

Production of Hydrogen and Aluminum Hydroxide by Electrochemical Dispersion of Aluminum Alloys D16 in Sodium Hydroxide Aqueous Solution

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Abstract

Kinetics experimental results of the interaction of an aluminum alloy D16 with a sodium hydroxide aqueous solution under the alternating electric current are presented. It is stated that the reaction rate under the AC is much larger than the reaction rate without applying an electric current. The use of an alternating electric current makes it possible to obtain smaller particles of $\text{Al}(\text{OH})_3$ with a narrower particle size distribution range.

Keywords: Aluminum; Aluminum alloys; Aluminum hydroxide; Hydrogen production; Sodium hydroxide solution; Ceramics

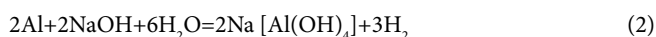
Introduction

One of the most promising ways to solve the problems of depletion of natural energy carriers and pollution of the environment as a result of their use may be the transition to alumina hydrogen power [1]. To organize the wide use of hydrogen as fuel, not only hydrogen production is needed, but also the accumulation, storage and transportation to places of consumption, which causes significant technical problems. These problems can be solved by using metallic aluminum as an energy carrier at the point of consumption, that is, on autonomous power plants and mobile generators of hydrogen production, for example, on a car board [2].

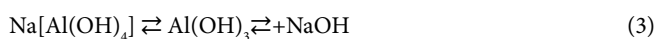
At normal conditions aluminum is coated with a thin oxide film thus is inert. The oxide film on the aluminum surface is easily removed by reaction with an aqueous solution of sodium hydroxide:



Without the oxide film, the interaction of aluminum with the alkali solution is described by the reaction:



At the point of consumption, hydrogen generated from this reaction can be used to produce energy without storing, storing and transporting it. The easily soluble complex compound $\text{Na}[\text{Al}(\text{OH})_4]$ decomposes reversibly according to the reaction:



Thus, sodium hydroxide is not eliminated from the reaction sphere. According to these reactions, the products of the interaction of aluminum and its alloys with an aqueous solution of sodium hydroxide are hydrogen and aluminum hydroxide $\text{Al}(\text{OH})_3$. On the one hand, the obtained aluminum hydroxide can be used for the production of metallic aluminum, on the other hand, it can produce an ultradisperse aluminum oxide powder widely used as a raw material for the production range of materials such as ceramics, composites, electrical insulating, abrasives, adsorptives, catalytics, medical and others [3,4].

The kinetics of the interaction of aluminum and its alloys with aqueous hydroxides solutions of alkaline elements has been studied in detail in a number of papers [5,6]. In these studies, the influence on the speed of the process of alloying alloy components has been determined [7-9].

Using hydrogen as an energy carrier in mobile systems, the issue of controlling the hydrogen evolution rate arises. In the author's opinion, one of the ways to control the rate of the hydrogen evolution reaction can be the effect of electric current on the process of aluminum dispersion.

The aim of this work is to study the influence of alternating electric current on the process of chemical dispersion of aluminum alloy D16 in a sodium hydroxide solution and on the properties of the reaction products.

Experimental Method

The reaction rate of an aluminum-based alloy in a sodium hydroxide solution was determined by a volumetric method by the volume of hydrogen evolved at 25°C.

Disk samples with the same surface area, were made of alloy D16 and connected to the electrode-holder. Samples were put in pairs in a thermostated reactor, which was a conical flask containing 0.5 L sodium hydroxide solution at a concentration of 1 mole/litre. The reactor was hermetically connected to a volumetric system.

Beforehand, without passing an alternating electric current, 2 samples connected to the electrodes and contained in a solution of sodium hydroxide were chemically dispersed, and the volume of hydrogen gas evaluated was measured. Then, the same samples in the same solution were dispersed by an alternating current of 50 Hz, a voltage of 6.4 V and a current strength of 0.3 A and 1.5 A, and the volume of hydrogen evaluated was also measured.

The reaction rate r was calculated from the equation:

$$r = \frac{\Delta V}{S \cdot \Delta t}$$

where ΔV is the volume of hydrogen evolved in time Δt , S is the area of the electrode.

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Received June 15, 2017; Accepted July 10, 2017; Published July 18, 2017

Citation: Reznichenko AV, Rybalchenko VV, Badaev FZ, Ponomarev SG, Vasin AA, et al. (2017) Production of Hydrogen and Aluminum Hydroxide by Electrochemical Dispersion of Aluminum Alloys D16 in Sodium Hydroxide Aqueous Solution. J Chem Eng Process Technol 8: 347. doi: 10.4172/2157-7048.1000347

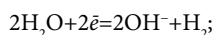
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Results and Discussion

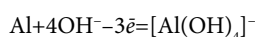
Kinetic curves of hydrogen evolution under different experimental conditions are shown in Figure 1.

