for NaOH was 264 ml, for KOH – 260 ml; at −20 °C: 100 ml for NaOH, and 225 ml for KOH. For KOH solution at temperatures of −30 °C and −40 °C the yields were equal to 192 and 49 ml respectively.

Oxidation of granulated non-activated aluminium (2.5 g of aluminium per 300 ml of solution) with hydrochloric acid solution in the presence of $CuCl_2$ (2.5 g per 300 ml of solution) resulted in generation of more than 2000 ml of hydrogen during 300 min. For $FeCl_3$ solution the total value of hydrogen obtained during 180 min was equal to 70 ml, it also has been observed partial freezing of this solution.

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Introduction

The problem of the development of power supply systems for infrastructure facilities operating in Arctic zone is becoming of great importance, especially for Russia in the development of its Arctic territories. Today to realize stand-alone heat and power supply in the Russian Federation Arctic regions diesel power units are mainly used. However, these units are characterized by poor environmental performance and low efficiency of fuel chemical energy conversion.

If storage and transportation problems are solved, hydrogen may be well represented as an energy carrier in Arctic zone. Combustion of hydrogen does not result in harmful emissions, and efficiency of conversion of its chemical energy into usable kinds of energy can achieve rather high values than for diesel. However, hydrogen has two considerable disadvantages which are its low density and high explosiveness. An alternative energy carrier is represented by aluminium that has an energy potential close to one for hydrogen. Furthermore, the application of aluminium is not restricted by above limitations. Aluminium is the most widespread metal and the third widespread element in Earth's crust. Today the price for hydrogen is from 2 to 5 USD per kg. It is expected that it can be reduced to 3 dollars USA per kg. Heat value of hydrogen combustion in oxygen is 142 MJ/kg. World market prices for commercial purity aluminium are currently from 1.2 to 1.5 dollars USA per kg. Enthalpy of aluminium oxidation by oxygen with aluminium oxide formation is 31.3 MJ/kg.

It is necessary to point out that the products obtained from aluminium oxidation in water (aluminium hydroxide and oxide) can be valuable products. By realization of these products the costs for aluminium-based energy generation can achieve or even be lower than those for hydrogen-based energy generation. If obtained aluminium oxide is used in aluminium production process then there is no any need to increase production of bauxite and some other aluminium-containing minerals. The power is generated so that the original materials (aluminium and water) are fully regenerated without resulting in any air pollution emissions. If the power for aluminium electrolyses is supplied by renewable energy sources such as hydroelectric power stations, wind turbines, etc., then the development of "aluminium-hydrogen energy industry" is not expected to cause increased negative impact on the environment. Moreover, providing wide use of the power units applying aluminium and its alloys as an energy carrier, effective aluminium waste recycling [1] can be realized.

The present study is devoted to the development of power units which use aluminium as an energy carrier and water as an oxidant and operate at low temperatures. Aluminium as an energy carrier in Arctic regions has some extra advantages including relatively high energy density, convenient and safe storage and transportation, and the possibility of aluminium oxidation products regeneration (or safe utilization in situ). Aluminium-water reaction results in generation of heat and hydrogen which chemical energy can be again effectively converted into useful heat (for example, by means of infrared burners) or electric energy (for instance, by using fuel cells).

To date a number of researches have been attempted to investigate hydrogen generation in aluminium–water reactions. Direct reaction between aluminium and water does not occur at standard conditions due to immediate formation of oxide film on the aluminium surface effectively preventing further oxidation. Employing high-temperature techniques for aluminium oxidation leads to decrease in economic efficiency of aluminium application. Thus, one of the major problems is to develop new methods of aluminium activation allowing performing aluminium oxidation under conditions close to standard.

There is a variety of aluminium activation methods: production of ultrafine aluminium activated by NaCl [2]; introduction of activating agents such as silicon, graphite, bismuth, sodium chloride powders [3]; application of TiO_2, Co_3O_4, Cr_2O_3, MoO_3, Bi_2O_3, CuO additions; aluminium amalgam treatment [4]; activation of aluminium by Ga–In–Sn–Zn and Ga–In mixtures (Rehbinder effect) [5,6]; application of lithium compounds [7].

To date a great amount of studies have been published devoted to generation of hydrogen by oxidation of aluminium in water or different water solutions at ambient pressure and temperatures from 20-25 °C to 90–95 °C. A number of studies are devoted to aluminium oxidation at elevated pressures and temperatures [8–11]. However, the authors of the present paper have not found any articles on low-temperature aluminium oxidation processes.

The present research is devoted to the development and investigation of different methods that allow us to provide quick start of low-temperature aluminium oxidation with hydrogen generation. A number of experiments on aluminium oxidation in different water solutions stable to freezing at temperatures down to −40°C have been carried out. The data obtained have been analysed to define the effects of the temperature and composition of aqueous solution on the rate of aluminium oxidation and the hydrogen yield.

Experimental

Original reagents

Non-activated aluminium granules (see Fig. 1) and activated aluminium powder (see Fig. 2) have been used in aluminium oxidation experiments. Diameters of aluminium granules were about 5 mm. Aluminium with a purity of 99.96 wt. % was used. Oxidation of non-activated aluminium granules has been carried out in KOH, HCl, and $FeCl_3$ solutions.

For the manufacture of activated aluminium powder the commercial aluminium powder with average particle size of 300 μm was used. Aluminium with purity of 99.3 wt. % was used. Aluminium was activated by milling the commercial aluminium powder with liquid eutectic on the basis of gallium. To produce the liquid eutectic gallium of 99.9999% purity, indium (chemical purity 99.999%), and zinc of 99.96% purity have been taken in ratio 60:20:20 respectively. Milling was carried out using ball crusher S 100 Retsch during 10 min at rotation velocity of 550 rpm in an argon atmosphere. As to the costs for production of activated aluminium powder containing 10 wt. % of additives (gallium-indium-zinc taken in ratio 60:20:20), prices for gallium, indium and zinc are equal to