In the process of electrolysis of an aqueous sodium hydroxide solution NaOH with electrodes made of an aluminum-based alloy, the following reactions occur:

Cathode (-):

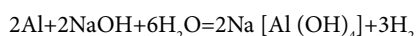


Anode (+):



In the process of electrolysis (comparing with the process without the flow of electric current), the rate of aluminum dispersion increases, as it is subjected to dispersion according to the reactions as electrochemical:

Anode (+): $\text{Al} + 4\text{OH}^- - 3\bar{e} = [\text{Al}(\text{OH})_4]^-$, and chemical:



1 - Chemical dispersion; 2 - passing an alternating electric current $I=0.3$ A; 3 - passing an alternating electric current $I=1.5$ A.

The consumption of OH^- ions during electrochemical dispersion is completely compensated by their formation by the cathodic reaction proceeding at the same electrode when the electric pole is changed:



The flowing cathodic process of water recovery on the aluminum electrode causes additional hydrogen evolution and an increase in the total rate of its release. On the cathode, simultaneously with the evolution of gaseous hydrogen, OH^- ions are formed, which causes a sudden increase in their concentration in the near-electrode layer. In the same layer, the concentration of Al^{3+} ions suddenly increases due to the anodic reaction occurring in the next phase of the alternating current. The Al^{3+}

and OH^- ions react with the formation of a complex ion $[\text{Al}(\text{OH})_4]^-$, which decays to form $\text{Al}(\text{OH})_3$ aluminum hydroxide. Consequently, when electric current is passed through the solution increases not only the rate of hydrogen gas evolution, but also the dispersion rate of aluminum and, accordingly, the rate of synthesis of $\text{Al}(\text{OH})_3$.

With electrochemical dispersion at 0.3 A current strength, the rate of hydrogen evolution compared to chemical dispersion increases approximately 5 times and is $9 \text{ l}/(\text{m}^2 \cdot \text{min})$. With 1.5 A current strength, the hydrogen evolution rate is approximately $12 \text{ l}/(\text{m}^2 \cdot \text{min})$. In the same way, the speed of dispersion of the alloy increases.

It is known that when precipitating from solutions of high concentration and under conditions of sufficiently low temperatures, ultradispersed and slowly settling particles are formed [10]. In the process of electrochemical dispersion of aluminum and its alloys, the concentration of both Al^{3+} ions and OH^- ions in the near-electrode layer increases significantly in comparison with chemical dispersion. For this reason, in our opinion, in the electrochemical dispersion of an aluminum alloy, products in the form of $\text{Al}(\text{OH})_3$ with more dispersed particles should be formed.

The particle size was studied on a FRITTSCH Analysette 22 Nanotec plus laser particle analyzer. The results of the studies are presented in Table 1.

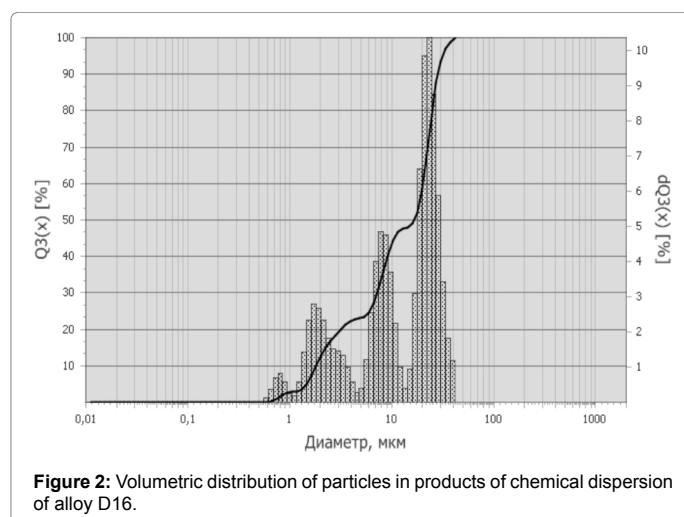
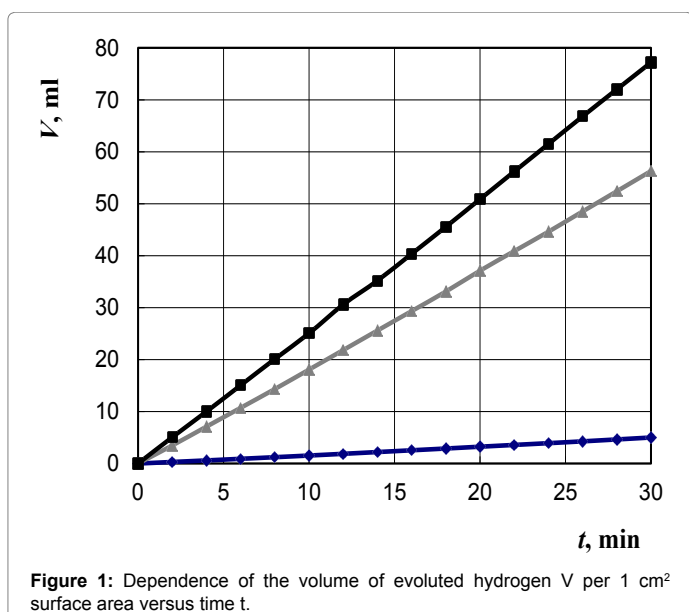
It has been stated that in the $\text{Al}(\text{OH})_3$ products obtained by chemical dispersion, 90% are particles with a size of less than $29 \mu\text{m}$. In this case, a four-modal particle size distribution is observed (Figure 2).

In products of electrochemical dispersion with 0.3 A alternating electric current, 90% particles are smaller than $18 \mu\text{m}$. In this case, a narrower three-modal particle size distribution is observed (Figure 3). When the AC power is increased to 1.5 A, 90% of the dispersion products of the D16 alloy are

Impact type	$d_{10}, \mu\text{m}$	$d_{50}, \mu\text{m}$	$d_{90}, \mu\text{m}$
Chemical dispersion	1.8	18	29
Electrochemical dispersion 0.3 A	3.7	8.3	18
Electrochemical dispersion 1.5 A	1.8	5	11

Here the value of d_n is such that the number of particles with a characteristic size less than d_n is $n\%$ of all particles

Table 1: Granulometric characteristics of powders.



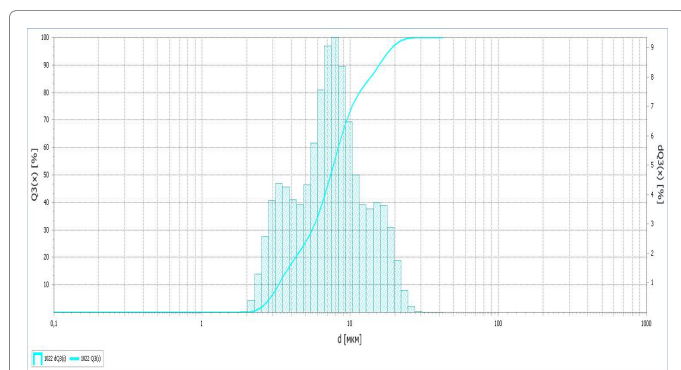


Figure 3: Volumetric distribution of particles in products of electrochemical dispersion of alloy D16 (current strength 0.3 A).

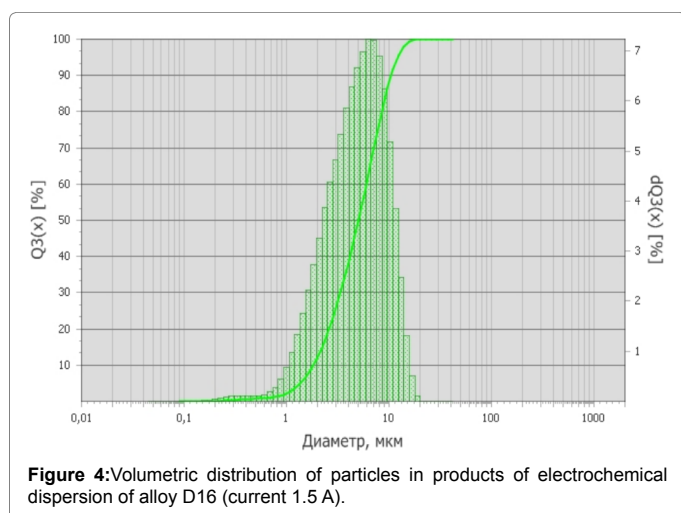


Figure 4: Volumetric distribution of particles in products of electrochemical dispersion of alloy D16 (current 1.5 A).

particles smaller than 11 μm . An even narrower single-modal particle size distribution is observed in this case (Figure 4).

Conclusions

1. The possibility of accelerating the process of dispersion of

aluminum and its alloys in an aqueous solution of sodium hydroxide at a concentration of 1 mole/litre and controlling the rate of generation of hydrogen gas by an alternating electric current has been experimentally studied and established.

2. Electrochemical dispersion of aluminum alloy D16 produces aluminum hydroxide with particles of smaller size than aluminum hydroxide during chemical dispersion of this alloy.
3. An increase in the AC power from 0.3 to 1.5 A leads to a decrease in the average particle size. The distribution by particle size becomes narrower.

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